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Influence Copolymers of Ethylene with Vinyl Acetate On the Physicochemical Properties of Bitumen.

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ABSTRACT

The results of experiments are presented concerning the modification of road bitumen by ethylene copolymer with vinyl acetate (EVA). This polymeric additive make a strong structure-forming influence on bitumen. At that the penetration value changes most rapidly at 25 °C. The higher the concentration of copolymer and the content of the ester groups in it, the less the penetration depth of the binder needle. The introduction of excess amount of copolymers with vinyl acetate groups develops a spatial structure conjugated with asphaltene associates, and providing the stability of all bitumen heterogeneous system. The reduction of elongation and brittleness temperature is revealed at the introduction of low molecular EVA, which allows to obtain the binders with improved low temperature properties. The most intensive change of properties is achieved by the introduction of EVA into bitumen with the molecular weight of 25,000, which is manifested in softening temperature increase with brittleness temperature reduction, and the extension of plasticity range by 8-20 °C. At the same time the introduction of granulated EVA into bitumen with high molecular weight leads to a significant increase of softening and brittleness temperature and ductility interval decrease. The study results showed that the bituminous compositions modified by EVA with a high content of vinyl acetate groups are somewhat inferior to the softening temperature and the extensibility of the compositions, modified by EVA with a low content of ester groups, because of the greater initial plasticity of the copolymer in the second case.
Keywords: road bitumen modifiers , ethylene-vinyl acetate copolymer

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INTRODUCTION

High-viscosity oils are the main source for the production of road bitumen [1-4]. Asphalt-concrete pavements are the objects in which oil bitumen operate under the highest strain. The provision of relaxation, resulting in cyclic deformation coatings is possible providing bitumen with the ability to resist violation of asphalt concrete uniformity and the formation of cracks in contact places with a foreign surface under the influence of actual loads in the operating temperature range. This problem can be solved by the introduction of polymer additives into bitumen, which are prone to the formation of a spatial flexible structure in the dispersion medium of a binder. Thus, almost all polymers produced in the industry nowadays were tested in bitumen compositions. The effect of their action is different, but, as a rule, if it is possible to obtain a homogeneous mixture, the composition has a fraction of valuable polymer properties. Among the existing classes of polymers, thermoplastic elastomers are the most effective additives for bitumen. However, they are not without drawbacks - the binders on their basis are not resistant to an oxidative effect of atmospheric oxygen, and consequently, pavements based on these materials do not have a high durability [5-8].

RESEARCH METHODS

In present work thermoplastic elastomers - ethylene copolymers with vinyl acetate (EVA) - were chosen as a polymer additive with different molecular weight and the concentration of vinyl acetate links. Physical and chemical properties of ethylene copolymer with vinyl acetate: the mass fraction of vinyl acetate makes from 7 ÷ 10 to 26 ÷ 30%; the density makes from 0.925 to 0.9500 g/cm3; melt flow rate makes from 1.0-5.0 to 12-18 g/10 min; tensile strength makes makes 11,3 ÷ 9.0 MPa; elongation at break of makes no less than 600%.

Besides, a by-product was chosen for the production of EVA - a substandard low molecular copolymer (an average molecular weight makes 200 - 30,000, penetration makes 0.1 ÷ 30 mm). In its turn, the selection of ethylene copolymers with vinyl acetate as a polymeric additive is substantiated by their properties analysis results. Copolymers with different content of acetate groups have a set of attractive properties, namely high waterproofing properties, a broad range of operating temperatures, chemical resistance, high impact resistance, the resistance to cracking at low temperatures, a good adhesion, harmlessness, low cost, and also strength and elasticity. It is known that with an increase of ester group content in the copolymer range from 7 to 30% its deformation, strength and adhesion properties are also increased.

In order to prepare modified bitumen in a laboratory a planetary mixer equipped with a thermostatic container was used. In order to obtain a homogeneous composition in the dehydrated bitumen heated to a temperature of 110-120 0C was injected with copolymers at the amount from 2 to 12 % wt. The compound temperature was further increased to 130-150 0C and stirred vigorously for 0,5-1,5 h.

Polymers were introduced into heated bitumen in a particulate form, their complete dissolution in the bitumen took place for 30-90 minutes depending on the administered amount, complete dissolution period of low molecular copolymer in the bitumen decreased, and made 15-30 minutes. Thus, the merits of this class of polymers are presented by their ability to decompose quickly and easily enough into the bitumen without the third component.

During modification EVA particles are introduced into the dispersed bitumen system. These particles are capable to absorb the part of maltene fractions to form a three-dimensional spatial structural grid due to the physical-chemical bonds between vinyl acetate fragments of copolymer macromolecules and the active centers of high molecular components of bitumen, which in the future will determine its improved performances.

Electronic-microscopic studies were conducted in the paper for the visual evaluation of the modifying effect. The microstructure of obtained samples was photographed and studied using MIM 7 microscope.

