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The use of Plant Oils for Gaining the Colored Plastoconcrete

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Development of road infrastructure is an indispensable condition for economic and social progress of many countries. In this paper we studied in detail the patterns of interaction between components studied in order to obtain a binder for color plastoconcrete based on thermoplastic resins and the mixtures of unsaturated and saturated acids of vegetable origin – from plant oils as solvents, with addition of ultrathene, pigments. There is some evidence about the nature and quality of interaction obtained in the synthesis of binders. The main performance properties of the obtained binder systems were analyzed as well as softening point, penetration, ductility, adhesion to mineral particles.

Key words: plant oil, binder, colored plastoconcrete, Ultrathene, performance properties, road bitumen.

The practice of using bitumen as an adhesive, binder, hydrophobic construction material has more than 8 thousandyears. There is, in particular, data on the use of natural bitumen in the construction of warships in the Sumerian state (about 6000 BC). It is believed that the word bitumen has Sanskrit roots. Initially the word meant a resin obtained from certain species of trees[1].

Bitumen is a tar-like solid mixture of carbohydratesand their derivatives formed by weathering of the oil. Natural bitumen contains 60-75% asphaltenes.

In Russia, for example, the lack of asphalt-bitumen highways remains one of the main problems: 50 th.of settlements, which are home to 12 million people still do not have paved roads. Russian roads are usually compared with the Canadian, as countries are in similar climatic conditions. However, in issues of bitumen production per capita Russia lags behind Canada nine times, we have four times less facilities for its release, and the service life of the roads made of Russian bitumen is five times shorter than that of Canada. Physical and mechanical properties of marks of petroleum bitumen for road purpose (BND), which constitute 61% of the total produced in domestic refineries bitumen, do not meet the requirements of GOST 22245-90 (GOST – Russian State standard)[2] for at least one of the indicators. The situation is further complicated by the fact that there is practically no naphthenic base oil with a high asphaltene content providing producing qualitative vacuum distillation bitumen. In addition, imperfect vacuum unit of CDU (crude distillation unit) in most cases does not allow maintaining the process parameters (temperature and residual pressure) at a level that would provide enough deep recovery of vacuum distillates to obtain the residual bitumen. For example, an important feature of the Russian bitumen production (and the refinery in general) is a significant change in recent years of a quality of commercial mixtures of oil flowing through the pipeline system of JSC "Transneft" to the oil refineries. It is subject, above all, to increasing paraffinicity of feedstock. However, it

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is known that even a slight increase in the concentration of n-paraffinic hydrocarbons in the oil, and hence in the tar, and in the oxidized product – bitumen – leads to a rapid deterioration of their performance properties. And that is, especially, low-temperature and plastic characteristics, which are accompanied by a decrease of fracture toughness and durability of the asphalt coatings derived from such bitumen[3-6]. Domestic refineries, unfortunately, for a number of reasons cannot carry on the processing of heavy oils with high content of wax to produce bitumen and oils, as happens in most developed countries.

Thus, there is now the need to produce bitumen, and therefore binders possessing a set of specific characteristics, due to climatic conditions of use. Solving this problem is a priority, and getting a "synthetic" binder with unique properties can enable to obtain colored asphalt concretes and roads with European standards lifetime of 18-20 years. Development of road infrastructure is an indispensable condition for economic and social progress of many countries, and Russia particularly.

Binders for color plastoconcrete based on petroleum resins and plasticizers derived from petroleum.

Binders for colored plastoconcrete similar by quality to cementing materials Pave Bright of firm "Neville Sindhu Chemistry" were obtained on the basis of petroleum-polymer or indene-coumarone resins and plasticizers of petroleum origin.

The fraction 140-200 °C separated from the "light" oil of various pyrolysis products (kerosene-gasoil fractions, low-octane gasoline, gases, et al.). is commonly used as the raw material for the production of petroleum polymer resins.

The raw material for the production of indene-coumarone coke-chemical resins is "heavy" benzene obtained by distillation of the solvent naphtha of coke-chemical production. To obtain these resins, a catalytic or thermal polymerization of said fractions is used.

Depending on the feedstock and the conditions of polymerization resins of different color are obtained: from pale yellow to nearly black with a softening point ranging from 60 to 140 °C. They are transparent and are colored by adding pigments to the corresponding color. The consumption of the pigment is the less and the color is the brighter, the lighter is the original resin. The resins are resistant to water, acids and alkalis, and therefore can be used in anti-corrosion coatings. The main disadvantage of resins is their high brittleness. To eliminate this drawback, they are used in admixture with other resins or different plasticizers are use.

