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Modification of Asphalt-Free Super Viscous Oil Using Ethylene Copolymer with Vinyl Acetate.

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ABSTRACT

In this work the composition as well as the physical and mechanical properties of deasphalted bitumen of the Ashalchinsky field compounded by ethylene vinyl-acetate copolymer was studied. The possibility of development of an asphalt concrete pavement based on bituminous binding material, containing as dispersed phase, not asphaltene associates, but ethylene vinyl-acetate copolymer was looked into. The characteristics of the new asphalt binder are presented, on the basis of which it follows that the resulting binding material has ultra-high reserve of strength, elastic-deformation , low temperature and adhesion properties.

Keywords: bitumen, ethylene vinyl-acetate copolymer, penetration, asphalt-free, softening temperature, adhesion.

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INTRODUCTION

The durability of the functioning of the roadway plays a huge role in the socio-economic development of any country. The solution of this problem allows to reduce the amount of costs on the reconstruction of existing roads and enables the construction of new road communications. A continuously increasing load carrying capacity and the intensity of vehicular traffic lead to a significant increase in dynamic load on the roadway. In order to exclude the damaging effects of above mentioned factors on the pavements more qualified binders are required, which allow to operate roads for a long time. One of the most common and the most promising methods of bitumen technological parameter improvement is the modification of various additives. These additives are intended for the improvement of bitumen quality indicators by the change of its structure.

Nowadays the trend of the heavy hydrocarbon feedstock is developed, designed to preserve the existing needs of humanity against the background of easily accessible standard oil depletion. These oils include, first of all, heavy oil and natural bitumen. The main disadvantages of these energy resources are the low content of fuel fractions, sulfur content, a large number of resins and asphaltenes. The presence of such materials leads to a high viscosity and low thermal stability. Unlike conventional oils, which are weakly and averagely concentrated colloidal systems, heavy oils and natural bitumen are highly concentrated disperse systems [1]. But, despite all these shortcomings, one of the main factors, covering all disadvantages are their geological volumes which far exceed conventional oil reserves [2-6]. According to many scientists and experts in the field of a heavy hydrocarbon feedstock development, it follows that the most promising trend is its processing on the production site [7-9].

In terms of economic feasibility in order to achieve this trend initially heavy hydrocarbons should be subjected to deasphalting by solvents. In this case, deasphalting viscous oil will be supplied to a refinery. The scheme is presented on Figure 1.

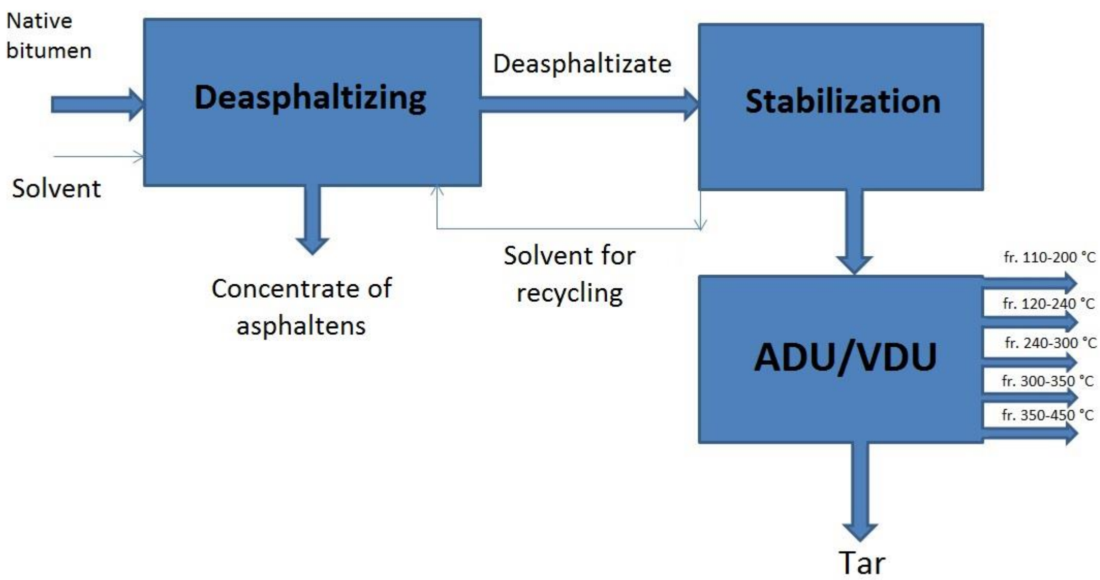

Fig. 1 – Scheme ofnativebitumen processing

METHODS OF STUDY

The aim of this work is the study possibility of a polymer-bitumen binder obtaining for asphalt concrete mixtures, based on heavy oil residue with a missing disperse phase in the form of asphaltenes. In this paper the residue of above 420 °C after the vacuum distillation of natural bitumen deasphalted oil at Ashalchinsky deposit was the object of the study [10-11]. The test samples of residue were obtained by the means of asphaltene sedimentation in 40-fold volume of petroleum ether with the boiling temperature of 40 - 70 °C.

