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EFFECT OF PHENOL-CRESOL-FORMALDEHYDE RESIN ON ADHESIVE AND PHYSICO-MECHANICAL PROPERTIES OF ROAD BITUMEN

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Abstract. The phenol-cresol-formaldehyde resin (PhCR-F) obtained from phenolic fraction of coal tar has been synthesized *via* the polycondensation method of "raw" phenols with formaldehyde. The modification of road bitumen by this resin was carried out. PhCR-F in different concentrations was found to be effectively used as a modifier of road bitumen. It was shown that PhCR-F is an effective adhesive additive for road bitumen. The structural types of the oxidized and modified bitumen were determined according to the group-chemical composition and calculated criteria.

Keywords: bitumen, adhesion, modifier, phenol-cresol-formaldehyde resin.

1. Introduction

The main reasons for the destruction of road coatings are the increase in traffic volume, the growth of freight transport volumes, the masses of vehicles, axial load, as well as the weather impact. Today, traditional asphalt concrete based on unmodified bitumen is not able to provide the necessary physico-mechanical properties of coatings and their durability under existing density of traffic [1-11].

Among all components of asphalt concrete, bitumen is the most sensitive to the impact of transport loads and weather conditions. Therefore, its behavior has a decisive influence on the service time of road coatings with given characteristics. Bitumen (first of all, the oxidized one) has a poor adhesion to the most stone materials used in road construction (granites, quartzites, andesites, diorites and other acidic rocks). This causes the formation of road chipping, cracking, potholes, a sharp decrease in water and frost resistance, and, consequently, the durability of asphalt concrete. To avoid these damages, it is necessary to use substances (adhesive additives) that provide a complete, irreversible and waterproof bond between bitumen binder and stone material. When using surface-active adhesive additives, two types of adhesion are distinguished: an active one (encapsulation of the material, forming and maintaining a strong chemical bond between the stone and bitumen in the presence of water with the effect of water displacement) and a passive one (forming and maintaining a strong chemical bond between the surface of dry stone material and bitumen). Modern adhesive additives are, in most cases, cationic surfactants of different structures based on aliphatic amines (mono-, di- and polyamines) or their derivatives, as well as quaternary ammonium compounds, which are quite expensive.

On the basis of previous studies [1-3, 5, 7-12] it was established that phenol-formaldehyde resins (PhFR) may be the effective modifiers of bitumen. But these resins, which are produced from pure phenol, are not widely used as polymer modifiers first of all due to their high cost. On the other hand, the phenolic fraction containing about 65 % of phenols and cresols is one of the products of coking process. Its cost is by 35–40 times lower than a pure phenol cost [11]. Therefore, this work is devoted to the detailed study of the possible improving the bitumen adhesion properties with the help of PhFR, obtained from cheap raw materials – the phenolic fraction of coal tar. The changes in colloidal structure of bitumen after adding PhFR, and thus the changes in the rheological properties, have been examined as well.

2. Experimental

2.1. Initial Materials

The phenolic fraction of coal tar was withdrawn at JSC "Zaporizhkoks" (Ukraine). Its characteristics are given in Table 1.

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To obtain the modified bitumen, we used the oxidized bitumen BND 60/90 produced by PJSC "Transnational financial and industrial oil company Ukrtatnafta" (Kremenchuk, Ukraine), as well as the distillation bitumen BD 60/90, withdrawn at Frankivsk Road Construction Department (Lviv, Ukraine). Characteristics of bitumen are given in Table 2.

2.2. Experimental Procedure

Novolac phenol-cresol-formaldehyde resin was obtained according to the scheme given in Fig. 1 by the method of formaldehyde condensation polymerization with the "raw" phenols extracted from these fractions. Synthesis conditions for the resins are shown in Table 3. As recommended by [13], the obtaining of novolac phenol-formaldehyde resins requires maintaining the mole ratio of phenol to formaldehyde at 1.12–1.42, while for novolac cresol-formaldehyde resin it should equal 2.27. Considering that the "raw" phenols that were derived from the phenolic fraction of coal tar, contain both phenols and cresols at various ratios, the synthesis was carried out at the molar ratio "raw" phenols: formaldehydes equal to 1.42. For calculations of reactor loading, it was assumed that the molar weight of the resulting "raw" phenols was 94.1 g/mol, which is equal to the molecular weight of pure phenol.

