Reinforcement of asphalt concrete pavement by segments of exhausted fiber used for sorption of oil spill

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Abstract. The paper is aimed at construction of the experimental road pavement made of dispersed reinforced asphalt concrete. Electronic paramagnetic resonance, infrared spectroscopy and fluorescent bitumen studies were used to prove that disperse reinforcement of asphalt concrete mixtures with fibers of exhausted sorbents reduce the selective filtration of low polymeric fractions of petroleum bitumen and improve its properties in the adsorption layer. Sesquioxides are neutralized as catalysts aging asphalt binder. This leads to improvement in the elasticity of bitumen films at low temperatures and provide better crack resistance of coatings to reduce the intensity of the aging of asphalt binder, and, therefore, to increase the durability of road pavements. The experimental road pavement made of dispersed reinforced asphalt concrete operated during 4 years and demonstrated better transport-performance properties in comparison with the analogue pavements.

1. Introduction
The main disadvantage of asphalt concrete as a material for pavements is considerable influence of air temperature on its strength properties (low resistance to shear forces at high positive temperatures and lack of fracture toughness at low temperatures). The mentioned disadvantage results in pavements deformations such as cracking, rutting, buckling and shifting.

Dispersion-reinforcement of asphalt concrete with discrete segments of chemical fibers is able to improve its rheological, physical and mechanical properties, thereby reducing probability of asphalt concrete pavements deformation occurrence and it has been confirmed by the research held in Russia, France, Switzerland, Netherlands, Poland and United States. There have been proved that introduction of dispersion-reinforcement into asphalt concrete mixture increases both its shear strength at temperature of 50°C by 25-30% and its tensile strength at negative temperatures by 40-80%. In this case deformability is improved up to 90-200% at temperature below zero and it mostly influences fatigue strength (improvement reaches by 200-500%) [1-3].

Disposal of fibrous sorbents wastes used for containment and oil skimming is an important of today. Existing methods of used sorbent disposal have disadvantages related to contamination of environment. Sliced fibers of waste sorbents used as dispersion – reinforcement in asphalt concrete are suggested being more environmentally friendly.

2. The theoretical studies of cross-linking processes of asphalt concrete
It is well known that asphalt concrete aging is caused by physico-chemical processes in mastic asphalt while asphalt mixtures preparing and pavements operation. The main processes affecting mastic asphalt aging intensity are selective filtration of oil bitumen components in pores and capillaries of
mineral materials, change of oil bitumen fractional composition under influence of climatic factors and sesquioxides as catalyzators of aging [4].

Oils being the least viscous components of bitumen penetrate in pores of mineral materials in the process of selective filtration. Mastic gums fill small pores and asphaltenes are adsorbed on the mineral materials surface. Changing fractional composition of adsorbed layers of bitumen under influence of climatic factors and sesquioxides is accompanied by transition of oils to mastic gums and mastic gums to asphaltenes. Adsorption layers of oil bitumen on the mineral materials surface are impoverished with low molecular weight fractions becoming more viscous, and consequently more brittle under temperatures below zero. This effect happens due to selective filtering components of bitumen, fractional composition changes of its films and negative influence of sesquioxides, accelerating processes of negative fractionation. Crack resistance of asphalt concrete pavements is reduced and the terms of their operation are shortened.

These negative processes can be eliminated using dispersion-reinforced asphalt concrete mixtures with fiber slices of their sorbents. They contain hydrocarbon feedstock collected at skimming that occur in case of a tanker sinking, accidents at oil pipelines and drilling rigs, spilling sludges and other wastes. Using this technique it’s possible to process mineral materials with organic binders in two steps [5]. Fibrous sorbents containing the controlled oil collected are added to mineral material (the first stage) then oil bitumen is added (the second one). Mineral material contacting with fibrous sorbents is processed with their hydrocarbon feedstock (mostly oil, fuel oil, mastic gums of different origin, shale and carbolic sludges) at the first stage. Perfect adhesion of the organic binder to the mineral material’s surface is provided due to this feedstock containing large amount of surface-active substances (phenols, ketones, carboxylic acids). These components interacting with the mineral material’s surface ensure availability of chemisorption bonds and waterproof-soluble compounds formation on this surface. At the same time they neutralize sesquioxides that are catalyzators of aging. The obtained organo-mineral mixture is treated with oil bitumen at the second stage.

