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Impact of the Group Content on the Properties of Bitumen of Different Grades

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Abstract: In this study, the group composition of different grades of bitumen was studied by SARA-analysis. Also, the physical and chemical properties and the test properties of studied bitumen were examined. The conclusions on the effect of group composition of bitumen on their physical-chemical and performance properties were presented. According to the analysis of obtained data, we may conclude about close relationship of bitumen chemical composition with its physical-chemical and operational performance. Comparing the physicochemical properties of the studied bitumen with the requirements of the relevant regulatory documents, it is expected to improve the low-temperature and adhesion-strength properties. This is due to a large concentration of hydrocarbon paraffin concentration in bitumen, the presence of which is clearly pronounced in the composition. The reason for such a “contrast” content of heavy resins with pyrobitumen and with lower molecular paraffinic-naphthenic hydrocarbons is the small number of intermediate compounds such as average molecular aromatic hydrocarbons.

Key words: Bitumen, physical-chemical properties, SARA-analysis, contrast, chemical

INTRODUCTION

Modern industry cannot be imagined without a huge range of different bitumen composite materials (Pokonova, 2005; Anonymous, 2003). According to modern concepts, (Cesare *et al*., 2015) bitumen is a mixture of high molecular weight hydrocarbons and compounds with hetero atoms of different molecular weight and structure. The composition of bitumen which is determined by the nature of a native hydrocarbon material has a great influence on its basic physical and chemical properties and performance (Zakieva *et al*., 2015a, b). The absolute necessity was and remains still the enrichment and development of the fundamental concepts concerning the composition and structural organization of high-molecular oil systems. For example, the accumulated data will help to design new methods of high-quality bituminous materials obtaining.

According to recent publications, the content and nature of pyrobitumen and maltenes plays an important role in the formation of the colloidal structure of bitumen which also determines their properties. There is an opinion that tarry pyrobitumen aggregates play an important role in the formation of intermolecular interactions in a bitumen system. There are two kinds of structural organization in nature, presented on Fig. 1. The belonging of bitumen to a particular structure depends on the number and distribution of flocculated pyrobitumen in it and the content and structure of arene hydrocarbons. The presence of alkane substitutes and the number of links in the chain is the most significant one (Nosal *et al*., 1978). If a dispersion medium contains a large number of arenes, large aggregates are not formed due to the high solvent power of medium. This structure is called sol. Otherwise, this structure is a gel (Rehbinder and Fuchs, 1973).

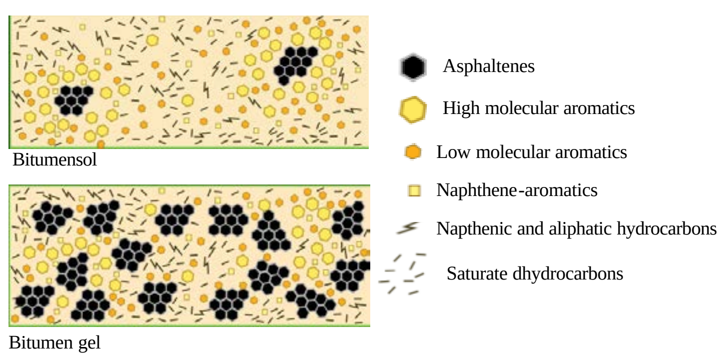

Fig. 1: Bitumen sol and bituman gel structure

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Figure 1 demonstrates a schematic view of two variants concerning the structural organization of bituminous systems.

The study of bitumen change property regularities on its composition is a relevant and forward-looking theme and certainly will form the basis of the methodological approach to an effective development of materials based on it.

MATERIALS AND METHODS

The following objects were selected for the study: Petroleum Road Bitumen PRB 90/130 and 60/90; Petroleum construction bitumen PB 70/30 construction; Petroleum Insulating Bitumen PIB V.

The group chemical composition of bitumen was determined by SARA-analysis method (saturates, aromatics, resins, asphaltenes). Using it, one may divide the objects of study into four groups of components: saturated hydrocarbons, aromatic hydrocarbons, resinous matters, asphaltene substances. Asphaltenes are isolated by precipitation of low molecular alkanes. The precipitation of asphaltenes was carried out from topped oils with 40-fold excess of C5-C8 alkanes. The separation of deasphalted sample concerning the above specified components was performed by the method of column chromatography using a mixture of C5-C8 alkanes, carbon tetrachloride, benzene and isopropyl alcohol. The rheological studies of samples were carried out using the system “cone-plate” in the range of shift speeds from 3-1312 s^{-1} in the temperature interval ranging from 10-80°C. According to the measured shear stress and shear rate the dynamic viscosity was calculated. According to experimental results the dependencies of a group chemical composition, the viscosity of bitumen from on the time of oxidation were developed. The determination of penetration involves the measuring of depth to which a needle is immersed at a given load in a test sample, in units relevant to tenths parts of a millimeter. The definitions of a sample softening temperature consisted in the fixing of temperature at which the bitumen located in a ring of specified sizes, softens and moves under the steel ball impact to the bottom plate. The maximum length was taken as extensibility according to which the bitumen is poured into a special form, spread at a constant speed. It can be stretched without breaking. Brittleness temperature was measured at cooling and the periodic bending of a bitumen sample determining the temperature at which cracks appear.