For obtaining binders suitable for production of plastoconcrete with high plasticity range, good heat and freeze resistance and high strength properties plasticizers must meet the following requirements[7-10]:

a) A good compatibility with resins at elevated temperatures and preserving the homogeneity of the mixture at the lowered temperature;
b) The low glass transition and fragility temperature (brittle temperature should be no lower than minus 30 °C on Fraas);
c) High boiling temperature (over 350 °C);
d) Flash point in open crucible is not lower than 220 °C;
e) Light color: color by iodine scale up to 120 units
f) Low content of unsaturated hydrocarbons - iodine value not exceeding 20;
g) Stability and resistance to atmospheric factors: light, oxygen, temperature variations, etc.;
h) A definite value of viscosity (35-55 cSt at 100 °C) and flatter curve of viscosity changes from temperature;
i) Low coefficient of volumetric expansion, which reduces the risk of cracking and deformation at varying temperatures;
j) Being cheap and a readily available;
k) Lack of toxicity and odor.

With a view to the selection of plasticizers a number of different products have been investigated, including synthetic fatty acids C_{10}-C_{16}, fatty acid esters, such as isobutyl and isoamyl, stearic acid esters, chlorinated paraffin, plasticizer "ANAS" (esters of naphthenic acids), dibutylsebacate and dibutyl phthalate, various mineral oils (transformer oil, MS-20, etc.).

The investigated plasticizers did not provide binder with the necessary physical and chemical properties. Physical and chemical properties of the plasticizers are shown in Table 1.

Table 1 . Physical and chemical properties of the plasticizers

Indicators	Binders of MINH&GP (present – RGU N&G – Russian State University of Oil and Gas called after I.M. Gubkin) based on resins: Oil-polymer			Coke-chemical			Binder Pave Bright of “Neville Sindhu Chemistry”	Norms of GOST 22245– 90 [2]* for road bitumen		
	90/130	60/90	40/60	90/130	60/90	40/60		BND - 90/130**	BND – 60/90	BND - 40/60
1	2	3	4	5	6	7	8	9	10	11
The depth of penetration of the needle: At 25 °C, 100g. 5 seconds;										
At 0 °C, 200g.	92-128	70-90	44-58	90-124	62-78	46-59	90	91-130	61-90	40-60
60 seconds; extensibility	38-54	28-38	18-21	40-53	32-46	27-30	-	28	20	13
at 25 °C, cm softening point, °C Brittle point °C	35-68	22-78	25-70	-	-	-	110	65	55	45
	55-41	50-43	58-45	40-43	49-45	49-48,5	46,7	43	47	51
	-12	-12	-10	-22	-16	-19	-	17	-15	-12
The softening point change after warming at 160 °C, 5h.,° C	to -30	to -18	to -15	to -15	to -17	to -14				
	55-45	42-45	58-47	-	51	-	-	5	5	-5
			-	51	-		5	5	-5	

*GOST – Russian State standard **BND – mark of road bitumen derived from petroleum

Table 2. Exemplary compositions and mechanical properties of compacted plastoconcrete mixtures

Indicators	Plastoconcrete mixture based on MINH&GP binder				Pave	GOST 9128-97 on
	actual data		Norms of MINH&GP		bright	asphalt concrete
	sand	finely grained	sand	finely grained		mixtures
1	2	3	4	5	6	7
Composition, % 25A.:						
Mineral chips with a size of 0 to 15 mm.						
sand	-	82-84	-	56	-	-
mineral powder	73-78	-	77.5	20	-	-
pigment	14-20	10	13	15	-	-
binder	3-Jan	0.7-1.0	3-Feb	3-Feb	-	-
Physical and mechanical properties:	7-Jun	6	7.0-8.0	6	-	9-May
bulk density, g/cm^3						
water saturation, % vol.						
swelling, % vol.	2.35-2.50	-	2.3-2.5	-	2.27	2.25-2.35
compressing strength, kg/cm^2, in dry condition, at: 50 >!	0.1-4.0	-	1.0-3.0	-	4.7-7.8	1.5-3.0
20 >!	0.0-0.4	-	< 0.5	-	-	No more than 0.5
0 >!						
The same in water-saturated condition at 20 >!						
heat resistance	10.5-2.7	-	10-Aug	-	-	No less than 10
water resistance	25-82	-	over 22	-	-	No less than 22
The loss of strength after 30 freeze-thaw cycles	60-78	-	< 120	-	-	No more than 120
Marshall stability,						
Amer. pounds						
Fluidity, 1/100 inch	25-72	-	-	-	-	No less than 22.5
	2.5-3.0	-	-	-	-	Not normed
	1.0-0.9	-	0.85	-	-	No less than 0.9
	Not observed					
		-	-	-	-	-
	-					
	-	-	-	-	2680-2890	-
		-	-	-	12-Jun	-

Only when using a complex of refined products such as deasphalted oil (DAO), extract of phenolic purification of residual oil and petrolatum, is possible to get the binders with the necessary physical and chemical properties that meet the basic requirements of GOST 22245-90 [2] for the improved road bitumen.

