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PRODUCTION OF BITUMEN MODIFIED WITH LOW-MOLECULAR ORGANIC COMPOUNDS FROM PETROLEUM RESIDUES. 9. STONE MASTIC ASPHALT USING FORMALDEHYDE MODIFIED TARS

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Abstract. The work is devoted to a completely new binder for asphalt-concrete mixtures, in particular, crushed stone-mastic mixtures. In the role of a binder, it is proposed to use raw materials for the production of bitumen − tars modified with a forming agent (catalyst and formalin). The paper proves the advantage of using tar modified with formalin, in comparison with standard oxidized bitumens, on the example of established physical and mechanical properties of bituminous binders and crushed-mastic asphalt concrete SMA-15.

Keywords: stone mastic asphalt, tar, formalin, formaldehyde, catalyst.

1. Introduction

Road bitumens are the main binding material used to produce asphalt concrete mixtures used in highway construction. For the production of road bitumen, residues from oil processing are used, most often these are residues after processes vacuum distillation of oil (tars).[1-4] A number of problems arise when obtaining road bitumens from tars and their application. The first of them is the impossibility of obtaining high-quality road distillation (residual) bitumen at oil refining enterprises, including Ukraine, which is explained by the lack of heavy aromatic oils on the market, which are actually the optimal raw materials for the production of road bitumen. The second is their unsatisfactory operational characteristics, mainly heat resistance and adhesion between the binder and the aggregate, which, with an increase in the intensity of traffic, an increase in the volume of heavy-duty transportation, the mass of cars, together with the influence of weather and climate factors on the structure, leads to the destruction of the road surface. Thirdly, in order to improve the operational properties of bitumen (both distilled and oxidized), it is necessary to add expensive industrial polymers and adhesives to them. Most polymer modifiers are poorly compatible with bitumen, which leads to delamination of such bitumen-polymer mixtures during their storage. It should also be noted that Ukraine does not have its own production of polymer bitumen modifiers, they are imported, which causes their high cost in our market.[5-8]

Therefore, the use of new bituminous materials obtained by the method of chemical modification of oil residues (tars) and bitumen with inexpensive substances produced by Ukrainian industry is relevant. The authors in previous studies proved[6-10] that the use of the chemical modification method will allow to obtain heat-resistant bitumen with excellent adhesive properties. Stone mastic asphalt (SMA) is currently the most effective material in Ukraine for covering road structures, both for highways and bridges.Therefore, it is proposed to study this material on the basis of a new binder using formalin.[11-12]

2. Experimental

2.1. Raw Materials

Two samples of oxidized bitumen, OB2 and OB5, respectively, were obtained from two selected samples of tars (T1 and T2) at different time intervals under factors controlling the oxidation process at JSC Ukrtatnafta (Kremenchuk, Ukraine). Physico-mechanical properties of tars (T1 and T2) and oxidized bitumen obtained from them (OB2 and OB5) are given in Table 1 and Table 2 respectively.

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Table 1. Physico-mechanical properties of tars

Index	Unit	Value	
		T1	T2
Density at 293 K	kg/m^3	982.9	1.0087
Boiling point	K	659	426
Flash temperature	K	555	568
Penetration at 298 K	dmm	247	208
Softening point	K	312	314
Ductility at 298 K	cm	58	>100
Fraass breaking point	K	255	-29

Table 2. Physico-mechanical properties of road bitumen 70/100 (OB2; OB5)

Index	Unit	Value	
		OB2	OB5
Penetration at 298 K	dmm	82	75
Softening point	K	320.4	322.0
Ductility at 298 K	cm	>150	>150
Fraass breaking point	K	261	260
Flash temperature	K	549	571

Technical formalin (37 % aqueous solution of formaldehyde; colorless transparent liquid) was used as a tar modifier to create a bituminous binder, the following acids were used as a process catalyst: concentrated hydrochloric acid technical, 37 % aqueous solution of HCl (density at 293 K – 1.19 g/cm^3); concentrated sulfuric acid technical (density at 293 K – 1.8356 g/cm^3); concentrated technical orthophosphoric acid, 73 % aqueous solution of H_3PO_4 (density at 293 K – 1.572 g/cm^3); concentrated acetic acid (glacial), the content of the main substance is not less than 99.85 wt. %.[13-19]

2.2. Experimental Procedure

2.2.1. Modification of tars with formalin

During the chemical modification of tars with formalin (a 37 % aqueous solution of formaldehyde), products were obtained, the quality characteristics of which allowed to classify them as commercial bituminous road materials that meet the requirements of the relevant regulatory documents.