Table 1

Characteristics of the phenolic fraction withdrawn at JSC "Zaporizhkoks" (Ukraine)

Index	Values
Distillation, K:	
Initial boiling point	378
10 % distilled at the temperature	437
20 % distilled at the temperature	445
30 % distilled at the temperature	447
40 % distilled at the temperature	450
50 % distilled at the temperature	452
60 % distilled at the temperature	455
70 % distilled at the temperature	458
80 % distilled at the temperature	470
90 % distilled at the temperature	475
95 % distilled at the temperature	481
Molecular weight	136
Bromine number (g Br_2/100 g product)	81.64

Table 2

Characteristics of oxidized and distillation road bitumens

Index	Values	
	Oxidized bitumen	Distilled bitumen
Penetration at 298 K, $m\cdot10^{-4}$	70	80
Softening point R&B, K	319	316
Ductility at 298 K, $m\cdot10^{-2}$	63	>100
Adhesion to glass, %	33	60
Adhesion to crushed stone, points	3	4
Change in properties after heating:		
mass loss, %	0.1	–
residual penetration, %	93	–
change in softening temperature, K	2	–
Fraass breaking point, K	255	257
Penetration index	–1.5	–2.1
Plasticity range, K	337	332

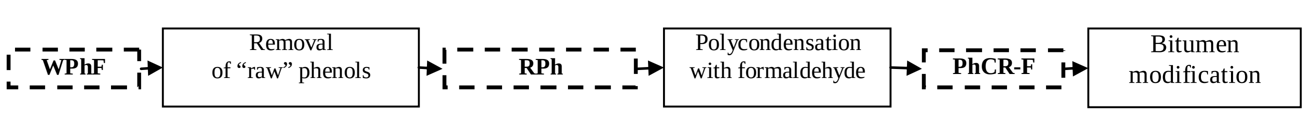

Fig. 1. Scheme of researches: WPhF – wide phenolic fraction; RPh – "raw" (technical) phenols; PhCR-F – phenol-cresol-formaldehyde resin

Table 3

Conditions for PhCR-F synthesis

Parameter	Value
*Molar ratio of "raw" phenols to formaldehyde	1.42
Weight ratio of "raw" phenols to formalin (formaldehyde content in formalin – 37 wt %)	1.78
Catalyst weight content (concentrated HCl), % by raw phenols	1.0
Temperature, K	373
Process time, min	60

Note: *the molar weight of "raw" phenols was proposed to be 94.1 g/mol.

2.2.1. Removal of "raw" phenols

Phenols from the phenolic fraction were removed using 20% NaOH solution. This removal is based on the reaction of phenols and alkali with the formation of water-soluble phenolates, which are converted into phenols with a concentrated hydrochloric acid. The yield of "raw" phenols from the phenolic fraction was 32.3 wt %.

2.2.2. Obtaining of PhCR-F

The polycondensation of phenols with formaldehyde was carried out according to the procedure described in [13]. The components were placed in a three-necked reactor under definite conditions (ratio of the components "raw" phenols/formaldehyde, time, temperature and catalyst amount) and stirred. The resulted resin was dried under vacuum at 373 K for 3 h.

2.2.3. Obtaining of polymer modified bitumen

The polymer modified bitumen (PMB) was prepared as follows: the definite amount of bitumen was heated to a fixed temperature, and then a modifier (2.4 wt %) was added. The mixture was stirred (Re = = 1200) at 463 K for 1 h. The process conditions were chosen on the basis of results, described in [14].

2.3. Analysis of Raw Material and Products

The physico-mechanical properties of bitumen were determined according to standard techniques. The heating was carried out using the following procedure: bitumen (50 ± 0.1 g) was poured into metal cups and uniformly distributed along the bottom. After cooling bitumen to room temperature in the desiccator, the samples were weighed (± 0.01 g). Then they were placed on a horizontal grill of the drying cabinet preheated to (436 ± 1) K. The samples were heated for 5 h. After finishing the cups were removed from the drying cabinet, placed in a desiccator, and after cooling to room temperature, weighed with an error of ± 0.01 g. The changes in the values of softening temperature, residual penetration (as the ratio of penetration after and before heating, %) and adhesion to the mineral materials were determined.

