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Theoretical Substantiation of the Possibility of Regulating the Properties of Cold Coating Polymer Bitumen Emulsion Mastics.

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ABSTRACT

Understanding the effect of the structure and properties of the basic structure-forming components of bitumen on its physical and mechanical properties allow carrying out targeted control of properties of the complex organomineral binders based on them. Increase of mastic cohesive strength depending on the negative and positive boundary values of type is possible due to the hardening of the asphaltene coagulation carcass by adding mineral filler having a particle size comparable to the one of asphaltenes and the distance between them. Increase of deformability of complex organomineral binder is expected due to the addition of the polymer solution in the plasticizer into the bitumen, which shall improve the elasticity of the dispersion medium, and a small concentration of "acidic" filler creates a thick layer without reducing the ductility of the dispersion medium, and, at the same time, the filler grains are the orientation centers of the polymer fibers, and that creates the spatial elastic structure in a dispersion medium. Increase of adhesion of bitumen binder to concrete surface of transport facilities structures is possible due to a uniform application and small thickness of binder film on the insulated surface, which determines the type of material, such as an aqueous emulsion based on a complex organomineral binder.

Keywords: Mastic, waterproofing, polymer, filler, plasticizer.

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INTRODUCTION

The main components of coating waterproofing polymer bitumen mastics are bitumen, polymer and filler. The preparation technology of cold polymer bitumen mastic involves making an aqueous emulsion based on an integrated organic-binder, which is composed of the components listed above. Therefore, the properties of such compositions depend substantially on the structure and properties of the matrix bitumen, the amount and type of polymer and filler used, and the mastic preparation technology. Widely used hot coating mastics have some significant drawbacks, the main of which are high temperature, toxicity, complexity of their preparation and use technology, which gave occasion to the development of cold coating polymer bitumen emulsion mastics including a separate preparation of bitumen complex organic binder with aqueous solution of an emulsifier, a plasticizer and finely divided filler with their further combining in the disperser.

The main requirements imposed on cold coating polymer bitumen emulsion mastics are strong adhesion with the surface insulated, reliable operation without thermal cracking and plastic deformation in a wide range of operating temperatures, and manufacturability of their application. It is obvious that the strength of the adhesive bond with the insulated surface will be determined by the choice of adhesive additives. The targeted regulation of the high and low temperature properties of the mastic is achieved considering properties features of bitumen having different structural type, kind and amount of polymer and filler due to the dispersion degree of the latter.

MAIN BODY

Resistance of bitumen as a dispersed system depends on the degree of affinity of maltenes (amount of oils and resins) and asphaltenes, that can be regarded with a certain approximation as the difference between the degree of asphaltenes and maltenes aromaticity (ratio of number of carbon atoms in the aromatic structure to the total number of carbon atoms in a molecule) [2-4]. Operating experience of waterproof coatings indicates that the influence of low temperatures and humidity may cause cracks. To prolong lifetime of waterproofing it is necessary to create a strong organomineral mixtures. The chemical composition of the bitumen, certainly, affects its properties, however, the crucial factor is not only the amount of particular components in the system, but also their structures and the relation between them. The most simple dependence can be seen between the softening temperature and the composition of bitumen. In the first approximation we may assume that the softening temperature increases together with the concentration of asphaltenes in the bitumen. Depending on the concentration of asphaltene bitumen may form structures such as a sol, sol-gel or gel. Destruction of these structures requires different energy, therefore bitumen with a high content of asphaltenes, having a gel-like structure, are characterized by a higher softening point.

The effect of bitumen composition on their brittleness temperature and penetration is more difficult, as these values depend largely on the properties of the dispersion medium. Basically, the brittleness temperature of bitumen, as well as the softening point, increases with the amount of the dispersed phase (asphaltenes) as their hard carcass becomes more brittle. However, this phenomenon can be seen from the other side: the brittleness temperature rises because the amount of the dispersion medium decreases and its solidus temperature rises. In other words, the brittleness temperature characterizes the moment when the entire system loses its flexibility and becomes an amorphous solid body. Penetration, being essentially the viscosity parameter, also characterizes the change in the plasticity of the medium depending on change in its quantity and composition. To increase the penetration and reduce brittleness temperature at a predetermined softening point it is necessary to reduce the viscosity and the pour point of the dispersion medium [5, 6].