Best by all indicators binders are obtained using binary plasticizers: extract-DAO or extract-petrolatum.

Brittleness temperature (brittle point) of binder is determined by the viscosity of the extract, the higher it is, the lower is the brittle point of the binder. In this case, the binder composition contains an increased amount of the extract, and that accordingly reduces the consumption of the more expensive component – the resins. Cohesion of the binders is the higher the better is compatibility of the resins with the extract and the higher the softening point of the resin as well as the viscosity of the extract. The color of binders (they should be light, not darker than 150 units of iodine scale) depends mainly on the color of the extract and the resin as DAO and petrolatums are painted much weaker.

Highly viscous DAO with high content of naphthenic hydrocarbons are poorly combined with resins and give binders with high brittle temperature and low cohesion. The highest softening point for the binder is provided by DAOs with a high viscosity or a specific content of paraffinic hydrocarbons. However, the latest worsen extensibility. Adding petrolatum improves brittle and softening point and somewhat impairs extensibility, cohesion and compatibility of the resins with plasticizers. Naturally, by their nature, composition, structure and physical and chemical properties petroleum resins and asphaltenes of the binders differ from the same components contained in the bitumen.

Technology for industrial production of color plastoconcrete based on petroleum binder

Color plastoconcrete is a mixture of mineral materials (mineral chips, sand, mineral powder), a pigment colorant and a thermoplastic binder[11-12]. As mineral chips the products of fragmentation of marble granite and other rocks, or of artificial stone material, having a particle size of from 2 to 10 mm, are used. Natural sand, quartz sand or obtained by fragmentation of the above mentioned materials are used. As the mineral powder white or colored, natural or artificially crushed materials are used, with the following particle size: 100% of the powder should pass through a sieve with holes of 1.25 mm, as through a sieve with holes of 0.071 mm, not less than 70% of the powder should pass. Pigments used for color plastoconcrete must be heat resistant (to withstand temperatures up to 200 °C) and light and water resistant. Thermoplastic binder – is a mixture of petroleum-polymer or indene-coumarone resins and plasticizers. Compacted plastoconcrete mixtures

Table 3. Properties of the gained solutions based on MUAVO and EVAC (ethylene-vinyl acetate copolymer

Solution	EVAC concentration	Softening point, °C
1	30	70.5
2	20	63.85
3	15	58
4	12.5	56
5	10	22.35

Table 4. The performance characteristics of the prepared solutions based on TPR and MSAVO with addition of EVAC

No	Concentration of EVAC, % mass.	Softening point, °C	Bending at -25°C	Adhesion to mineral particles	Ductility, mm	Penetration, mm	Heat resistance (85°C)	Water saturation
1	-	30,4	-	1	>80	>200	-	-
2	5	33	-	1	>30	>100	-	-
3	10	84.3	+	1	8	35	+	+
4	20	88.5	+	1	7	28	+	+
5	30	88.8	+	1	5.8	21	+	+
6	40	90.2	+	1	4.5	15.5	+	+

should meet the requirements of GOST 9128-97 [13] on the fine-grained or sand asphalt concrete mixtures. In Moscow, one of the asphalt plants, in 1967, a pilot plant for the production of colored plastoconcrete was established. The binder was prepared in boilers by mixing certain amounts of heated plasticizers with fractured petroleum-polymer resin until gaining a homogeneous molten mass. During preparing process, the temperature was maintained within 100-140 °C. Ready binder was mixed in a conventional asphalt concrete mixer with mineral materials heated up to 150-170 °C. The pigment was injected into the mineral material before the addition of binders.

Exemplary compositions and mechanical properties of compacted plastoconcrete mixtures are presented in the Table 2.

Solutions based on organic oils to obtain binders for the production of color plastoconcrete Petroleum resin, ethylene-vinyl acetate copolymers, EPDM rubber (ethylene-propylene-diene monomer rubber), low-molecular polymers pentaerythritol was used as the most suitable as raw material for the synthesis of binders.

As solvents, when choosing the most suitable components, a mixture of unsaturated acids of vegetable origin (MUAVO) with a composition of C_{20-26} was used. Calcined IM 2201 (yellow-green), that is also used as polymerization initiator, zinc oxide (white) were used as pigments

While carrying out the work solutions of different composition were synthesized. Then their properties were assessed (determination of softening point by so called ring and ball method, extensibility, penetration, fragility, adhesion), as well as an important criterion for evaluating the properties and characteristics of the binder – a visual analysis. The filling by pigments was followed by the estimation of resulting binders in the regards of homogeneity of the resulting solution (visual analysis) and all the combined properties.