There have not been any selective filtration of the oil bitumen components in pores and capillaries of mineral material since these pores and capillaries have already been filled with components of organic binder at the first stage. Consequently, adsorption layers of oil bitumen on the mineral materials surface won’t be impoverished with low molecular weight fractions and this fact positively impacts their elasticity under negative temperatures.

Furthermore due to large amount of these fractions in the adsorption layer of oil bitumen transition of oils to mastic gums and mastic gums to asphaltenes will be less intense. As a result, crack resistance of asphalt concrete pavements is increased.

3. Experimental procedure

According to the theory of professor F.G. Unger free radicals of mineral materials surface can be the centers in which the asphaltenes are deposited. Then their combination and further increase of amount happen. Since asphaltenes are almost 100% concentrate paramagnetic materials, intensity indicator of the aging process of the oil disperse system can be paramagnetic centers concentration in it, indicating concentration of asphaltenes [6].

The investigations of mastic asphalt aging by electronic paramagnetic resonance method (EPR) have been conducted using the radiospectrometer “RADIOPAN” SE / X-25-44, frequency of 9 GHz and wave length of 3.2 cm. The spectra of EPR mixtures have been obtained immediately after mixing components, as well as mixtures subjected to aging at 160 °C in a thermo-stabilized cell for 6 hours. Concentration of paramagnetic centers in mixtures has been defined. The investigation results are presented in Table 1.
### Table 1. Impact of technology of bituminous mixture preparing on concentration of paramagnetic centers

| No. | Composition of mixture | Concentration of paramagnetic centers in the mixture, г⁻¹ | Relative concentration of paramagnetic centers in the mixture |
|-----|------------------------|----------------------------------------------------------|------------------------------------------------------------|
|     |                        | before aging                                             | after aging                                                |
| 1.  | Granite + Bitumen      | 0,24х10¹⁷                                               | 0,7х10¹⁷                                                   |
| 2.  | Granite + Mastic gum + Bitumen | 0,3х10¹⁷                                               | 0,3х10¹⁷                                                   |
| 3.  | Limestone + Bitumen    | 4,5х10¹⁷                                               | 6,9х10¹⁷                                                   |
| 4.  | Limestone + Mastic gum + Bitumen | 0,5х10¹⁷                                               | 5,0х10¹⁷                                                   |

The data of the Table 1 demonstrate that modification of the granite surface with coal tar pitch doesn’t considerably effect on the concentration of paramagnetic centers. One can see that the concentrations in mixture No. 1 (prepared according to the traditional technology) and No. 2 (prepared using the proposed technology) are approximately the same. Apparently it happens due to the fact while granite surface processing with oil bitumen there is no active interaction between them.

It’s obviously that concentration of paramagnetic centers is changed after aging very significantly. Granite treated with bitumen contains 0,7х10¹⁷ paramagnetic centers. The same granite treated with coal tar pitch first, and then with oil bitumen contains only 0,3х10¹⁷ paramagnetic centers, which is 42%. It testifies that less asphaltenes (by 42%) have been appeared in the mixture and the intensity of the granite mixture aging with organic binder using the proposed technology is significantly lower.

Effect of the proposed technology on intensity of limestone mixtures and organic binders interaction is more discernable. Mixture of limestone and bitumen which hasn’t been subjected to aging is paramagnetic centers concentration within 4,5х10¹⁷ г⁻¹ which testifies active interaction of bitumen and limestone surface. Coal tar pitch has been treated with limestone first and then with bitumen. Limestone free radicals interact with coal tar pitch components and lose their activity. After addition of oil bitumen to this mixture the number of centers where asphaltenes are associated and combined decreases. As a result concentration of paramagnetic centers (testifying asphaltene concentration) in the mixture prepared by two-stage technology (mixture No. 4) is reduced to 0,5х10¹⁷ г⁻¹ which is only 11%.

Study of mixtures of limestone with organic binders subjected to aging testifies concentration of paramagnetic centers decreasing if two-stage technology of addition of organic binders is used. Concentration of paramagnetic centers in mixture No. 8 (prepared according to the proposed technology) is 28% lower than in mixture No. 7 (prepared using the traditional technology).

The method of luminescence analysis [7] has been used to study selective filtering of organic binder components in case of its interaction with mineral materials surfaces. This method is based on oil bitumen components’ ability to luminesce under ultraviolet (UV). Each component luminesces with its color using certain characteristic features. Selective filtering of organic binders components those treat fine pore rocks has been studied during the experiment. Some portions of crushed stone have been taken as samples. The first one has been dried to a constant weight and treated with organic binder. The second portion has been treated with oil bitumen and another portion has been treated with oil. The third portion has been treated with oil first and then – with oil bitumen. Each portion has been cut and examined selective filtration of organic binders components after cooling.
The selective filtration process has been observed using the universal biological microscope MBI-15 with ultraviolet source. The microscope is equipped with a digital camera and electronic devices which automatically determine exposure.