RESULTS AND DISCUSSION

Using the method of SARA-analysis, the chemical composition of commonly encountered brands was studied: PRB 90/130 and 60/90 viscous petroleum bitumen road; PB 70/30 bitumen building; PIB V oil insulation bitumen is presented in Table 1.

All brands of bitumen in oil part are characterized by a high content paraffin naphthenic hydrocarbons (14-17%) and aromatic hydrocarbons (28.0-41.5%). Paraffin naphthenic hydrocarbons (Saturates) is the fraction extracted by SARA analysis, comprising of isoalkane and alkane hydrocarbons as well as of aliphatic cyclic compounds of different composition including polynuclear and hybrid compounds of mixed structure.

The content of resins according to the studied bitumen ranges from 23.0-25.7. The resins extracted from bitumen by SARA-analysis have a similar structure like the oil molecules but in this component the main representatives are highly condensed hybrid molecules composed of arene rings and naphthenic rings.

It is known that the resins and asphaltenes recovered from bitumen have a high content of heteroatoms (Ganeeva *et al*., 2011). Asphaltenes are the most complex components, most of which is a layered block structure of particles (Fig. 2) containing 4-6 aromatic rings, a small amount of paraffin branching and the significant amounts of sulfur, nitrogen and oxygen in the molecules (Fig. 2).

All samples of bitumen were tested using standard procedures. Their basic physical, chemical and performance indicators were identified. These indicators are presented in Table 2.

The temperature of fragility and the depth of a needle penetration are determined by the amount and composition of a low molecular weight components of the bitumen. At that, if the amount of high-molecular

Table 1: The group composition of different grades bitumen (Results of SARA-analysis)

Bitumen brand	Oil part hydrocarbons			
	Paraffine-naphthenic saturates	Aromatics	Resins	Asphaltenes
PRB 90/130	17.0	41.5	23.0	18.5
PRB 60/90	16.2	39.3	23.8	20.7
PB 70/30	14.5	34.2	24.7	26.6
PIBV	13.9	28.3	25.7	32.1

Table 2: Physical-chemical and performance properties of bitumen

	Bitumen brand			
Index names	PRB 90/130	PRB 60/90	PB 70/30	PIB V
The depth of a needle penetration at 25°C (0.1 mm)	100	63	14	8
Softening point (°C)	44	50	81	102
Elongation at 25°C (cm)	78	97	5.5	2
Brittleness temperature (°C)	-16	-13	-	-
Plasticity range (°C)	77	74	-	-
Coupling with a mineral filler (adhesion)	Score 5	Score 5	Score4	Score 4
Softening temperature change after heating (°C)	7	5	5	-
Penetration index	-1.12	-0.65	1.68	3.05

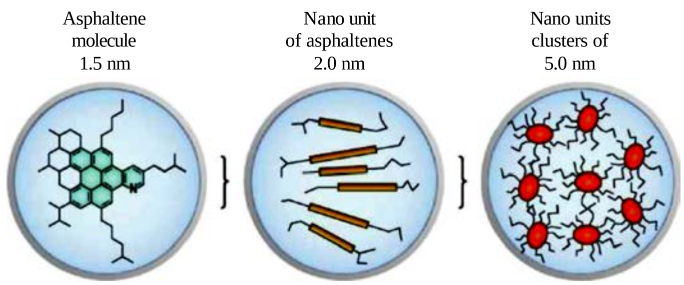

Fig. 2: Modified model of Jena (Mullins *et al*., 2013)

components, namely asphaltenes increases the thermal properties change accordingly. Table 2, data confirm the theoretical patterns, the bitumen of brand PIB V has the smallest value of a needle penetration depth and the asphaltene content is a maximum one. And, the bitumen of PRB 90/130 grade has an inverse relationship (Fig. 3).

The plastic properties of bitumen are also largely determined by its group composition. These properties have a huge impact on the quality of bitumen and determine the temperature range in which the bitumen composite does not lose its operational performance. The brittleness temperature as the penetration (a needle penetration depth), largely depends on the group composition of an original product. They try to reduce brittleness temperature gradually in composite bituminous materials.