Previous results indicate fundamental differences in the technical and rheological properties of bitumen belonging to different structural types [15]. Structural type of bitumen is determined, first of all, according to the group chemical composition (GCC): the content of asphaltenes and malthenes (*i.e.*, resins plus oils). The most cited classification of bitumen is the classification according to Kolbanovska and Mikhailova [16], who distinguish three types of bitumen colloidal structure: 1 – gel, 2 – sol, 3 – sol-gel (see Table 4). The group chemical composition was determined according to Markusson method [17].

The type of structure was also determined using certain calculation criteria. The simplest criterion is the plasticity range (*PR*). Such a criterion is an algebraic difference between the softening point R&B and brittle temperature ($PR = T_s - T_b$). In accordance with this index, bitumen with $PR \geq 348$ K can be attributed to the "gel" type; bitumen with $PR \leq 328$ K – to the "sol" type. Intermediate type "sol-gel" has *PR* = 328–348 K [15].

In Western European countries, for the classification of viscous bitumen according to the type of structure penetration index (I_p) is widely used. This value is based on the penetration temperature dependence, which is very sensitive to the group composition of bitumen.

Table 4

Structural types of bitumen according to GCC criterion

Type of structure	Group chemical composition, wt %			Ratio·100 %	
	Asphaltenes (A)	Resins (R)	Oils (O)	A/(A+R)	A/(R+O)
1 – gel	>25	<24	>50	>50	>35
2 – sol	<18	>35	≤47	<34	<22
3 – sol-gel	21–23	30–34	45–49	39–49	25–30

In accordance with the standards of the European Union countries – EN 12591 [18], the penetration index is determined by the formula:

$$I_p = \frac{20T_s + 500\lg P_{298} - 1952}{T_s - 50\lg P_{298} + 120} \quad (1)$$

where T_s is a softening temperature, °C; P_{298} is a penetration at 298 K, m·10^{-4}.

Bitumen with $I_p < -1.0$ can be conventionally classified as "sol", with $I_p > +1.0$ – as "gel" type and bitumen with I_p from –1.0 to +1.0 – as "sol-gel" type.

In order to simplify the experiments needed to determine the structural type of bitumen, V. Zolotaryov [15] proposed a coefficient taking into account the softening point (T_s), the brittle temperature (T_b) and ductility (D) at 298 K:

$$K = \frac{(T_s - T_b)\cdot L}{25D} \quad (2)$$

where L is the neck length (3 cm) of the "eight" shape to determine the ductility of bitumen; 25 is a temperature, at which ductility is determined, °C.

According to Zolotaryov's classification bitumen with $K > 0.13$ refers to the "gel" type, bitumen with $K < 0.08$ – to the "sol" type, and bitumen with intermediate values – to the "sol-gel" type. Calculated criteria for determining the structural type of bitumen are summarized in Table 5.

3. Results and Discussion

On the basis of experimental results the mass balance for obtaining PhCR-F was calculated (Table 6). The yield of the resulted resin was 29.65 g.

To confirm the positive effect of PhCR-F as a modifier, we compared the main characteristics of pure (oxidized and distilled) bitumen and modified ones. They are given in Table 7.

Table 5

Calculated criteria for defining the structural type of bitumen

Structural type	Values		
	Plasticity range (*PR*), K	Penetration index (*PI*)	Zolotaryov's index (*K*)
1 – gel	≥ 348	> +1.0	> 0.13
2 – sol	≤ 328	< –1.0	< 0.08
3 – sol-gel	328–348	from –1.0 to +1.0	0.08–0.13

Table 6

Mass balance for obtaining PhCR-F

Components	g	wt % relative to the reactor loading
Loaded		
"Raw" phenols	32.30	63.64
Formalin	18.13	35.72
Concentrated HCl	0.32	0.64
Total:	50.75	100
Obtained		
PhCR-F	29.65	58.42
Water and unreacted components	21.10	41.58
Total:	50.75	100