The following is data of results obtained during the selection of the necessary combination of substances and their concentrations to obtain a solution with the physical and chemical properties most similar to those of binder having a bituminous or polymer-bituminous nature.

The solutions obtained have a homogenous structure under a look with an

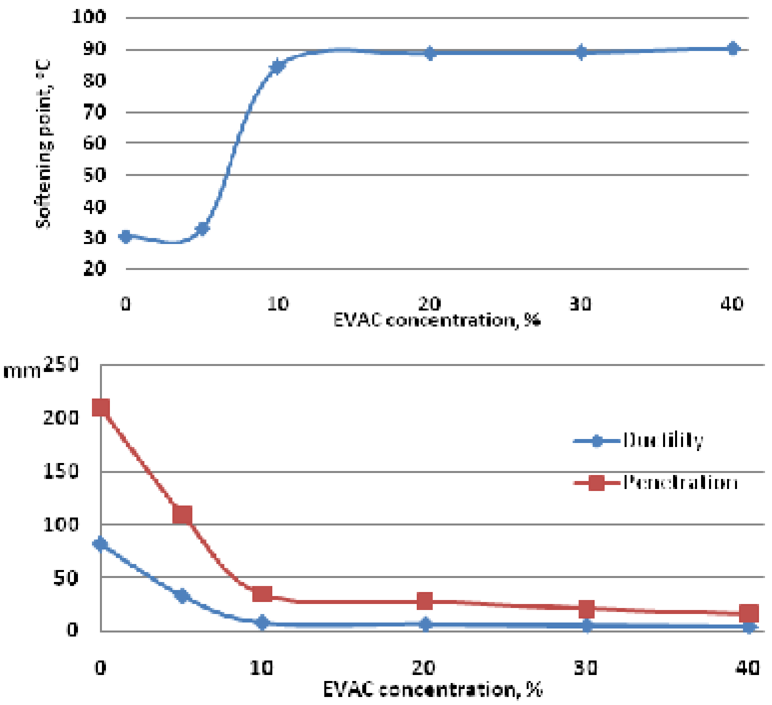

Fig. 1. Dependence of the softening point (a), penetration and ductility (b) change from the concentration of ultrathene (EVAC) in the TPR-MSAVO (70/30)

unarmed eye, and transparent, but when exposed to the slightest mechanical stress – start to form a loose broken nonplastic mass. After pigmentation of the solutions, these properties are preserved. These solutions cannot be used as a binder for plastoconcretes.

The resulting solutions prepared by adding IM 2201 to a mixture of TPR (thermoplastic resins) and MUAVO in different concentrations (from 5 to 50 per cent to the mixture) are very well painted. Their visual analysis shows, that depending on the concentration of powder of IM 2201 they have different viscosities, though look homogeneous in composition. Only the solution with the highest amount of pigment shows a loss of fluidity.

The performance characteristics of the prepared solutions based on TPR and MSAVO (a mixture of saturated acids of vegetable origin) taken with a mass ratio of 70/30 with addition of EVAC are shown on the table 4. The properties were determined according to GOST 30547-97, for Roofing and hydraulic insulating materials in rolls[14]. According to the data obtained the solutions at numbers 3, 4, 5, 6 on the set of characteristics stand GOST to the roll material.

The abovementioned solutions based on TPR and MSAVO with average concentrations of EVAC was also modified by adding of zinc white. It is observed that the softening point decreases to 67 and 79.6 >! and the penetration depth is increasing to 60 and 150 mm with adding 25 and 50 % of pigment, respectively. Visual analysis indicates that these solutions have a loose structure, aggregative unstable, there is a lack of adhesion to mineral materials therefore they cannot be used as a binder.

Thus, the best properties were obtained by adding of low-molecular polymers into TPR-MSAVO system, with the addition of pigment MI-2201. Visually, the resulting solution is homogeneous and has no looseness.

CONCLUSION

In all developed countries of the world equipment and technologies are constantly improving that will positively affect the quality and durability of roads. This is currently central area, especially for Russia, the largest country in the world, having millions of kilometers of roads with one of the great evils that is a lack of qualitive roads, in the presence of all climatic regions. Also the hallmark of a developed country is the development of such topics as getting colored asphalt that can be used as a marking or simply to obtain coatings of different colors. Thus, the subject of this research – obtaining colored asphalt binder is relevant today. The experimental data obtained in the present work allows suggesting the optimal compositions of binders based on oils of vegetable origin with the performance properties no worse than that of binders produced from petroleum products. That is especially important when there is a lack of proper petroleum raw materials.

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