STUDY RESUYLTS AND THEIR DISCUSSION

The photographs of modified compound structure with different polymer composition obtained by microscopy showed that the introduction of high molecular (granulated) EVA additives results in the formation

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of the spatial structural grid in the bitumen. Further increase of copolymer concentration only leads to the thickening of already set modified structure at 2% wt. Despite the visual homogeneity of the modified sample, EVA forms the dispersed phase in bitumen, the copolymer particles are enveloped by bitumen medium, an additional structural formation of the system takes place through the development of an independent structural mesh of a polymer within the coagulation framework of asphltenes. The introduction into the binding structure of excess copolymer amount with vinyl acetate groups forms a spatial structure conjugated with asphaltene associates. This structure ensures the stability of the entire heterogeneous bitumen system.

The features of basic physical and mechanical properties of modified bitumen obtained samples are shown on Figure 1 and 2. During the research of bitumen properties standard test methods were used. It should be noted that the curves of needle penetration depth, extensibility, softening temperature change for the bitumen modified with different amounts of the copolymer are of the same nature, the difference is usually, only in the absolute values of property indicators. On the other hand, a revealed extreme dependence of the binder performance properties on the vinyl acetate group content of the copolymer is related, in our opinion, with the introduction of excessive amounts of active molecular groups into bitumen. These groups are capable to create the field of additional associative forces that provide an enhanced adhesion and a dispersion system stability.

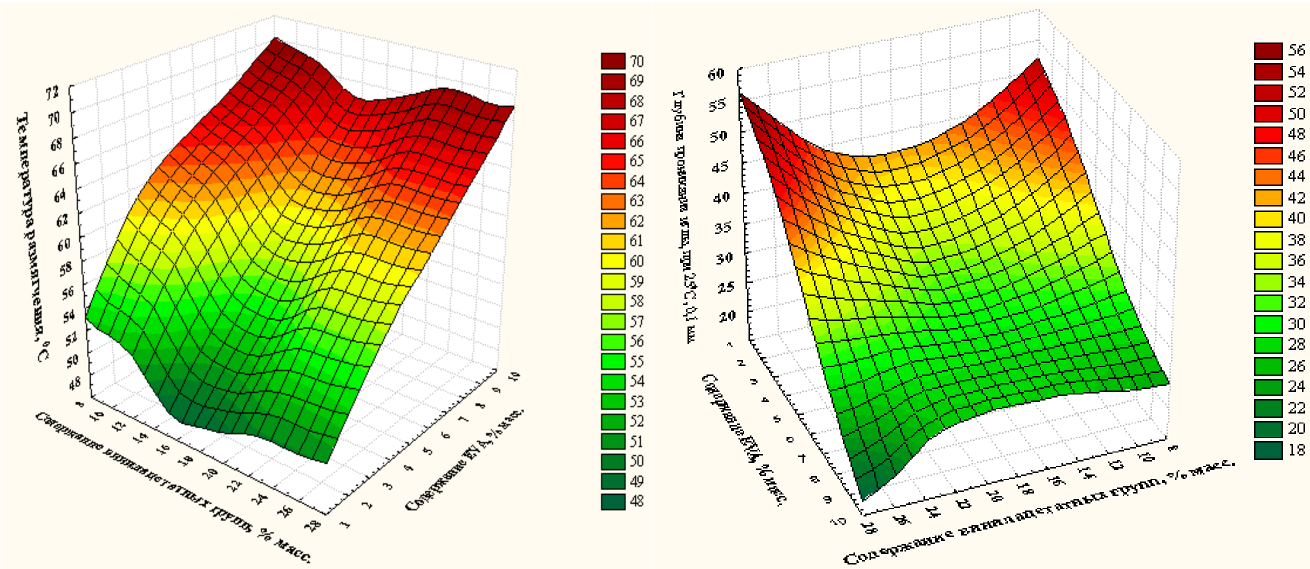

Fig 1 - Dependence of softening temperature and the penetration depth of the needle at 25 ° C ENPU bitumen concentration of EVA with different content of vinyl acetate groups

EVA has a very strong structure-forming influence on the bitumen. At that penetration value changes most rapidly at 25 °C, the higher the concentration of copolymer and the content of the ester groups there, the less the depth of a binder needle penetration. The observed pattern is associated with the structural type of bitumen, its group chemical composition and the nature of intermolecular interactions in vinyl acetate EVA fragments with the active centers of high-molecular bitumen components. The increase of EVA content of more than 2% wt. provides a structural transition a binder from the structural type sol-gel with the penetration index from -2 to +2 into gel-type structure with the penetration index of more than +2. The possibility of such a structural transition by the way of copolymer concentration change may be an extremely useful and effective means to control the properties of the binder when it is used in various climatic conditions.

EVA introduction into the bitumen leads to a significant temperature increase and bitumen softening (Figure 2). A non-linear dependence character of this index on the content of vinyl acetate groups in EVA should also be mentioned. So with the increase of vinyl acetate groups in the copolymer up to 16% wt. the reduction of softening temperature is visible, a further increase of ester group concentration results in a significant increase of the binder softening temperature. The raise of softening temperature for the modified compositions may be related with dissolving, copolymer dispersing int maltene fraction bitumens. Let's note that the formation process of the spatial structure in modified bitumen is associated with a very sharp decrease of the binder elongation at 25 °C (Figure 2), which indicates its structure formation increase. In this case, the break has a plastic nature.