Modern physicochemical bitumen production technologies allow improving properties of binder and widening the raw material recourses of road construction. The existence of genetic dependence of formation of certain structure in oxidized bitumen on the disperse state of feed materials gives background to the predicted control of bitumen structure through targeted regulation of raw material dispersion. Complex of properties inherent to bitumen I "gel", II "sol" and type III "sol-gel", has been generalized by V.A. Zolotarev [7, 8] due to standardized properties, which shows that the three-component system - asphaltenes (A), resins (R) and oils (O) can show the following relations: penetration increases, softening point decreases, and the brittleness temperature increases with the increase of O/A ratio, and are almost independent of R. Extensibility reaches its maximum (> 100 cm) at a O/A ratio in the range 2 to 5. Such behavior is specific to the bitumen with "sol" structure.

Bitumen with “gel” structure is slightly affected by resin content. Generally, plastic range is directly proportional to asphaltene content, and, in some cases, the increase in the O/A ratio leads to the increase in plastic range.

The simplest indicator of the change in the structural type of “sol” to “gel” is the increase in the penetration index, which is standardized for construction and road bitumen [9, 10].

Bitumen modifier shall satisfy the main conditions such as cheapness of raw material base, ease of modifier technological process and environmental safety. Unfortunately, many of the improving substances meet only one or two conditions, ignoring other indicators. The main objective can be a search for universal multifunctional modifier.

One of the modification examples is the introduction of paraffin waxes, FT-paraffines into the bitumen, intended to improve the mechanical characteristics of bitumens at moderate operating temperatures and reduce the viscosity of the binder at high processing temperatures. Introduction of high-melting-temperature paraffin additives to 3% standard bitumen causes their practical transition in terms of penetration index to a more grease mark, sharply improves their softening temperature, decreases ductility to a level below the regulatory requirements, enhances penetration index due to vast softening temperature to excessively high and unacceptable for conventional bitumen values. However, paraffin additives reduce the preparation technological temperature of asphalt mixtures and coatings rather than improve the quality of bitumen and insignificantly compensate energy costs.

Polymer modifiers are high in demand on the modern road construction market. They can be divided into two major groups: thermosetting, solidifying irreversibly at a certain temperature (increase deicing pavement properties when used in surface finish), and thermoplastic, which can be softened reversibly many times and become plastic under the influence of heat (used in combination with the bitumen forming the mixture of more or less viscous liquid at a high temperature). The most typical name for such compositions is a polymer-modified asphalt binder (PMAB), which is most encountered in the literature. To properly assess the effectiveness of different polymers in relation to a particular bitumen we should consider the composition and structure of the original bitumen. Chromatographic analysis is the most commonly used method for these purposes, which allows sharing bitumen into two main fractions: the asphaltene (precipitated) and maltene (soluble). This must be taken into account when adding any polymer compounds. The addition of polymers with molecular weights similar or higher than those of asphaltene leads to the phase imbalance, since both the polymer and asphalt have the ability to swell in maltene phase, thereby affecting its solubility.

For the preparation of polymer modified bitumen waterproofing mastics it is advisable to use polymers of thermoplastic elastomers (styrene-butadiene-styrene). This type of two-phase polymers is a thermoplastic copolymer block with polystyrene spherical domains dispersed in a polybutadiene matrix. Thermoplastic elastomers give elasticity and strength to the matrix filled with them by linking molecules into three-dimensional network [11]. This is achieved through the consolidation of the polystyrene blocks in separate domains, which ensures the creation of intermolecular bonds for three-dimensional matrix of polybutadiene. Blocks of polystyrene give strength to the polymer network, and medium polybutadiene blocks - elasticity.

Since the beginning of combining components of polymer-modified bitumen composition a multiphase heterogeneous system arises, which has maltene portion of bitumen as a dispersed medium, and asphaltenes and polymer beads as a dispersed phase. Concentration of asphaltenes in the bitumen composition, its viscosity and the temperature have significant effect on the rate of diffusion, the swelling and dissolution of the polymer. The rate of the above processes increases as the temperature rises. It is necessary to limit the heating temperature of the bitumen to 195 °C, in order to avoid the danger, occurring while prolonged stirring, of thermal degradation of the polymer and the partial bitumen aging.

After completing the diffusion phase of low molecular weight components of the bitumen in a polymer bead another phase starts, when low-molecular components of bitumen penetrate into the surface layer of styrene-butadiene-styrene macromolecules, which increases the mobility of the macromolecules of

the polymer [12]. This initiates the swelling of a polymer under the influence of saturated and aromatic bitumen hydrocarbons [13], which is accompanied by a decrease in free energy in the polymer-solvent system [14, 15]. The polymer macromolecules dissolved after swelling begin to diffuse into the bitumen. This process ends after reaching a uniform polymer concentration in the entire volume of the bitumen. As a result of dissolution a polymer network is created in the bitumen, providing it with flexibility and elasticity, and improving its heat resistance. At a concentration of SBS more than 6-10% a polymer has a dominant influence on the properties of the polymer-modified bitumen composition [16, 17]. Critical content of polymer, which causes inversion of the composition phases, depends on the viscosity of the matrix bitumen. In this case, SBS-type polymers with a branched structure promotes a greater increase in the softening point of polymer-modified bitumen compositions in comparison with the linear SBS, which has determined their use in complex organomineral binder.