Chemical modification with formalin without stirring was carried out in hermetic stationary reactors capable of working under excess pressure (Fig. 1). This is due to the toxicity[20] and the ability to evaporate formaldehyde at the operating temperature of the process (333–433 K). First, a formulating mixture was prepared separately – a mixture of formalin and catalyst in the required ratio. First, tar (oil residue) or oxidized bitumen and solvent (if necessary) were loaded into the reactor and mixed until a homogeneous mass was reached. After cooling the mixture, a forming agent (a mixture of formalin and catalyst) was added. The reactor was hermetically closed and placed in a silicone bath heated to the required temperature, and the time of the start of the chemical modification process was recorded. At the end of the modification process, the depressurized container was placed in a vacuum cabinet to remove water and unreacted components. Vacuum drying was carried out for 4 hours at 393 K and a pressure of less than 10 mm Hg.[21-22]

Fig. 1. View of reactors for modification of tar or bitumen with formaldehyde without mixing

After vacuum drying of the obtained products, their analysis was carried out according to the indicators that are standardized for bituminous materials. In order to obtain modified bitumens for testing them in asphalt concrete, a reactor with a larger volume was used. Performance characteristics of the products obtained under the same conditions of modification of oil residues and bitumen with formaldehyde when using small and large volume reactors practically did not differ. This also indicates the effectiveness of using reactors without mixing.

2.2.2. Preparation of SMA

The preparation of different versions of stone mastic asphalt and his mixture met Ukrainian standards.[23-24] Granite crushed stone and limestone mineral powder were used for the production of stone mastic asphalt. The granulometric composition of the mineral part of stone mastic asphalt mixtures was selected according to the average curve in accordance with the requirements for SMA-15.The composition of SMA was selected for type SMA-15 (Table 3). The manufacturing and compaction temperatures of SMA comply with those required by standards.

Table 3. Composition of SMA-15

Name of material	Content of material in asphalt concrete, wt.%
1. Aggregates including factions	85.0
10/15 mm	50.0
5/10 mm	20.0
0,071/5 mm	15.0
2. Limestone filler aggregate	15.0
Total	100.0
3. Stabilizing additive	0.4
4. Bitumen binder (OB2, OB5, FMA-1, FMA-2, FMA-3, FMA-4, FMA-8, FMA-10, FMA-11, and FMA-12)	6.5

2.2.3. Testing of SMA

The study of SMA in the form of cylindrical samples (diameter and height 71.4 mm and weight 655.0 g) was carried out according to Ukrainian research methods. since the materials used are local.

The average density of SMA was determined by hydrostatic weighing. Residual porosity was determined by the pores volume in the SMA based on the given average density of the cylindrical samples and the actual density of the SMA mix. Water-saturation was determined by the quantity of water, which is absorbed by a sample at pre-set mode of saturation in vacuum unit. The compression strength at 293 and 323 K of SMA was determined on mechanical presses with press-plate movement speed of (3.0 ± 0.1) mm/min. For testing, SMA samples are placed under the press plates with flat upper and lower faces of the cylinder. Before testing the samples are thermostat-conditioned in a vessel with water for (60 ± 5) min at temperatures: (323 ± 1) K, (292 ± 1) K. The samples for testing compression strength at 323 K are placed (before the thermostat-conditioning) into the tight polyethylene bags – to prevent their contact with water.[25]

