Abstract

The theoretical postulates of designing of modified paving concrete, made of organic bindings by combined modification of asphalt- and tar-concrete have been formed, namely: by modification of binding polymers, integrated with them; doping into the composition of bindings the complex additives, consisting of polymer and active dispersed filling agent; superficial activation with mineral powder by oligomers and polymers. It has been proved experimentally that complex and modified asphalt-concrete and tar-concrete are characterized by elevated values of resistance to water and frost, resistance to thermooxidizing aging; are distinguished for the wide interval of binding and elastic behaviour of paving, uprated of shift resistance and elasticity index.

Keywords: paving concrete at organic binding agents, modification, oligomer, polymer, longevity.

The structural and mechanical properties of paving concrete at organic bindings from their operational conditions in structural course of paving concrete must provide shift resistance at high positive and crack and fracture resistance at negative temperatures, water-, frost-, atmospheric- and wear-tear resistance and also calculation values of elasticity index and strength limit to bending at paving tension [1-5].

Integral features of asphalt-concrete paving, determining their longevity are: deformation criteria of shift resistance [6]; glasstemperature determined as $R_{\text{max}} = f(T)$ (where $R_{\text{max}}$ is a maximal value of the strength limit to bending at paving tension [1-5].

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bending at a tension curve, T is testing temperature) and the glazing region determined at dependence \( Eg E^* = f(T) \) (where \( E^* \) is a dynamic elasticity modulus), is equal to temperature when elasticity module value reaches \( 10^4 \) MPa [3, 7, 8]; the coefficients of water stability at protracted water saturation and frost-resistance [9] having regard to pulsating hydrodynamic pressures to asphalt-concrete [10]; the wear-and-tear coefficient of roadway paving [11]; stability criteria of material against thermooxidant factors is an air-accessibility coefficient [12] and the critical loss at asphalt-concrete covering of bitumen [13, 14]; tolerated elastic sag, shift stress in spreading ground and poorly bound materials of structural layers, the layers strength from monolith agents to tension at bend with introduction of a dynamic coefficient to static load and agent fatigue coefficient [15-17].

Properties of asphalt- and tar-concrete are identified, first of all, by matrix quality represented by organic binding (OB) and mineral powder (MP). In this case, the asphalt-concrete production with given structure and properties are reached at optimal quantitative relationship between micro-, mezo- and macro-structures, namely: at designing of lasting of asphalt-concrete and tar-concrete it is expediently to specify such structure of concrete that is represented by optimal characteristics of macro-structure, micro-structure and threshold space [3, 18, 19]. It is necessary to make a stable spatial framework at asphalt-concrete, strain and relaive with high adhesive and cohesive properties of asphalt- and tar-binding agent and a volume of residual pores at concrete must be minimal.

To produce shift and stable concrete it should be designed the II type of macro-structure of asphalt-concrete (tar-concrete) which will allow to use efficiently as properties of films of organic binding agent dividing polydisperse mineral particles and three dimensional frame formed by grains of broken stone and facilitating to increase of shift and stable at the expense of increase of sliding planes and their roughness (maximal values of deformation index are reached, internal friction and catching being the formulation of Professor Zolotaryov V.A. [3]).

On qualitative components and optimal structure of concrete, physical and chemical modification of “solid” and “structural” organic binding agent with polymeric additives (bitumen by temperature controlled formations and reactioncapable; coal-mining binding agents – polyvinyl chloride or polystyrene and complex additives (polymer + active disperse filler) and also with energy stepping-up of interaction at the interface of phases (IP) organic binding agent is the mineral powder activated with oligomer, which contains functional groups (carbamiidoformaldehyde resin (CFR), epoxides (E), stillage residues of styrene rectification (SRSR), etc. or polymerbearing wastes of production of epoxides and etc., or polymer solutions, e.g. SKMS-30, Elvaloy AM and others is the most advantageous way of control structural formation of asphalt-concrete and tar-concrete [18-23].

