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BITUMENS AND POLYMER BITUMENS - NANODISPERSE SYSTEMS

Abstract. This work shows the data regarding the elemental and chemical group compositions of the road bitumens. The short characteristic has been shown for the components of the bitumens - the asphaltenes, the resins and the oils. The properties have been described for the bitumens on which they have the direct impact. The description is given for the micellar model of the bitumens from the point of view of the colloid chemistry.

The analysis has been performed for the results of the study by other authors for the asphaltenes of a bitumen and an oil. The group chemical compositions are given for the bitumen of the grades BND 50/70, BND 70/100 and BND 100/130 produced by the plants of Kazakhstan. It has been shown that the content of the asphaltenes in them is from 15.8% to 24.3%; in most cases, the content of the asphaltenes is within the range of 20-25%, i.e. the asphaltenes nanoclusters are almost a fourth of the bitumen by weight.

The brief description is given for the best known polymers used for the modification of the road bitumen: 1) the reactive polymers Elvaloy 4170 and Elvaloy AM; 2) the polymers of the group SBS - Kraton D 1192A, Calprene 501, SBS L 30-01 A, KUMHO KTR and Butonal NS 198.

It is proposed to consider the bitumen and the polymer bitumen as the peculiar nanodisperse systems. The structures are described for the polymer bitumen nanodisperse systems occurring during the modification of the road bitumen with the polymers of the above two groups.

Key words: Bitumens, polymers, polymer bitumens, asphaltenes, oils, resins, nanodisperse systems.

Introduction. The bitumen is one of the main road materials. The need for it is growing due to the increase in the volume of the road construction and the repair works. For example, over 1 million tons of the road bitumen were used in Kazakhstan in 2020.

Despite the fact that the bitumen content in an asphalt concrete is only 5-6% (by weight), many physical and mechanical, almost all the rheological properties of the asphalt concrete depend on the bitumen.

Currently, there are both practical methods for assessing quality and calculation models for predicting the properties of the road bitumen. But many of them are based on the ideas about the bitumen as viscous liquids and colloidal systems with dispersed particles of macro dimensions.

This paper proposes to consider the bitumen and the polymer bitumen as the peculiar nanodisperse systems.

Bitumen nanodisperse systems. The bitumen is a complex mixture of the residual high molecular weight hydrocarbon compounds also comprising different chemical structures in a relatively small amount. An estimated elemental composition of the bitumen (by weight): carbon is 80-85%; hydrogen is 8-11.5%; oxygen is 0.2-4%; sulfur is 0.5-7%; nitrogen is 0.2-0.5%. The metals - iron, nickel and vanadium - are in a small amount in the composition of the bitumen [1-3].

At present, it is common to characterize the bitumen by the group of chemical compounds included in their composition. Meanwhile, all chemical compounds in the bitumen are divided into the following 3 groups:

1) Asphaltenes are the highest molecular weight part of the bitumen which is dissolved in carbon disulfide and chloroform and it is not dissolved in light alkanes (n-pentane, n-hexane, n-heptane, petroleum ether, etc.);

2) Resins are red-brown solids consisting of cyclic and heterocyclic structures interconnected by aliphatic chains;

3) Oils are the mixture of cyclic hydrocarbons of light yellow color.

The synthesis of the results for the numerous studies [4] made it possible to determine that the asphaltenes are a structural framework of the bitumen, they give hardness and heat resistance to the bitumen; resins characterize plasticity, ductility and cementing properties of the bitumen; oils cause plasticization of the bitumen, they reduce viscosity and heat resistance, increase fluidity and frost resistance.

Many properties of the bitumen, including rheological ones, can be explained using the so-called micellar model. It considers the bitumen as a colloidal system. Colloidal systems are known to be the dispersion of one body (disperse phase) in another body (disperse medium). The dispersed particles are not individual molecules, but aggregates of molecules in colloidal systems.

Back in 1940, it was proposed to consider the bitumen as a colloidal system [5]. In such a colloidal system, the micelles are formed that play the role of a dispersed phase. Micelles consist of asphaltenes. The disperse medium is maltenes (mixture of oils and resins).

The results for the analysis of the known works [4, 6-15] show that at present the following ideas are the most common among the specialists about the structure of the asphaltenes and their structural parameters: asphaltenes are the ordered polycyclic condensed aromatic structures (with the inclusion of heterocycles and lateral substituents) in the form of a packet of flat sheets with the radius of 0.85-1.5 nm and the thickness of 1.6-2.0 nm; the distance between the layers in the packet is 0.355-0.370 nm; the number of layers in the packet is 5-6; the distance between the elements in the saturated structures is 0.55-0.60 nm.