3. Results and Discussion

3.1. Tar modification

The selected T1 and T2 bitumens are characterized by high values of P298 (247 and 208 dmm) and low values of SP (312.0 and 314.2 K), which does not allow them to be used as binding materials in road construction. Tars modified with formaldehyde (FMT-1, FMT-2, and FMT-3 were obtained from T1; T2 – FMT-8 and FMT-9) were obtained using concentrated sulfuric acid as a process catalyst with optimal values of process control factors.[26] It was also established that other inorganic acids are effective catalysts of the process (HCl та H_3PO_4). Therefore, for comparison, FMTs were obtained using concentrated hydrochloric and orthophosphoric acids as catalysts of the process with the values of the factors that coincide with the values when modifying with the use of sulfuric acid (Table 4). The formalin/catalyst mass ratio for all FMTs is the same and equal to – 1.0. The temperature and duration of modification also do not differ significantly and are 378–403 K and 0.6–1.0 hours, respectively. The only difference is the amount of the modifier - forming agent (mixture of formalin and catalyst). To obtain a bituminous material with approximately the same softening temperature, a different amount of forming agent is required depending on the nature of the catalyst used. For example, FMT-8, FMT-10, and FMT-11 were obtained from T2, which are characterized by approximately the same softening temperature of 325.4, 321.8, and 324.2 K, respectively. They differ in the amount and composition of the forming agent: FMT-8 – 4.0 wt.% for raw materials (2.0 wt.% of formalin and 2.0 wt.% of concentrated sulfuric acid); FMT-10 – 6.0 wt.% for raw materials (3.0 wt.% of formalin and 3.0 wt.% of concentrated hydrochloric acid); FMT-11 – 6.0 wt.% for raw materials (3.0 wt.% of formalin and 3.0 wt.% of concentrated orthophosphoric acid).

Physico-mechanical properties of modified tars are shown in Table 5.

Guided by the current regulatory documents, the obtained samples of FMT correspond to the brands of binding materials in terms of their main physical and mechanical properties (Table 6).

Table 4. Control parameters of the chemical modification of tars with formaldehyde

Variable parameter of process	Units	FMT-1	FMT-2	FMT-3	FMT-4	FMT-5	FMT-6	FMT-7	FMT-8	FMT-9	FMT-10	FMT-11	FMT-12
Raw	–	T1							T2				
Amount of formalin (including formaldehyde)	% wt. for raw materials	1.0 (0.37)	1.9 (0.70)	3.0 (1.11)	3.2 (1.18)	1.0 (0.37)	2.0 (0.74)	3.0 (1.11)	1.0 (0.37)	2.0 (0.74)	3.0 (1.11)	3.0 (1.11)	3.0 (1.11)
Type of process catalyst	–	H_2SO_4			HCl	H_3PO_4			H_2SO_4		HCl	H_3PO_4	CH_3COOH
Amount of catalyst	% wt. for raw materials	1.1	1.7	3.2	3.1	1.0	2.0	3.0	1.0	2.0	3.0	3.0	3.0
Mass ratio formalin / catalyst	–	0.91	1.12	0.94	1.0	1.0	1.0	1.0	1.0		1.0	1.0	1.0
Modification temperature	K	383	378	383	373	403	403	403	403		403	403	403
Duration of modification	h	0.6	0.6	0.8	1.0	1.0	1.0	1.0	1.0		1.0	1.0	1.0

Table 5. Physico-mechanical properties of modified tars

Index	FMT-1	FMT-2	FMT-3	FMT-4	FMT-5	FMT-6	FMT-7	FMT-8	FMT-9	FMT-10	FMT-11	FMT-12	BND100/150[27]	BND 70/100[27]	BMPA 70/100-55[28]	BMPP 35/50-70[28]
Penetration at 298 K, dmm	144	89	47	131	139	95	83	58	43	78	99	157	101–150	71–100	71-100	35-50
Softening point, K	321	332	356.4	320.4	319.4	324.6	331.8	325.4	345	321.8	324.2	316.1	314–320	318–324	≥328	≥338
Ductility at 298 K, cm	42	16	4	59	79	111	134	15	12	>100	86	>100	≥70	≥60	–	–
Elasticity at 298 K, %	14.6	16.7	17.3	11.2	22.0	18.5	19.3	14.6	14.6	16.5	24.6	23.6	–	–	≥55	≥55
Fraass breaking point, K	256	258	264	259	253	256	259	253	256	249	250	247	≤257	≤260	≤255	≤260