The necessary condition of efficient impact of polymer to characteristics of organic binding agents is compatibility of these components which is determined first of all by capability of polymer to dissolve at the binding agent up to molecular and abovementomolecular level. Just only at this condition one can get considerable improvement of structure and properties of organic binding agents (e.g. parameters equality of polymer solubility and components (solvents) of dispersion medium OB). Optimal temperature and temporary conditions of coincidence should provide solubilization of polymer in OB without destruction of the last at attainment of maximal value of bitumen and tar-polymer binding agent of elasticity.

Macro-molecules of polymer at OB medium must show tendency to association. Substances of this sort can be high-molecular compounds containing in their formulation functional group (NH, OH, CCL, etc.) for example, polyvinylchloride, diastratum, chlorinated rubbers at their modification of the coal-mining binding agents, or, for example Elvaloy AM at bitumen modification. Macro-molecules of polymer in the OB medium must have display tendencies to association. It will allow at minimal content of polymer at OB to form thermal fluctuating spatial net, the strength of which will be determined by strength of bonding in the knots of net (even at elevated temperatures) and by number of knots and elasticity of flexibility of networks between them (at low temperatures). Specifically, at production of bitumenpolymeric binding agents, polymer should form at polymer such structural net which preserves strength at temperature not lower 60°C and elasticity up to minus 60°C [21].

The structure of tar-polymeric (TP) and bitumen-polymeric (BP) binding agents should be characterized by optimal combination of changed by polymer dispersion medium of OB structurally and mechanical characteristics of disperses of dispersion phase of OB. To do this, OB should have optimal and structural medium.

Structural network of polymer should be formed at OB after finishing of consolidation of asphalt-, tar-concrete mixture or reversible being destructed at critical stresses.

Injection of polymer at OB should increase or does not lower its adhesion to the surface of mineral material.

TP (BP) at storage at bitumen - boilers should be thermostable and kinetic thermostable.
At modification of low-binding OB together with polymers, it is necessary to inject active dispersion fillers (technical sulfur, wood hydrolytic lignin, distillation cubic residues of phthalic anhydride, etc. Dispersion filler should be moisten by tar-polymeric (bitumen-polymeric) medium well, that will facilitate to its more even distribution in the OB volume. To provide sedimental stability of filled DPBA (BPBA), density of filler should be compared with density of modified bitumen (tar-polymeric) binding agent. The filler should contain polar and even reaction capable groups, promoting to strengthening of bond at bitumen polymeric (tar polymeric) binding agent. Strengthening of structuring action can be reached by its maximal dispersion with allowance for aggregating at storage. The dimension of the filler particles should be within the range of (1-100)·10⁻⁶ m. Injection of optimal concentration of dispersion filler to (BPBA) or TPBA of interlayer of plasticized polymer [20, 22]. At bitumen-polymeric (tar-polymeric) binding agent the three dimensional conjugate net spring-up, which determines manufacturing properties of the concrete mixes and structural and mechanical indices of concrete.

The decisive significance for the physical mechanical properties of composite materials is state and properties of boundary layers on the surface of phases division.

According to the offered conceptual pattern [20] (Fig. 1), activation with solutions of oligomers or polymers of mineral powder surface will bring to better coincidence of activated MP with modified organic binding agents (at correct selection activator and modifier), e.g. with tar and polyvinylchloride one, that will provide its complete moistening by tar-polymeric binding agent (DPBA). In the result of intermolecular interaction and diffusive processes on the boundary of phases “activated” MP – modified binding agent structural and strengthening layer, providing high adhesive strength at PRF of asphalt- and tar-concrete ([2], Fig. 1).

The research has shown that at optimal proportion of grinding packings and milled material (limestone) at dispersing during four hours the optimal size of surface of MP has been reached. Milling of MP at the activator medium transforms to decrease of its integral surface in comparison with non-activated MP, because of calmatation of pores and capillary tubes of MP particles by molecules of oligomers.

Dependence of strength limit at compression of tar-concrete from mass concentration of activators passes over maximum [23].