The conducted experimental studies of the crushed stone section of fine-porous limestone that had been treated with oil bitumen before have revealed fractionation of oil bitumen components. Oils penetrate deeper into mineral material and mastic gums are closer to the surface. Asphaltenes are adsorbed on the surface. Thus, as has been expected, oil bitumen films providing link between mineral particles of asphalt bitumen mixture are essentially impoverished with low molecular weight fractions. It causes their brittle increasing and consequently acceleration of asphalt concrete aging. Luminescence of crushed stone of fine-porous limestone treated with oil has shown that oil penetrates into mineral material deeper than oil bitumen. Radiation of its components is expressed with less bright and less saturated with colors. Luminescence of crushed stone of fine-porous limestone treated with oil first and then with oil bitumen testifies absence of oil bitumen components filtration in mineral material, as pores and capillaries have been already filled with oil components.

Investigations of the sesquioxides interaction processes with active ingredients of products absorbed by sorbents as well as the processes of mastic asphalt aging have been carried out using IR spectroscopy. The results of these studies are presented in Figures 1 and 2.

**Figure 1.** IR- spectra: 1-shale sludges; 2 - ferric oxide; 3-ferric oxide modified with shale sludges.

**Figure 2.** IR-spectra of mastic asphalt after aging: 1- ferric oxide + oil bitumen; 2 – ferric oxide + shale sludges + oil bitumen.
Figure 1 shows that there are broad absorption bands in the spectrum of shale mastic gum. They are extending from 3000 to 3799 cm\(^{-1}\), showing oscillations of free or associating OH groups and confirming the presence of phenolic compounds. There are absorption bands of 1050 and 1100 cm\(^{-1}\) in the spectrum of shale mastic gum associated with the stretching vibrations of C-\ OH [8]. Disappearance of these absorption bands at transition from mastic gum to its mixture with ferric oxide can be explained by carboxylic acids active interaction with oxide resulting in neutralization of the catalyzer of aging as organic binder.

Effect evaluation of the interaction processes of shale sludges and ferric oxide on binder aging intensity has been made later (Figure 2). The depth of carbonyl absorption at 1600 cm\(^{-1}\) indicating the presence of aromatic compounds in the mixture has been adopted as a criterion for evaluation aging intensity. Analyzing this figure it should be noted that mixtures of ferric oxide and oil bitumen are characterized of less intense carbonyl absorption band rather than mixture of oil bitumen and oxide modified with shale sludge. This testifies higher concentration of aromatic compounds in the mixture of oil bitumen and ferric oxide modified with shale sludge. It can be explained by processes slow up of asphaltene formation from low molecular weight fractions of oil bitumen due to neutralization of sesquioxides as catalyzators of aging during their interaction with phenols.

The suggested technology was tested in a pilot operating construction (site of the national department of highways "Gorno-Altayavtodor"). The experimental section of the road using asphalt concrete pavement dispersion reinforced with fibers obtained from waste fibrous sorbents subjected to centrifugation after skimming in 2010.

The construction process is shown in Figure 3. Operation of the pilot area for four years has proved that its performance is significantly better than similar ones of the standard zone.

![Figure 3](image)

**Figure 3.** A section of the road using asphalt concrete pavement dispersion reinforced with segments of chemical fibers obtained from waste fibrous sorbents.

4. Conclusion

There has been conducted experimental research using the methods of electron paramagnetic resonance and fluorescent bitumen studies. They testify that at dispersion reinforcement of asphalt concrete mixtures with fibers of sorbents used for containment and oil skimming it’s advisable to enter first sorbents containing recovered oil products into the mineral material, mix them and then oil bitumen can be added to this mixture.

Advanced processing of mineral materials with oil containing in the fibrous sorbents provides modification of their surfaces. Oil products penetrate into pores and capillaries filling them. In case of the further mixture processing with oil bitumen selective filtration of its components in pores and
capillaries of mineral materials doesn’t happen because they have been already filled with oil contained in the fibrous sorbents. As a result adsorption layers of bitumen on the surface of mineral materials are not impoverished with low molecular weight fractions that improve their elasticity at low temperatures, providing increased cold check resistance in winter and consequently durability of pavements.

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