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CHARACTERISTICS OF ROAD BITUMEN MODIFIED WITH CARBON NANOPOWDER

Abstract. In the paper the improvement of low temperature properties of blown road bitumens by means of modification with a carbon nanopoweder is shown. The bitumens of grade BND 70/100 and BND 100/130 have been produced by the Pavlodar petrochemical plant. The nanopowder has been obtained from a coal in the "Saryadyr" deposit ("ON-Olzha" corporation). Stiffness of the bitumens has been measured by a bending beam rheometer. Group chemical composition of the bitumens has been determined by the "Gradient" chromatograph. It was found that the Fraas point of the modified bitumens after short term aging on the RTFO method is not less than of the bitumen in non-modified and non-aged condition. Stiffness of the modified bitumen is considerably decreased at low temperatures (44%, 38% and 28% at the temperatures of -24 °C, -30 °C and -36 °C respectively). It has been stated that modification of the bitumens with the crbon nanopowder transforms the resins into compacted asphaltenes and decompacted oils consuming little energy for the process.

Key words: bitumen, carbon nanopowder, Fraas point, bending beam rheometer, stiffness, group chemical composition.

Introduction. The results of numerous investigations [1-10] show that conventional bitumens produced in plants do not practically always satisfy the requirements of operational conditions (including climatic ones) in many countries of the world, especially in the regions with sharp continental climate. As a rule to improve bitumens quality they are modified with polymers. Addition of polymers varies considerably the characteristics (physical and mechanical, rheological, etc.) of bitumens [11-13].

Due to what the abovementioned variations occur for bitumens characteristics at their modification with polymers? The answer should be searched, first of all, in variation of chemical composition of binders. Usually the researchers confine themselves only to physical and mechanical and rheological characteristics at the analysis of polymer type and content effect on bituminous binders properties, i.e. their chemical composition is not considered.

Table 1 represents the results for determination of group chemical composition of the neat bitumen of grade BND 100/130 and polymer bitumen binders manufactured by addition of various polymers into the bitumen. The neat bitumen has been produced by Pavlodar petrochemical plant (PPCP) from crude oil of Western Siberia by method of direct oxidation. The group chemical compositions of the basic neat bitumen and the polymer modified bitumens were determined in the laboratory of the Kazakhstan Highway Research Institute (KazdorNII) by method of adsorptive chromatography on Gradient M chromatograph [14, 15].

As the data of the table 1 show, without dependence on type and content of polymers, the bitumen modification is followed by the decrease of light components content (oils) and the increase of heavier components content (resins and asphaltenes). The increase of asphaltenes content due to the decrease of oils in the composition of the bitumen of grade BNS 70/100 (PPCP) at short-term and long-term aging has been determined in the work [14].

Table 1 – Group chemical composition of the neat bitumen of grade BND 100/130 and the polymer bituminous binders

Name of chemical compounds	Bitumen BND 100/130	Name and content of polymers				
		Bitumen BND 100/130 + KUMHO KTP (SBS) (Korea) – 6.0%	Bitumen BND 100/130 + Interchi-mica SBS – 4%	Bitumen BND 100/130 + SBS (L 30-01 A) – 3%	Bitumen BND 100/130 + Elvaloy AM – 2%	Bitumen BND 100/130 + Butonal NS 198 – 3%
Parafinonaftenes	21.9	16.7	16.35	15.6	16.1	14.45
Aromatics light	8.0	8.2	9.1	6.95	7.55	8.35
Aromatics middle	3.51	8.1	7.6	5.5	6.0	5.75
Aromatics heavy	22.1	21.3	18.5	21,8	23.7	25.15
Resins 1	6.6	7.5	6.7	8.45	9.05	8.35
Resins 2	24.1	24.0	27.4	21.7	22.3	21.35
Asphaltenes	13.8	15.2	15.4	20.0	15.3	16.65
Group chemical composition						
Oils	**55.51**	**54.3**	**51.5**	**49.85**	**53.35**	**53.7**
Resins	**30.7**	**31.5**	**34.1**	**30.15**	**31.35**	**29.7**
Asphaltenes	**13.8**	**15.2**	**15.4**	**20.0**	**15.3**	**16.65**

Thus, one can conclude that as at thermal aging as well as at polymer modification the following variation for group chemical composition of bitumen occurs: content of more light components (oils) is decreased and the content of heavier components (asphaltenes) is increased, and the content of intermediate components (resins) remains constant or it is also increased.