An equally important factor influencing the choice of bitumen and its polymer-modified binder is adhesion, which is a parameter that determines the durability of building structures and pavement. It is explained by the formation of a double electric field on the separation surface of the bitumen film and solid mineral material. Properties of a thin layer of bitumen, adsorptive bonded with mineral material, depend on the chemical and mineral composition, the surface structure of the mineral material, the structure and properties of bitumen as well as the conditions of their interaction on the separation surface of phases. The adhesive properties of the bitumen consequently will depend on the polarity of its components and a modifier used. The adhesion compounds, in which there are simultaneously strong chemical and recoverable (resettable) molecular bonds with low activation energy (for example, due to functional groups with dynamic hydrogen atom - the carboxyl and hydroxyl groups), have the optimum properties. To exhibit binding properties the organic substance should contain an optimum number of functional groups and atoms with lone electron pair, nitrogen and sulfur atoms, and consist of flexible macromolecules.

This simplified model, however, allows predicting and adjusting properties of synthetic binding materials and choosing them. However, using only the polymer-modified bitumen composition as a waterproofing material does not solve the problem of increasing the cohesive strength, weather and shift resistance of surface waterproofing, enhancing its resistance to dynamic loads and effects of alternating temperatures. For this purpose fine-dispersion fillers are introduced into polymer-modified asphalt binder. In this case, the properties of the mastic are decisively affected by: a) the concentration of the filler; b) the particle size of low molecular weight oils, which give plasticity to a composition and elasticity and flexibility to mastic, deteriorates at a high concentration of the filler due to the adsorption on the surface of its grains, since the layer of adsorbed bitumen is characterized by a high viscosity due to the high surface energy of the filler. At the same time, the layer of film bitumen, which is directly on the surface of the filler particles, is characterized by the highest stiffness. When the concentration of filler decreases together with the increase in distance from its surface, the attractive force decreases, therefore, the layer of bulk bitumen, with smaller concentrations of filler, has a predominant importance, and ensures deformability of composition, and, in case of filler concentrations above the critical value, the system changes from plastic state into the viscous one, which leads to a sharp increase in the rigidity of the material and decrease in its deformability. This occurs by reducing the distance between particles of the filler, and, in case of sufficiently high concentrations, to coagulation interaction between these particles through the membranes of structured bitumen. The above facts are confirmed by the results of studies [18], which show that when adding 30% limestone filler in bitumen BN 70/30, its viscosity increases sharply as a result of interaction of individual filler particles through their diffuse structured membranes.

Adding a large amount of mineral filler (more than 30%) in the polymer-modified bitumen composition having poor maltene fraction (compared with matrix bitumen) leads to a sharp increase in its viscosity, which makes mastic non-manufacturable. In addition, increase in the filler content should lead to a reduction of deformability of polymer-modified asphalt mastics at low temperatures. Increase of deformability of the "filled" polymer-modified asphalt mastic is achieved by adding polymer solutions in plasticizers into their structure. This effect is achieved by increasing the low molecular weight components with low glass transition temperature due to the high kinetic energy of thermal motion of the molecules in the mastic. This results in increasing the mastic plasticity [19 – 21], since the plasticizer replaces some part of maltene fraction adsorbed by polymer and filler.

In connection with the foregoing a scientific hypothesis was formulated: the ability to simultaneously ensure the deformability and thermal resistance of waterproofing polymer-modified asphalt mastics at low and high operating temperatures, respectively, by combining "sol-gel" bitumen, a plasticizer, thermoplastic elastomers and powdered filler. Such waterproofing polymer-modified asphalt mastic will simultaneously have high heat resistance and flexibility due to the formation of three dimensional interpenetrating structures of asphaltenes, polymer and filler. According to A.S. Kolbanovskaya [1], bitumens are two-component dispersion systems, which can be classified into three types of dispersion structures depending on the volumetric ratio of the phase and the medium. A.S. Kolbanovskaya writes: "the optimum set of properties that characterize the performance of heat and crack resistance and resistance to aging processes is common to structural type III bitumen with the content of the dispersed phase - asphaltenes coinciding with the range of the critical structuring concentration (CSC) and makes $(C_v) 0.487 < C_v^{**} < 0.613$ in terms of volume of asphaltenes in the bitumen.