The more detailed studies have shown that the size of the asphaltene molecule is varied between 1.2-2.4 nm [7-9,14]. The sizes of nanoaggregates are increased to 10 nm with the increase in the concentration of the asphaltenes (up to 200 mg/l) in petroleum media [16]. Separate nanoaggregates, combining, create nanoclusters consisting of 8-10 nanoaggregates. The sizes of the nanoclusters reach 100 nm. The average size of the nanoaggregates is about 40-50 nm [17].

Thus, according to the concepts of the colloidal chemistry, the bitumen is a nanodispersed system where the maltenes (a mixture of oils and resins) are dispersed medium, and the asphaltene nanoclusters are dispersed phase.

Table shows group chemical compositions of bitumens of grades of BND 50/70, BND 70/100 and BND 100/130 produced by Kazakhstan plants. As it is seen from this Table, the content of the asphaltenes in them is within the range of 15.8% and 24.3%. In most cases, the content of the asphaltenes is within the range of 20-25%, i.e. the asphaltenes nanoclusters are almost a fourth of the bitumen by weight.

Group chemical composition of the bitumens produced by the plants of Kazakhstan

Group of chemical compounds	Plant-producer, bitumen grade				
	Pavlodar petrochemical plant		Caspiy Bitum		Gazpromneft
	BND 70/100	BND 100/130	BND 50/70	BND 70/100	BND 70/100
Paraffin-naphtenes	19.6	20.3	21.3	15.2	21.6
Light aromatics	6.2	5.5	4.2	5.0	5.4
Medium aromatics	2.1	4.3	4.6	3.9	3.6
Heavy aromatics	10.8	21.6	17.5	20.6	19.6
Petroleum-benzene	6.7	7.1	8.0	9.9	10.7
Alcohol-benzene	30.3	20.4	23.5	22.4	23.3
Asphaltenes	24.3	20.8	20.9	23.0	15.8
Group chemical composition					
Oils	38.7	51.7	47.6	44.7	50.2
Resins	37.0	27.5	31.5	32.3	34.0
Asphaltenes	24.3	20.8	20.9	23.0	15.8

Polymers. The best known polymers used for the modification of the road bitumen are Elvaloy 4170, Elvaloy AM, Kraton D 1192A, Calprene 501, SBS L 30-01 A, KUMHO KTR and Butonal NS 198.

Elvaloy 4170 and Elvaloy AM are chemically active elastomeric copolymers of ethylene with butyl acrylate and glycidyl methacrylate.

The modifiers Kraton D 1192A, Calprene 501, SBS L 30-01 A, KUMHO KTR and Butonal NS 198 belong to the same group of the polymer compositions; they are linear block copolymers of styrene and butadiene. The ratio of styrene and butadiene blocks is almost the same in them. For example, the content of styrene (% by weight): in Kraton - 30; Calprene - 31; SBS - 30±1,5; KUMHO - 30. However, Butonal NS 198 is a cationic aqueous dispersion of a styrene-butadiene copolymer. It contains 64% by weight of the solids.

Bitumen polymer nanodisperse systems. After mixing with the bitumen, the polymers of the SBS group (styrene-butadiene-styrene) swell in the maltene part (mixture of resins and oils) of the bitumen; their volume becomes 5-10 times higher compared to the initial one. Meanwhile, the polystyrene blocks are assembled into rigid domains, which are connected by rubbery (rubber-like) chains of the polybutadiene. Polystyrene domains have dimensions of the order of 10-40 nm [3]. Thus, when the bitumen is modified by the SBS group polymers, an additional spatial amorphous nanostructured mesh is created in bitumen in the initial nanodomain system, at the nodes of which there are rigid polystyrene nanodomains connected to each other by elastic chains of the polybutadiene. Rigid polystyrene nanodomains increase the viscosity of bitumen, thereby improving its high temperature characteristics, and polybutadiene chains give elastic properties to the bitumen, which increases their low temperature stability.

The butyl acrylate ethylene base of the polymers Elvaloy 4170 and ElvaloyAM imparts elasticity to the bitumen polymer system. The presence of an epoxy group in glycidyl methacrylate creates the possibility for its chemical effect with functional groups (-OH, -COOH, -NH_2, -SH, etc.) contained in the asphaltenes of the bitumen. Thus, rather than the polymers of SBS group, the asphaltene bitumen nanoclusters when modified with Elvaloy polymers will be rigidly (chemically) interconnected by a spatial elastic polymer network. In other words, a peculiar nanodisperse system is created where the dispersed phase - the nanoclusters of asphaltenes are located in the nodes of the spatial amorphous elastic nanostructured mesh. It is expected that the obtained nanodisperse system should have the improved high and low temperature characteristics.