That is, this method allows obtaining almost any bituminous materials for road construction. The intensification of the modification process (decrease in P298 and increase in SP) depends on the amount of the forming mixture (formalin/catalyst mixture). To obtain bitumens with high SP (FMT-3 and FMT-9) a larger amount of modifier (formulating mixture) is required. These data indicate the high flexibility of this process, in contrast to the traditional oxidation process, in which it is impossible to obtain such bitumens. Also, the advantage of the process of chemical modification of tar with formaldehyde in comparison with oxidation is a significantly shorter reaction time. Inorganic acids are the most effective catalysts in the process of chemical modification of tars with formaldehyde. If inorganic acids are compared with each other, their efficiency can be placed in the following order: $H_2SO_4 \rightarrow H_3PO_4 \rightarrow HCl$. If we talk about their shortcomings, then concentrated sulfuric acid is capable of sulfonation reaction of aromatic structures of bitumen, and the use of concentrated hydrochloric acid intensifies the corrosion processes of equipment, which requires the use of special expensive alloys during the construction of the installation. Concentrated orthophosphoric acid is devoid of these disadvantages. It should also be noted about another advantage of using orthophosphoric acid, which allows obtaining bituminous materials with higher values of the D298 indicator, which indicates the plasticizing effect of this acid.

A significant advantage of the process of chemical modification of tar with formaldehyde is that the obtained materials with approximately the same SP have a higher value of the P298 index in comparison with the oxidation process. This can be explained by the fact that the process of oxidation of tar with air oxygen at 444–453 K leads to thermo-oxidative destruction of paraffinic and naphthenic hydrocarbon structures (oxidation gases and black solar are formed in the process), which leads to an increase in hardness and a decrease in plasticity of the obtained products. In the process of chemical modification of tar with formaldehyde, which takes place at lower temperatures and without the participation of oxygen, the probability of such processes is much lower, these paraffin and naphthenic structures remain in the product, which leads to high P298 values. Such bituminous materials (FMT) are good raw materials for the process of modification with polymers (for example, SBS, terpolymers, waxes, *etc.*) in which P298 is significantly reduced. It will also allow to reduce the polymer content, which will be necessary to bring the E298 indicator to the required values.

Table 6. Physico-mechanical properties of modified tars

No.	Binder	Types	Methods
1.	Petroleum road viscous bitumen	– BND 150/220 – FMT-12; – BND 100/150 – FMT-1, FMT-4, and FMT-5; – BND 70/100 – FMT-2, FMT-6, FMT-7, FMT-10, FMT-11; – BND 50/70 – FMT-8.	[27]
2.	Bitumen modified with polymers (according to the softening temperature)	– BMPA 70/100-55 – FMT-2, FMT-7; – BMPP 35/50-70 – FMT-3, FMT-9.	[28]
3.	Bitumen modified with synthetic waxes	– BMW-S 60/90 – FMT-2, FMT-7; – BMW-S 40/60 – FMT-3, FMT-9.	[29]
4.	Bitumen modified with adhesive additives	– BND-A 70/100 – FMT-6, FMT-7, FMT-10; – BND-A 35/50 – FMT-3, FMT-9.	[30]

Table 7. Physico-mechanical properties of SMA-15 using oxidized bitumens (for comparison) and tars modified with formaldehyde