EVA bitumen modification effect is confirmed by the data of other physical and chemical parameters of brittleness temperature (Figure 2), the index of penetration, the change of softening temperature and the mass after heating. Apparently, a large amount of vinyl acetate links in copolymer immobilizes a significant portion of bitumen light hydrocarbons, resulting in a marked reduction of indicators indirectly characterizing the aging of a binder with EVA content increase to 12% wt. in the latter.

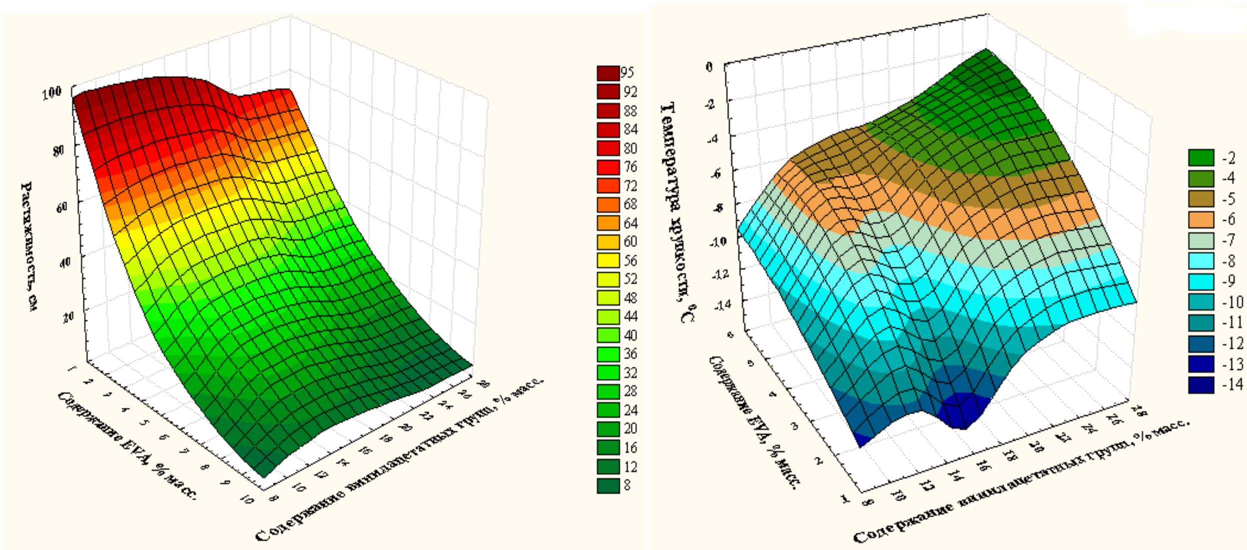

Fig. 2 - Dependence of elongation and temperature brittleness of bitumen ENPU by EVA concentration with different content of vinyl acetate groups

It is necessary to emphasize that the structure forming EVA impact at low temperatures which manifests itself in the increasing fragility temperature of bitumen with the increase of vinyl acetate content in copolymer (see Figure 2). In its turn, Fraas brittleness temperature should be equal to or lower than the temperature of coating operation area coldest day. For example, EVA modified bitumen in the selected quantity interval does not meet standard requirements according to fragility temperature values.

CONCLUSIONS

In road bitumen standards, the temperature dependence of their rheological properties is noted by embrittlement and softening temperature through the following relationship: the lower the embrittlement temperature and the higher softening temperature, i.e. the wider the plasticity range, the more preferable is the binder for asphalt mixtures. Thus, the binders obtained by bitumen modification have a wide plasticity interval of 72 °C and more, compared to the initial bitumen with the plasticity interval of 60 °C.

The results of studies in this part of the work showed that the bituminous compositions modified by EVA with a high content of vinyl acetate groups are somewhat inferior by softening temperature and extensibility to the compositions, modified by EVA with a low content of ester groups, because of the greater initial plasticity of the copolymer in the second case. It should also be noted that the bitumen, modified by polymers begin to acquire their properties and, as several researchers noted, the standard bitumen test methods do not allow to reflect these changes completely.

SUMMARY

The introduction of EVA into bitumen leads to elongation and brittleness temperature decrease. At that the plasticity interval in these compositions with copolymer content up to 5% wt., is 5-15 °C higher than that of pure bitumen, mainly due to softening temperature increase. This allows to obtain the binders with improved low temperature properties. The most intensive change of properties is achieved by the introduction of EVA into bitumen with the molecular weight of 25,000, which is manifested in softening temperature increase with the reduction of brittleness temperature, and the extension of plasticity range by 8-20 °C. At the same time the introduction of the granulated EVA into bitumen high molecular weight leads to a significant increase of softening and brittleness temperatures and to ductility interval decrease.

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