At present the possibility has been shown for application of nanoparticles of different structure as functional additives for bitumens [16]. Meanwhile, carbon nanoparticles are the closest to bitumen, as a component of petrol. It is considered that in this case the effect of modification will be a maximal one [17-19].

Materials and methods. Bitumens of grades BND 70/100 and BND 100/130 produced by PPCP have been taken for investigation of the impact of carbon nanopowder content on a group chemical composition. Nanopowder has been manufactured from a coal of 'Saryadyr" deposit belonging to "Corporation "ON-Olzha" LLP (Akmola region, Kazakhstan), and it has dimensions of 150-200 nm.

For the purpose of provision of the uniform distribution of the nanopowder particles in bitumen the nanopowder has been first dispersed in kerosene through the action of ultrasound with the frequency of 20 kHz for 5 minutes at a room temperature. Then the dispersed solution (kerosene+nanopowder) has been added to the bitumen at the temperature of 160 °C and constant stirring for 30 minutes. In such a way the samples of the nanocarbon bituminous binder (NCBB) have been prepared with the content of the carbon nanopowder from 0.1 to 2.0 % by weight.

Rational quantity of the nanopowder was determined according to the indicators of the bitumen resistance to aging. Bitumen "is aged" in the process of preparation of a hot asphalt concrete mix, light fractions are volatilized, bitumen becomes more brittle, less frost resistant.

The following main standard indicators for NCBB have been determined by appropriate methods of laboratory tests: needle penetration depth at the temperature of 25 °C under the standard ST RK 1226 [20], softening point on ring and ball under the standard ST RK 1227 [21], ductility at the temperature of 25 °C under the standard ST RK 1374 [22], Fraas point under the standard ST RK 1229 [23].

Aging of a binder at stirring of an asphalt concrete mix in a mixing device and during its laying occurs in conditions of a high temperature and air inflow. To model this form of aging the method of rolling of a thin film in the oven (RTFO) is used under the standard ST RK 1224 [24] and AASHTO T 240 [25].

To model the aging in the process of operation the accelerated method of aging is used in the device PAV under high pressure and at a high temperature for 20 hours under standard ASTM D 6521 [26]. The samples of a binder aged in PAV have already been subjected to aging under method RTFO. Binder residue after aging under method PAV represents the binder subjected to the action of all the factors of the environment which it has during production of an asphalt concrete mix and operation of an asphalt concrete pavement.

In accordance with the Technical system Superpave the low temperature stability of bituminous binders is evaluated under the stiffness modulus value, determined at load duration of 60 seconds under the standard ASTM D 6648 [27] on a bending beam rheometer (BBR). In this work the stiffness modulus of the neat bitumen and NCBB was determined at the temperatures of -24 °C, -30 °C and -36 °C.

Group chemical compositions of the original and the nanomodified bitumens were determined on the chromatograph "Gradient".

Results and discussion.

Standard indicators. Main standard indicators of the bitumen and NCBB, determined under the abovementioned standards, are represented in table 2.

Table 2 – Main standard indicators of the neat bitumen and NCBB

Indicators	Content of nanopowder, %								
	Neat bitumen	Neat bitumen after aging (RTFO)	0.1	0.2	0.3	0.5	0.7	1.0	2.0
Depth of needle penetration at 25°C, 0.1 mm	75	55	47	61	62	59	59	64	61
Softening point, °C	47.5	51	55	53.5	53	53	52	51	51
Ductility at 25°C, cm	118	69	41	53.5	45	32	54	31	51
Fraas point, °C	-28.5	-24.5	-27.1	-27.2	-26.9	-28.5	-28.0	-24.3	-27.6

The results of table 2 data analysis have shown that adding of the nanocarbon powder decreases ductility to 26 %; softening point is practically not changed, and depth of the needle penetration is increased for 16 %.

It should be specially noted that bitumen aging under the method RTFO increases Fraas point for 4°C from -28.5°C to -24.5°C, and adding of the nanocarbon powder reduces Fraas point and already with the nanopowder content of 0.5 % the Fraas point of the neat bitumen is recovered, i.e. becomes equal to -28.5°C.

Stiffness. Table 3 gives stiffness modulus values for the neat bitumen and NCBB at lower temperatures, obtained by testing at BBR.