![Fig. 1. Assuming scheme of formation of interphase contact layer in the system "tar-polyvinylchloride (PVC) binding agent – mineral powder activated by oligomer": 1 – particle of mineral powder; 2, 3, 4 – structural, diffusive and solid layers of binding agent, correspondingly; 5 – polar substance of tar; 6 – alpha-fraction; 7 – beta-fraction; 8 – associative complex; 9 – crystal of polycyclic hydrocarbon; 10, 11 – fragments of coagulation and condensation structures; 12 – oligomer layer of MP surface activator; 13 – a pore structures filled with oligomer; 14 – a fragment of polymeric net; 15, 16 – fragments of structures with autogezionic interactions.](image-url)
Optimal concentration of an activator on the MP surface depends upon chemical and mineralogical composition, of MP structure and capability of oligomer or polymer to form hemoabsorption bonds at the phases division surface. Optimal mass concentration of CF-MT at the dolomite dust surface – 1% and POES – 2%.

Fig. 2. Dependence of strength limit at compression of fine-aggregate tar-concrete R from mass concentration at the surface of mineral powder (dolomite dust) of polymer containing industrial wastes of epoxy resins C\textsubscript{mf}: 1, 2, 3 – 0°C, 20°C, 50°C, correspondingly; viscosity of tar at concrete C\textsubscript{m0} = 180c.

At the same time, the optimal mass concentration at the surface of limestone MS – 0.5%, POES – 1%, of butadiene-methylstyrol rubber SKMS-30 – 0.5%. At the given concentration of activator at the surface MP oleafilling layer KF-MT, POES, SKMS-30 is formed which facilitates to strengthening of coagulating of structural forming at tar- and asphalt-concrete.

Electronic photographs show that at mass concentration, for instance, KF-MT 0.25% to MP, there is a partial activation of surface of mineral powder with oligomer molecules (Fig. 3) [24]. Further increase of content at system C\textsubscript{mf}, % «MF-KF-MT» leads both to formation at the surface MP the optimal structural and strengthening layer KF-MT, sorbated at larger part of mineral powder and to formation of polymolecular layers of oligomer at the surface of MP (characteristic even of oligomer layers formation, if concentration KF-MT in binary mixes MP-KF-MT is 1.25%) (Fig. 3).

Oligomer layers, being in free state, are planes of sliding at concrete deformation with complex modified microstructure, that and makes oneself out at strength of tar-concrete (Fig. 2).

Fig. 3. Electronic micro-photographs of activated KF-MT of limestone mineral powder (x900): a, b, c – mass concentration KF-MT at the surface IMP 0.25%, 0.5% and 1.25%, respectively.
Calorimetry research of the system: tar $C_{10}^{30} = 215^\circ C$ with 1.5% of PVX (1); «tar, $C_{30}^{10} = 215^\circ C$ with 1.5% of PVC and 60% of dolomite dust» (2); «tar, $C_{30}^{10} = 215^\circ C$ with 1.5% of PVC and 60% of dolomite dust, activated of 2% POES» (3) have shown that temperature of dissolution of PVX at of the systems 1, 2, 3 set up 110-115°C, 125-135°C and 150-160°C, respectively.

It witnesses of stronger energetic interaction at the surface of phases division in the system of “tar-polymeric binding agent – MP, activated oligomer”.

It is confirmed by electronic and microscopic research. So, for instance, tar-polyvinylchloride binding agent forms the complicated adsorption and solvated film at the surface of activated mineral powder (Fig. 5). Simultaneously in the system, where mineral powder is not activated, surface layer of tar-polymeric binding agent is not continuous. There are some sections of mineral powder which are not covered with TPBA.

The reological methods have adjusted that thickness of TPBA layer at the surface of neutralization station sludge (SN), activated by 2% of POES is at the temperature 25 °C $h_{35} = 3.22 \times 10^{-6}$ m, at 40 °C $h_{40} = 2.87 \times 10^{-6}$ m. If SN is not activated, then $h_{35} = 1.66 \times 10^{-6}$ m, and $h_{40} = 1.28 \times 10^{-6}$ m [26].

Thus, efficient way of increase of adhesion and cohesion of modified organic binding agent, providing elasticity of asphalt-binding agent and tar-polymeric binding agent, and strong bond at the surface of phases division “modified bitumen (tar) – mineral material” is activation of the mineral powder surface with oligomers containing functional groups (AD, POES, KORS, KF-MT) and polymer (SKMS-30). At optimal concentration of activators at the mineral powder surface, the structural layer of modifier leading to strengthening of intermolecular interaction at surface of phases division “modified organic binding agent – mineral powder”.