The operational performance of commercial products in addition to the group component composition was greatly influenced by the ratio of the dispersed phase and the dispersion medium and the ratio of aromatic hydrocarbons to paraffinic hydrocarbons. One of the most important operational parameters of bitumen composite is its softening temperature. Figure 4 shows the effect of the component composition on this property. The dependencies have the form of straight lines which suggests a direct effect of such component content as saturates, aromatics, resins, asphaltenes, non plastic bitumen properties. In order to break the rigid frame of asphaltenes, it is necessary to apply more stringent conditions (such as bitumen PIB V characterized by a

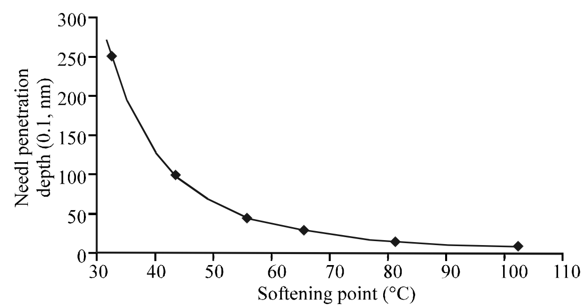

Fig. 3: The dependence of a binder softening pointon its penetration 25°C

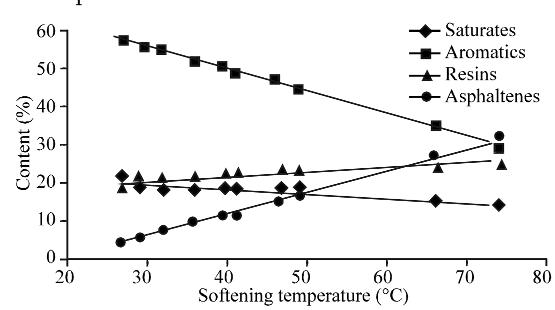

Fig. 4: The dependence of the bitumen softening point on the content of rich aromatic hydrocarbons, resins and asphaltenes

rather high softening temperature). Pyrobitumen have the ability to structure bitumen and improve its thermal performance.

The influence of bitumen composition on their brittleness temperature and penetration is more difficult, since they depend largely on the properties and the composition of a dispersion medium. Bitumen temperature brittleness as the softening temperature increases with the increase of asphaltenes as their rigid frame becomes hard and brittle (Table 1 and 2). The bitumen frame may vary on ratio of high and low molecular components in a dispersion medium. Therefore, the temperature of fragility will reflect these changes. In other words, brittleness temperature characterizes the moment when the entire system loses its ductility, becoming an amorphous solid body. Penetration (a needle penetration depth), being a viscosity parameter, also characterizes the change in the plasticity of a medium depending on the changes in its quantity and composition.

The operational properties of bitumen products are characterized by simple dependences on the content of their components and the number of arene compounds in these components (Fig. 4).

It is known (Bonemazzi and Giavarini, 1999) that the structural organization of bituminous systems will be determined by the ratio of the components in their composition. The value of energy applied to break the bonds in the system will condition the temperature properties of bitumen. Proportionally high asphaltene content leads to a significant impact on these values of bitumen, raising, for example, its softening temperature as for PIB V bitumen. The polar properties of asphaltenes may have a direct impact on the environment ability to glue the particles of bitumen. The more molecular weight components form asphaltene aggregates the better the adhesive properties of bituminous materials are (Pocius, 1997).

The influence of paraffinic hydrocarbons on the performance properties of bitumen is complicated. But most researchers agree that a lot of their content impairs the quality indicators of bitumen. It is considered (Copeland, 2007) that high molecular paraffinic hydrocarbons have a crystalline structure and such a property as the ability to crystallization but it does not have the ability to adhere and are not characterized by plasticity. Therefore, there are some limitations on the content of this component in the bitumen, namely: the number of paraffinic hydrocarbons may be no more than 5% wt.

In general, according to the performed studies we may conclude a close relationship between the chemical composition of bitumen with their performance characteristics. Comparing the physicochemical properties of the test of bitumen with the requirements of the relevant regulatory documents, the improvement of low-temperature and adhesion-strength properties is expected. This is due to a large amount of paraffin hydrocarbons, the presence of which is clearly pronounced in bitumen composition. Thus, the study of the group chemical composition of bitumen and its performance, gives us the information about their quality.

Summary: In conclusion, one should note an unconditional fundamental importance of fundamental base expansion about the composition, structure and properties of such demanded oil products like bitumen. There is no doubt that the new information about the patterns of qualitative changes in the properties of bitumen depending on its group composition may be widely applied in the industry at the planning of a commercial product certain properties as well as during the prediction of its behavior in operational conditions. One should seek for the regulation of petroleum bitumen properties by changing and controlling the content of certain components.

CONCLUSION

The analysis result of the obtained data allows to make a conclusion about close relationship between the chemical composition of bitumen and their physical-chemical and performance characteristics. Comparing the physicochemical properties of the tested bitumen with the requirements of the relevant regulatory documents, the improvement of low-temperature and adhesion-strength properties is expected. This is due to a large concentration of paraffin hydrocarbons in bitumen, the presence of which is clearly pronounced in the composition. The reason for such a “contrast” content of heavy resins with asphaltenes and lower molecular paraffinic-naphthenic hydrocarbons is the small number of intermediate compounds such as average molecular aromatic hydrocarbons.

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