These data were obtained by the authors [22] after analyzing the Mooney formula for regular

concentrated systems, both for small and for large concentrations, in which the values $K = \frac{1}{C_v^{**}}$ are within $1.35 \leq K \leq 1.91$:

$$\eta^* = \exp\left(\frac{a \cdot c_v}{1 - K \cdot c_v}\right),$$

(1)

$$\eta^* = \frac{\eta}{\eta_s}$$

where η_s – relative shear viscosity of the system;

η – viscosity of the dispersed system;

η_s – viscosity of the dispersion medium;

$a = 2.5$

C_v – volume concentration of asphaltenes;

$$K = \frac{1}{C_v^{**}}$$

– a constant, selected according to the experimental data ($1.35 < K < 1.91$);

C_v^{**} – the critical volume concentration of spherical particles, when the particles have already touched each other, and the viscosity of the system sharply increases compared with the viscosity of the dispersion medium ($\eta^* \rightarrow \infty$).

In this case, the volume concentration $C_v^{**} = 0.487$ - is minimum concentration of asphaltenes required for generating the coagulation framework that will provide a minimum strength and deformation resistance at high and low operating temperatures [22]. $C_v^{**} = 0.613$ - corresponds to the volume of the critical concentration of asphaltenes, in which the thickness of the solvation shells (as a result of physical and chemical interactions) of asphaltenes and aromatic hydrocarbons contained in the oils and resins of dispersion medium due to their immobilization by asphaltenes will already be minimal [21].

Considering the asphaltene complexes in the dispersion medium, as a set of randomly arranged spherical particles, B.S. Radovsky obtained the value $c_v^{**} = 0,613$ as the most probable bulk packing when there is no change in volume during shift (the aggregate shows no dilatancy). This value c_v^{**} is right with the data of multiple experimental data.

The Mooney formula for bitumen shall be as follows:

$$\eta^* = \exp\left(\frac{2,5 \cdot c_m}{1 - 1,63 \cdot c_m}\right)$$

(2)

Since the method of adsorption-chromatographic analysis shows asphaltene weight content in the bitumen considering boundary criteria of variation range of asphaltene volume concentration, the optimum asphaltene content was calculated by weight based on the coefficients: bulk [λ] (the ratio of the volume of asphalt complex to the asphaltene volume, [λ] ≈ 3) and d (the ratio of the bitumen density to the density of the asphaltene, $d \approx 0,9$).

In this case, the expression of boundary criteria of optimal asphaltene weight content for structural type III bitumen shall be as follows [22, 23]:

$$\frac{0,487}{3 \cdot 0,9} \leq c_m \leq \frac{0,613}{3 \cdot 0,9}$$

Boundary values of asphaltene weight content will be determined mainly by the lyophilic degree (swelling) [24] of asphaltenes in the dispersion medium depending on the nature of the original oil and the appropriate bitumen manufacture technology, which ensures obtaining structural type III bitumen.

CONCLUSION

Theoretical ideas on the structure of bitumens and their properties depending on the type of dispersed structure and features of the phase and environment interaction allow determining the way of targeted control of performance characteristics of composite organomineral binder (COMB). Improvement of cohesive (intramolecular) strength of bitumen and, hence, its shift resistance at high summer temperatures, as well as increase of their resistance to dynamic loads is possible when hardening the asphaltene coagulation carcass by adding the fine mineral fillers, having particle size comparable to the one of asphaltenes and the distance between them, into the bitumen.

Increase of deformation property of complex organomineral binder, associated with the improvement of its flexibility (which is especially important in the context of the material performance at low negative temperatures), will be provided by increasing the elasticity of the bitumen dispersion medium when adding a solution of required number of polymers into the bitumen.

SUMMARY

- Understanding the effect of the structure and properties of the basic structure-forming components of bitumen on its physical and mechanical properties allow carrying out targeted control of properties of the complex organomineral binders based on them.

- Increase of mastic cohesive strength depending on the negative and positive boundary values of type is possible due to the hardening of the asphaltene coagulation carcass by adding mineral filler having a particle size comparable to the one of asphaltenes and the distance between them.
- Increase of deformability of complex organomineral binder is expected due to the addition of the polymer solution in the plasticizer into the bitumen, which shall improve the elasticity of the dispersion medium, and a small concentration of "acidic" filler creates a thick layer without reducing the ductility of the dispersion medium, and, at the same time, the filler grains are the orientation centers of the polymer fibers, and that creates the spatial elastic structure in a dispersion medium.
- Increase of adhesion of bitumen binder to concrete surface of transport facilities structures is possible due to a uniform application and small thickness of binder film on the insulated surface, which determines the type of material, such as an aqueous emulsion based on a complex organomineral binder.

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