Conclusion. 1. The asphaltenes of bitumens are the ordered polycyclic condensed aromatic structures (with the inclusion of heterocycles and lateral substituents) in the form of a packet of flat sheets with the radius of 0.85-1.5 nm and the thickness of 1.6-2.0 nm; the distance between the layers in the packet is 0.355-0.370 nm; the number of layers in the packet is 5-6; the distance between the elements in the saturated structures is 0.55-0.60 nm.

2. The sizes of the asphaltene molecule are varied between 1.2-2.4 nm. The sizes of nanoaggregates of the asphaltenes are increased to 10 nm with the increase in the concentration of the asphaltenes (up to 200 mg/l). Separate asphaltene nanoaggregates, combining, create nanoclusters consisting of 8-10 nanoaggregates. The sizes of the asphaltene nanoclusters reach 100 nm. The average sizes of the nanoaggregates are about 40-50 nm

3. The content of the asphaltene nanoclusters in the road bitumens produced by the plants of Kazakhstan is within the range of 15.8% and 24.3% by weight; in most cases, their content is within the range of 20-25%, i.e. the asphaltene nanoclusters are almost a fourth of the road bitumens by weight.

4. It is proposed to consider the road bitumens and the polymer bitumens as the peculiar nanodisperse systems.

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БИТУМДАР МЕН ПОЛИМЕРБИТУМДАР - НАНОДИСПЕРСТІК ЖҮЙЕЛЕР

Аннотация. Осы жұмыста жол битумдарының элементтік және химиялық топтық құрамы туралы деректер келтіріледі. Битумдардың құрамдас бөліктеріне, асфальтендерге, шайырлар мен майларға қысқаша сипаттама берілген. Олар тікелей әсер ететін битумдардың қасиеттері көрсетілген. Коллоидты химия тұрғысынан битумдардың мицеллярлық моделінің сипаттамасы келтірілген.

Битум және мұнай асфальтендері бойынша басқа авторлардың зерттеу нәтижелеріне талдау жасалды. Қазақстан зауыттары шығарған МЖБ 50/70, МЖБ 70/100 және МЖБ 100/130 маркалы битумдардың топтық химиялық құрамдары келтірілген. Олардағы асфальтендердің мөлшері 15,8 %-дан 24,3%-ға дейін; көп жағдайда асфальтендердің мөлшері 20-25 % аралығында болады, яғни битумның массасы бойынша төрттен бір бөлігі асфальтты нанокластерлер болып табылады.

Жол битумдарын модификациялау үшін қолданылатын ең танымал полимерлердің қысқаша сипаттамасы берілген: 1) Elvaloy 4170 және Elvaloy AM рективтік полимерлер; 2) СБС тобының полимерлері - Kraton D 1192A, Calprene 501, SBS L 30-01 A, KUMHO KTR және Butonal NS 198.

Битумдар мен полимербитумдарды нанодисперсті жүйелер ретінде қарастыру ұсынылады. Жол битумдарын аталған екі топтың полимерлерімен модификациялау кезінде пайда болатын полимербитумды нанодисперстік жүйелердің құрылымы сипатталған

Түйін сөздер: Битумдар, полимерлер, полимербитумдар, асфальтендер, майлар, шайырлар, нанодисперстік жүйелер.

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БИТУМЫ И ПОЛИМЕРБИТУМЫ - НАНОДИСПЕРСНЫЕ СИСТЕМЫ

Аннотация. В настоящей работе приводятся данные об элементном и химическом групповом составах дорожных битумов. Приведена краткая характеристика составляющих битумов-асфальтенов, смол и масел. Указаны свойства битумов, на которые они оказывают прямое влияние. Дано описание мицеллярной модели битумов с позиции коллоидной химии.

Выполнен анализ результатов изучения другими авторами асфальтенов битумов и нефтей. Приведены групповые химические составы битумов марок БНД 50/70, БНД 70/100 и БНД 100/130, произведенных заводами Казахстана. Показано, что содержание асфальтенов в них составляет от 15,8 % до 24,3 %; в большинстве случаев содержание асфальтенов находится в пределах 20-25 %, т.е. почти четвертая часть битума по массе – это асфальтеновые нанокластеры.

Дано краткое описание наиболее известных полимеров, применяемых для модификации дорожных битумов: 1) рективные полимеры Elvaloy 4170 и Elvaloy AM; 2) полимеры группы СБС - Kraton D 1192A, Calprene 501, SBS L 30-01 A, KUMHO KTR и Butonal NS 198.

Предложено рассматривать битумы и полимербитумы как своеобразные нанодисперсные системы. Описаны структуры полимербитумных нанодисперсных систем, возникающих при модификации дорожных битумов полимерами указанных двух групп.

Ключевые слова: битумы, полимеры, полимербитумы, асфальтены, масла, смолы, нанодисперсные системы.

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