Particularly, asphalt-concrete mixes with optimal combination macro-structure (asphalt-concrete of B type with concentration of broken stone of fraction of 5-15 mm – 40%) and micro-structure presented bitumen polymeric OB (bitumen is modified 2% by mass by butadiene-methylstiroil rubbers SKMS-30 and 40% by mass by technical sulfur) and activated by 0,5% SKMS-30 MP are distinguished by increased workability and compaction in wider range of temperatures (60-130°C) in comparison with traditional hot asphalt-concrete mixes (90-130°C).
Fig. 5. Electronic micro-photographs of tar-polymeric binding agents (x3000) by composition: a – tar $C_{20}^\text{op} = 215c$ with 1.5% of PVC, mineral powder of limestone is not activated; b – tar $C_{20}^\text{op} = 215c$ with 1.5% of PVC, mineral powder of limestone is activated 0.5% of KF-MT.

This process is promoted by thixotropic properties of modified asphalt-binding agent and more developed absorptive and solvated layers of bitumen-polymer-sulfur binding agent at the surface of MP [25].

Fig. 6. Temperature dependence of the complex modulus of elasticity $E^*$ (MPa) asphalt-concrete at strain frequency 0.05 Hz: designation of curves corresponds to indices of asphalt-concretes of Table 1.

Asphalt-polymer-sulfur-concretes are distinguished by wide interval of viscous and elastic behaviour in pavement (the temperature of glazing minus 32.5°C, and the temperature of transition into viscous and fluid state is 75°C) (Fig. 6), by increased resistance to shift (Table 1).

Asphalt-concretes with complex and modified micro-structures of optimal compositions are characterized by the following indices of quality: limit of strength at compression at 0°C $R_0 = 8-10$ MPa, at 20°C $R_{20} = 5.0-6.5$ MPa, at 75°C $R_{75} = 1.2-1.4$ MPa; swelling – 0; inundation 1.5-2.0% from the volume.

Table 1. Values of indices characterizing shift stability of asphalt-concretes according to Marshall (testing temperature is 60°C)

<table>
<thead>
<tr>
<th>Index of concrete</th>
<th>Formulation of asphalt binding agent in fine-aggregate asphalt-concrete (B type)</th>
<th>Conditional plasticity, 1/10 [mm]</th>
<th>Index of conditional stiffness, $A$, [H/mm]</th>
<th>Stability, $P$, [H]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Binding agent – bitumen – $P_{25} = 59$ [grad.] scales of penetrometer; mineral powder is not activated</td>
<td>46</td>
<td>3316</td>
<td>15256</td>
</tr>
<tr>
<td>2</td>
<td>Binding agent – bitumen – $P_{25} = 59$ [grad.] scales of penemeter, is modified 2 [% mass] SKMS-30 and 40 [% mass] of technical sulfur; limestone mineral powder is activated 0.5 [% mass] SKMS-30</td>
<td>39</td>
<td>5892</td>
<td>22981</td>
</tr>
</tbody>
</table>

Asphalt polymer sulfur concretes are characterized by great critical stresses ($\sigma_{kp} = 0.95$ MPa), than hot asphalt-concrete (0.45 MPa) (Fig. 7).

Consequently, pavements built using asphalt polymeric sulfur concrete mixes are more long-lived under action of transporting loads and atmospheric affects, then traditional ones. Coefficient of ageing of asphalt polymeric concrete (heat warm-up is made at the temperature 75°C and ultra violet radiation in climatic chamber IP-1) after 1200 hours of warm-up is $K_{AG} = 1.25$, and for hot asphalt-concrete is $K_{AG} = 1.5$. Coefficient of water durability at inundation
during 90 days and nights of asphalt-polymer-sulfur-concrete is $K_{WD} = 0.75$, and for traditional one is $K_{WD} = 0.57$.

Fig. 7. Dependence between stress in fine-aggregate asphalt-concrete and relatively strain at strain 0.5 Hz and temperature 20°C: designation of the curves corresponds to indices of asphalt-concretes of the Table 1.

References