Table 7

Comparison of the main characteristics of pure and PhCR-F modified bitumen

Index	BD 60/90	BD 60/90 + PhCR-F (2.4 wt %)	BND 60/90	BND 60/90 + PhCR-F (2.4 wt %)
Penetration at 298 K, 0.1 mm	80	65	70	60
Penetration decline, %	–	18.8	–	14.3
Softening point R&B, K	316	319	319	322
Softening point increase, %	–	7.0	–	6.5
Ductility at 298 K,	> 100	> 100	63	25
Adhesion to glass, %	60	94	33	94
Increase in adhesion to glass, %	–	56.7	–	184.8
Fraass breaking point, K	257	257	255	255
Penetration index	-2.1	-1.7	-1.5	-1.0
Plasticity range, K	332	335	337	340
Homogeneity	homogeneous	homogeneous	homogeneous	homogeneous

Table 8

Physico-mechanical parameters of pure and modified bitumen

Bitumen	Parameters							
	T_s, K	P_{298}, 10^{-4} m	D_{298}, m·10^{-2}	T_b, K	PR, K	I_p	Adhesion to	
							crushed stone, points	glass, %
BND 60/90	319	70	63	255	337	-1.5	3	33
BND 60/90 + PhCR-F (1.0 wt %)	321	68	46	255	339	-0.9	5	87
BND 60/90 + PhCR-F (2.4 wt %)	322	61	25	255	340	-1.0	5	94

So, the modification of both distilled and oxidized bitumen by PhCR-F increases the softening point by 3 K. Adhesive properties of PMB are increased for distillation bitumen by more than 1.5 times (from 60 to 94 %), for oxidized – by almost three times (from 33 to 94 %). This confirms that the resulting resin can be used as the adhesive additive, especially for oxidized bitumen.

In accordance with industrial requirements the amount of modifier approx. 1 wt % is technically and economically feasible; so we studied bitumen modification adding 1 wt % of PhCR-F and compared the results with previously obtained. Characteristics of the obtained PMB are given in Table 8.

The modification of BND 60/90 bitumen by different amount of modifier slightly increases the softening point, *i.e.* increases its heat resistance, reduces penetration and ductility, increases its hardness. However, the main effect of PhCR-F is a significant increase in bitumen adhesion to the crushed stone and glass (Fig. 2). The adhesion to crushed stone for BND 60/90 + PhCR-F (1.0 wt %) increases from 3 to 5 points, and the adhesion to glass – by more than 2.6 times. With increasing amount of PhCR-F additive (2.4 wt %), the value of adhesion to glass is somewhat higher (94 % *vs.* 87 %). Taking into account all mentioned above, the modifier amount of 1.0 wt % was acceptable for further investigations.

Bitumen in most road technologies is used in a hot form; therefore, it was necessary to investigate the characteristics of PhCR-F modified bitumen after its heating. The results are shown in Table 9 and Fig. 3.

Adhesion to crushed stone did not change, but adhesion to glass increased for both pure and modified bitumen. This fact can be explained by the decrease in bitumen penetration (the increase in viscosity) and possible better reaction of PhCR-F with bitumen due to heating.

In accordance with the described in Table 5 (Subsection 2.3) criteria for determining the type of bitumen structure, we determined the structural type of the obtained modified bitumen (Table 10).

Modification of BND 60/90 with the addition of PhCR-F in the amount of 1.0 wt % does not change the structural type of bitumen according to the proposed three calculated criteria. Both samples of bitumen belong to the structural type 3 (“sol-gel”).