Index	OB2	OB5	FMT-1	FMT-2	FMT-3	FMT-4	FMT-8	FMT–10	FMT–11	FMT-12	Requirements for SMA-15[23]
Raw material modification	–	–	T1				T2				–
Catalyst type	–	–	H_2SO_4			HCl	H_2SO_4	HCl	H_3PO_4	CH_3COOH	–
Physical and mechanical properties of SMA-15											
Average density, g/cm^3	2.41	2.37	2,39	2.37	2.38	2.40	2.37	2.37	2.35	2.37	–
Water saturation, % vol.	1.5	2.3	2.0	2.3	2.5	2.1	1.5	1.0	1.5	1.0	1.0-3.0
Compressive strength limit (MPa) at temperature:											
293 K	2.7	3.5	1.5	1.4	2.2	2.6	4.0	3.1	2.9	3.2	≥ 2.1
323 K	1.7	1.2	0.6	0.7	1.0	1.1	1.2	0.9	1.0	0.7	≥ 0.6
Compressive strength limit (MPa) after water saturation at temperature:											
323 K	1.8	0.9	1.3	1.7	2.3	1.2	0.9	0.7	0.6	0.8	–

Analyzing the data in the Table 7, we observe that all SMAs using FMT meet the regulatory requirements for SMA-15 according to DSTU B V.2.7-127:2015.

It can be seen that the physical and mechanical properties of SMA-15 are influenced by the raw material of the modification. With the use of FMT-8, FMT-10, FMT-11, and FMT-12, which are obtained from tar – T2, SMA-15 has better indicators of water saturation and strength at 293 and 323 K, compared to FMT-1, FMT- 2, FMT-3, and FMT-4, which are obtained from T1.

SMA-15 using FMT-8, FMT-10, FMT-11, and FMT-12 are characterized by low water saturation values (1.0–1.5 % by volume), which confirms the good adhesion ability of these bituminous materials to the surface of traditional acidic fillers asphalt concrete.

4. Conclusions

The influence of different types of catalysts on the process of chemical modification of oil residues with formaldehyde, namely concentrated sulfuric, hydrochloric, orthophosphoric and acetic acids, was investigated. It was established that the most effective catalyst for tar modification with formaldehyde is H_2SO_4, which is much more active than the others. A complete analysis of bituminous materials obtained by the method of modifying tars with formaldehyde using various process catalysts was carried out.

It was established that, in comparison with traditional oxidized bitumens, tars modified with formaldehyde are characterized by higher penetration values at the same softening temperatures, which is their advantage.

The design of the composition of crushed stone-mastic asphalt concrete mixtures and the formation and testing of samples of crushed stone-mastic asphalt concrete with the use of the investigated new binding materials were carried out. In most cases, crushed stone-mastic asphalt concretes correspond to the regulatory indicators of the SMA-15 brand in accordance with DSTU B V.2.7-127:2015.

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Abbreviations

OB	Oxidized bitumen
FMT	Formaldehyde modified tar
SMA	Stone mastic asphalt
T	Tar
D298	Ductility at 298 K (cm)
P298	Penetration at 298 K (dmm)
SP	Softening point (K)

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ОДЕРЖАННЯ БІТУМУ, МОДИФІКОВАНОГО НИЗЬКОМОЛЕКУЛЯРНИМИ ОРГАНІЧНИМИ СПОЛУКАМИ ІЗ НАФТОВИХ ЗАЛИШКІВ. 9. ЩЕБЕНЕВО-МАСТИКОВИЙ АСФАЛЬТОБЕТОН ІЗ ВИКОРИСТАННЯМ ГУДРОНІВ, МОДИФІКОВАНИХ ФОРМАЛІНОМ

Анотація. *Робота присвячена абсолютно новому в'яжучому для асфальтбетонних сумішей, зокрема і щебенево-мастикових. У ролі в'яжучого запропоновано використовувати сировину для виробництва бітумів – гудрони, що модифіковані формілюючим агентом (каталізатор та формалін). У роботі доведена перевага використання гудрону, модифікованого формаліном, у порівняні із стандартними окисненими бітумами, на прикладі встановлених фізико-механічних властивостей бітумних в'яжучих та щебенево-мастикового асфальтобетону SMA 15.*

Ключові слова: *щебенево-мастиковий асфальтобетон, гудрон, формалін, формальдегід, каталізатор.*