The component composition was determined according to standard methods [12]. The amount of asphaltenes was determined by asphaltene sedimentation with 10-fold excess, the mixture of n-alkanes of C5-C7 composition. The amount of resins and oils was determined by column liquid adsorption chromatography based on silica gel of GASK brand, the fraction of 0.25 mm, using standard alkanes C5-C7 as solvents, benzene and isopropyl alcohol. According to this methodology it was determined that deasphalted oil has the following group composition: oils - 48.6 %, resins - 53.1 %, asphaltenes – 0 %. And the original tar has the following composition: oils – 31.0 %, resins - 57.9 %, asphaltenes - 11.2 %.

Ethylene-vinyl acetate copolymer with a different content of ester groups in the range from 26 to 30% acted as a polymer phase in the present work [1, 13, 14]. This copolymer has the ability to bind a large amount of oil residue dispersion medium that is explained by the formation of a polymeric structure that retains strength and elastic parameters of modified bitumen at high temperatures, ensures a high rate of binder coupling with the mineral fillers of asphalt concrete pavement.

The samples of compounded bitumen are obtained by the introduction of heavy oil residue above 420 °C into deasphaltizate from 1 to 15% of the copolymer previously crushed to a grain size less than 0.05 mm. The compounding was performed at the temperature of 160 °C with the stirring for two hours. Since the copolymer has a sufficiently high molecular weight and a significant amount of acetate groups, it may be assumed that the modification of deasphaltizate will result in the formation of bound disperse system in it. Before the preparation of samples the samples copolymer was preliminary ground to a grain size of less than 0.05 mm. Then residue deasphaltizate of Ashalchinsky oil above 420 °C was compounded with 1 – 15 % of the copolymer. The mixing was carried out at 160 °C for two hours. Since the copolymer has a sufficiently high molecular weight and a significant amount of acetate groups, it may be assumed that the deasphaltizate modification will result in the formation of bound disperse system in it. The formation of spatial structure from the copolymer in deasphalted residue is characterized by a discrete change of softening temperature and penetration values. Based on the above described assumptions, one may say the following about hydrogenate structure: a weak development of coagulation frame made of a polymer and a small degree of its structuring leads to a smaller softening and penetration temperature gradient. Thus, the transfer of strength and adhesive properties by copolymer to deasphaltizate is carried out by the means of intermolecular interactions between copolymer particles and the formation of specific spatial structures subsequently.

STUDY RESULTS AND THEIR DISCUSSION

During the first stage of the research copolymer impact on the physical and chemical properties of the modified materials was evaluated. The physical and chemical properties of tar and modified deasphaltizate obtained experimentally, as well as the requirements to bitumen according to GOST 33133-2014 are shown in Table 2.

Table 2 – Physical and chemical properties of oil tar and modified deasphaltizate

Indicators	Tar	Deasphaltizate	The content of the copolymer, %				GOST 33133-2014	
			1	BND 100/130	BND 100/130	*15*	BND 100/130	BND 70/100
Penetration, 0,1 mmat 25°C	101	369	179	95	95	84	101-130	71-100
Ring-and-ball softening point, °C	33	28	37	60	63	66	no less than 45	no less than 47
Brittleness point, °C, no higher			-24	-10	-5	15	-20	-18
Mass variation after heating, %	0.19	1.36	0.2	0.33	0.4	0.52	No more than 0,7	No more than 0,6
Changing the softening point after heatingUke,byf , °C	1.9	4.5	3	1.75	1.5	1.0	No more than 7	No more than 7
Index penetrations	-3.7	-3.5	-2.9	1.9	5.4	5.5	-1 to +1	-1 to +1