Table 9

Physico-mechanical parameters of bitumen after heating

Bitumen	Parameters			
	Change in softening point, K	Residual penetration at 298 K, 10^{-4} m	Adhesion to	
			crushed stone, points	glass, %
BND 60/90	+2	93	3	43
BND 60/90 + PhCR-F (1.0 wt %)	+2	93	5	95

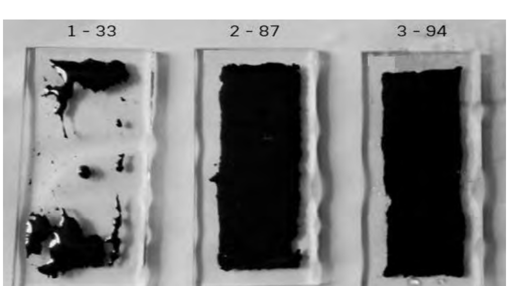

Fig. 2. Results of determining adhesion to glass surface for: BND 60/90 (1-33); BND 60/90 + PhCR-F (1 wt %) (2-87) and BND 60/90 + PhCR-F (2.4 wt %) (3-94)

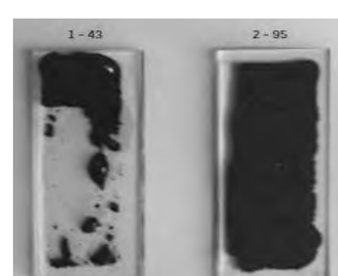

Fig. 3. Results of determining adhesion to glass surface for: BND 60/90 (1-43) and BND 60/90 + PhCR-F (1 wt %) (2-95)

Table 10

Structural type of bitumen according to the calculated criteria

Bitumen	Plasticity range (*PR*), K		Penetration index (*PI*)		Zolotaryov's index (*K*)	
	Value	Structural type	Value	Structural type	Value	Structural type
BND 60/90	337	3	-1.5	3	0.124	3
BND 60/90 + PhCR-F (1.0 wt %)	339	3	-0.9	3	0.172	3

Table 11

Structural type of bitumen according to GCC criterion

Bitumen	Group chemical composition, wt %			Ratio·100 %		Structural type
	Asphaltenes (A)	Resins (R)	Oils (O)	A/(A+R)	A/(R+O)	
BND 60/90	21.4	31.1	47.5	40.8	27.2	3
BND 60/90 + PhCR-F (1.0 wt %)	21.7	28.6	49.7	43.1	27.7	3

We also investigated the samples in accordance with GCC criterion (Table 11). The structural type determined by GCC coincides with that obtained according to calculated criteria. Thus, the modification of BND 60/90 bitumen by PhCR-F in the amount of 1.0 wt % does not significantly change GCC of the pure bitumen and, accordingly, its structural type.

4. Conclusions

"Raw" phenols were extracted from the phenolic fraction of coal tar with the yield of 32.3 wt %. Phenol-cresol-formaldehyde resin (yield is 29.65 wt % relative to phenolic fraction) was synthesized *via* polycondensation of "raw" phenols with formaldehyde. The synthesized resin was used to modify oxidized and distillation road bitumen. The addition of modifier slightly increases the softening point of bitumen and significantly increases the adhesion to crushed stone and glass. The increase in modifier amount from 1 to 2.4 wt % does not significantly affect the adhesion, therefore the content of 1.0 wt % should be considered as an optimum one. Structural types of pure oxidized and modified bitumen were determined according to the group-chemical composition criterion and calculated criteria. In both cases the type was found to be 3 ("sol-gel"). It was confirmed that the modification of BND 60/90 oxidized road bitumen with phenol-cresol-formaldehyde resin in the amount of 1.0 wt % does not change its structural type.

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ВПЛИВ ФЕНОЛО-КРЕЗОЛО-ФОРМАЛЬДЕГІДНОЇ СМОЛИ НА АДГЕЗІЙНІ ТА ФІЗИКО-МЕХАНІЧНІ ВЛАСТИВОСТІ ДОРОЖНІХ БІТУМІВ

Анотація. *Методом поліконденсації «сирих» фенолів з формальдегідом синтезовано феноло-крезоло-формальдегідну смолу (ФКФС) з фенольної фракції кам'яновугільної смоли. Проведено модифікування дорожніх бітумів цією смолою. За різного вмісту ФКФС встановлено можливість її ефективного використання у якості модифікатора дорожніх нафтових бітумів. Встановлено, що ФКФС є ефективною адгезійною добавкою для дорожніх бітумів. Визначено структурний тип окисненого та модифікованого бітумів за критерієм групового-хімічного складу та розрахунковими критеріями.*

Ключові слова: *бітум, адгезія, модифікатор, феноло-крезоло-формальдегідна смола.*