Table 3 – Stiffness modulus of the neat bitumen and NCBB at low temperatures

Temperature, °C	Content of nanopowder, %		
	0	0.5	2.0
-24	104.21	-24	104.21
-30	220.11	-30	220.11
-36	322.50	-36	322.50

As it is seen the nanopowder decreases considerably the stiffness modulus of the bitumen, i.e. increases low temperature stability. Modification effect is especially clearly shown with the content of the nanopowder of 0.5 %. So, the stiffness modulus of the bitumen with such concentration of the nanopowder at the temperatures of -24 °C, -30 °C and -36°C is 46 MPa (44.1 %), 83 MPa (37.7 %) and 91 MPa (28.2 %) respectively.

Thus, one can conclude that modification of the bitumen of grade BND 70/100 by the nanocarbon powder increases considerably its low temperature stability.

Group chemical composition. The obtained data on group chemical composition of the original bitumen and its modified samples have been tabulated into table 4.

Table 4 – Group chemical composition of the neat bitumen and NCBB

Bitumen	Asphal-tenes, %	Resins, %			Oils, %				
		Petrol-benzol	Spiritus-benzol	Sum of resins	Paraffin-naphthene	Light aromatic	Middle aromatic	Heavy aromatic	**Sum of oils**
BND 100/130 RTFO	**11.8**	24.5	20.4	**44.9**	20.6	3.6	4.3	14.9	**43.4**
BND 100/130 RTFO + 0.5% NANO	**17.0**	15.2	19.2	**34.4**	23.3	5.1	4.5	15.7	**48.6**
BND 100/130 RTFO + 0.7% NANO	**17.8**	17.0	16.6	**33.6**	23.6	4.3	4.6	16.1	**48.6**
BND 100/130 RTFO + 2.0% NANO	**20.8**	10.7	18.0	**28.7**	23.1	5.5	5.3	16.7	**50.6**

Progressing decrease of resins content with aggregate portion increase from 0.5% to 2.0% is seen from Table 4. At 2.0% of the added nanopowder portion the resins content is decreased for 16.2% by weight and the content of the asphaltenes and oils is increased for 9.0% and 7.2% by weight respectively.

Conclusion.

1. The possibility has been shown for considerable improvement of low temperature characteristics for road bitumens by their modification with a nanopowder from a coal: Fraas point of the modified bitumen after short-term aging under the RTFO method is not lower than for the original (non-aged) bitumen; stiffness is considerably decreased (at the temperatures of -24°C, -30°C and -36°C for 44%, 38% and 28% respectively).

2. Phenomenon previously unknown has been determined for differently directed weak energetic transformation of bitumen resins into compacted asphaltenes and non-compacted oils cumulatively forming a nanostructured bitumen with increased low temperature resistance during heating up to +160°C with addition of a nanopowder from a coal into a original bitumen.

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КӨМІР НАНОҰНТАҒЫ ҚОСЫЛҒАН ЖОЛ БИТУМЫНЫҢ СИПАТТАМАЛАРЫ

Аннотация. Мақалада тотыққан жол битумына көмір наноұнтағын қосу арқылы оның төменгі температуралық сипаттамаларын жақсарту мүмкіндігі көрсетілген. МЖБ 70/100 және МЖБ 100/130 маркалы битумдары Павлодар мұнай-химия зауытында өндірілген, ал өлшемі 150-200 нм наноұнтақ «ОН-Олжа» корпорациясының көмірінен алынды. Битумдардың төменгі температурадағы (-24 °С, -30 °С, -36 °С) қаттылығы иілгіш білікті реометрмен өлшенді, топтық химиялық құрамы «Градиент» хроматогрофында анықталды. Наноұнтақ қосылған битумның RTFO әдісімен қысқа мерзімді ескірген күйіндегі морттық температурасы бастапқы (ескірмеген) битумдікінен кем еместігі көрсетілген.

Наноұнтақ қосылған битумның қаттылығы елеулі (-24 °С, -30 °С және -36 °С температураларда тиісінше 44%, 38%, 28 %) төмендейтіндігі анықталды. Бұрын белгісіз, битумға көмір наноұнтағын қосқанда шайырлардың тығыздалған асфальтендерге және қопсыған майларға аз энергия шығынымен айналу құбылысы анықталды.

Түйін сөздер: битум, көмір наноұнтағы, морттық температурасы, иілгіш білікті реометр, қаттылық, топтық химиялық құрам.

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ХАРАКТЕРИСТИКА ДОРОЖНОГО БИТУМА С НАНОЧАСТИЦАМИ УГЛЯ

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