As is known, depending on such bitumen colloidal state, as "gel", "sol-gel" and "sol" the compounding mechanism is determined. The introduced modifier develops coagulation polymer grid in the bitumen of "sol-gel" and "sol" types, while polymer does not create its own grid in "gel" type bitumen, and develops the coagulating grid from asphaltenes. Therefore deasphaltizate modification with different quantity of copolymer to a predetermined softening temperature, results in the formation of bitumen with different dispersed structure with "sol-gel" and "gel" type in which penetration index is lower than minus two, from minus two and plus two. These penetration values correspond to "sol-gel" and "gel" structures with a high softening temperature and considerable elasticity. When a penetration index is above plus two the content of aromatic compounds in the maltene portion of bitumen is low one, thus the copolymer is coagulated, and the bitumen is in a "gel" state with a high softening temperature and a high plasticity. These trends of softening temperature change and deasphaltizate penetration depending on copolymer content showed that the concentration increase in the copolymer raw material is followed by its softening temperature sharp increase to 66 °C, which is conditioned by the formation of the polymer grid spatial structure in a dispersion medium of oil residue, which leads to its viscosity increase, and as a consequence, to a sharp decrease of the needle penetration depth.

The low values of weight loss indicators and the softening temperature decrease after heating indicate that the binder samples withstand the thermal stability tests (Table 2). This may be explained by assuming that a large amount of vinyl acetate in the copolymer contributes to the formation of the structure from the dispersed phase, which immobilizes the light portion of the dispersed phase light hydrocarbons. The immobilization of light hydrocarbon part of the dispersion medium system provides the system stability to evaporation at high temperatures.

High adhesive properties of binders to the stone material of asphalt concrete mixtures ensure the durability of road pavement. The following fact is noteworthy: the modified deasphaltizate by EVA copolymer has improved adhesion and low temperature properties. At that the adhesion is significantly improved with the copolymer content increase in tar. Low values of brittleness temperature are presented in the samples with a low content of copolymers which is explained by the large amount of the dispersion medium in obtained binder. The obtained binders have a high temperature range of performance. This can be explained by an effective influence of a polymer grid on bitumen at the temperature below 0 °C.

A necessary step of new binding compound study is the estimation of asphalt concrete mixtures strength characteristics on the basis of these compounds. From the standpoint of mechanics, an asphalt concrete pavement is a composite material based on mineral (stone) filler, where a binder component plays a major role [15-16, 18-19]. In general, the properties of the asphalt concrete may be considered as a consequence of internal cohesion and adsorption-adhesion forces of a binder to a stone material. The binder develops a mineral filler layer with the thickness of 2 microns using an adsorption interaction. This layer is determined by composite material strength. The parameters of this layer depend on bitumen viscosity and a binder interaction with a mineral filler which used crushed granite in practice in the asphalt concrete with the crushing mark of 100, its crushing screening, the sand with the fineness module of 1.25 and mineral limestone powder [16]. Hot dense asphaltic concrete of type B and grade II was taken as the most widely used prototype in Russia.

The resulting asphalt concrete samples containing modified binders have a high deformation ability at low temperatures, thereby preventing the cracking in the asphaltic concrete during winter period operation. The analyzed asphalt concrete mixtures demonstrate the increase of adhesion strength in the mineral and organic part of the composite material, which is explained by the basic physical and mechanical properties increase. It is noted that the increase of copolymer content in the binder to 10% of the magnitude of asphalt mixture compressive strength is higher at positive temperatures than with the use of conventional bitumen binder. In its turn, the reduction of asphalt concrete strength containing copolymer at the amount of more than 10 % can be associated with an increased binder viscosity, which greatly complicates the wetting of the mineral filler. Therefore a large part of it remains an uncovered one by a binding component. The tests revealed that the asphalt concrete coating shift resistance with the use of obtained binders is higher compared with classical bitumen binding component. It was noted that the samples containing the copolymer in a binder within the range from five to ten percent, have the highest thermal stability. The most dramatic increase in asphalt concrete strength at temperature reduction occurs in the binder with copolymer content up to 1 %. The lowest ratio of temperature sensitivity is observed in the binding sample containing copolymer in 5 %. I.e.

this sample has the resistance to shear deformation appearance at high temperatures and the resistance to cracking at low temperatures.

CONCLUSIONS

The results of performed studies showed that the obtained samples of the binders from deasphalted residue of heavy oil have improved low-temperature, high adhesion properties, and may provide high strength characteristics for asphalt concrete road coatings on their basis.

SUMMARY

Accordingly, the obtained data shows that the use of ethylene copolymers with vinyl acetate as the modifying additives of deasphalted bitumen is a promising trend, which provides a high-quality asphalt pavement.

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