

PRODUCTION OF BITUMEN MODIFIED WITH LOW-MOLECULAR ORGANIC COMPOUNDS FROM PETROLEUM RESIDUES. 5. USE OF MALEIC ANHYDRIDE FOR FOAMING BITUMENS

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Abstract. The possibility of using maleic anhydride as a foaming agent to produce foamed bitumen was investigated. The optimal content of maleic anhydride was determined according to the indicators of the growth of the binder volume and the half-life of the foam. Using maleic anhydride as a foaming agent, foamed bitumen was obtained and the latter was utilized to prepare two samples of stone mastic asphalt, which differed in mixing and compaction temperatures of a stone mastic asphalt mix. For comparison, the composition of a stone mastic asphalt mix was designed using non-foamed (BND 70/100 and BND 70/100 modified with maleic anhydride) and foamed bitumen (BND 70/100 foamed with maleic anhydride at two different temperatures). Stone mastic asphalt specimens were formed and tested.¹

Keywords: maleic anhydride, modified bitumen, foamed bitumen, warm mix asphalt.

Abbreviations

ACM – asphalt concrete mixture

BND – road oil bitumen;

FB – foamed bitumen;

FBP – Fraas breaking point;

HMA – hot mix asphalt;

MA – maleic anhydride;

MP – mineral powder;

PI – plasticity interval;

SMA – stone mastic asphalt;

SMAM – stone mastic asphalt mix;

SP – softening point;

WMA – warm mix asphalt.

1. Introduction

Based on the foreign practice,¹⁻⁵ it can be argued that the use of WMA is one of the most promising areas of the road technology. It is known that the degree of coverage of stone materials with bitumen is largely determined by the viscosity of the binder. Generally, the lower the viscosity of the bitumen, the faster and more evenly all the grains are covered with a bitumen. Traditionally, NMA is prepared and stacked at following temperatures: 423–443 K – preparation, 413–423 K – at the beginning of compaction, completion of rolling – not less than 353 K. 20–40 K are higher. It is also worth noting the benefits of using WMA, such as reduced CO₂ emissions, energy savings, reduced bitumen oxidation processes, increased distances and transport times, the ability to stack and seal in the cold season. At that time, no shortcomings were identified.

WMA mixtures can be produced by different techniques, using organic or chemical additives or foaming processes.^{6,7} The latter can be obtained by water-containing technologies or by water-based technologies.⁵ Water-containing technologies utilize incorporating additives which include water in their composition. Water-based additives for foaming bitumen are usually used in the form of powders. For example, in the form of zeolite – a natural or synthetic mineral with a high content of binded water, consisting of porous cubic crystals of a micro size. Zeolite-synthetic sodium

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aluminosilicate in the form of spherical white granules with a diameter of approximately 0.3 mm is used to prepare WMA.⁸⁻¹¹ In the water-based technologies, water is injected into the hot bitumen in small quantities and is immediately added to the aggregates in the asphalt

mixing chamber.¹² This process is usually more technically complex and requires a relatively large financial investment for plant modifications. For the production of FB by direct injection of water, air and water are injected in bitumen as shown in Fig. 1.

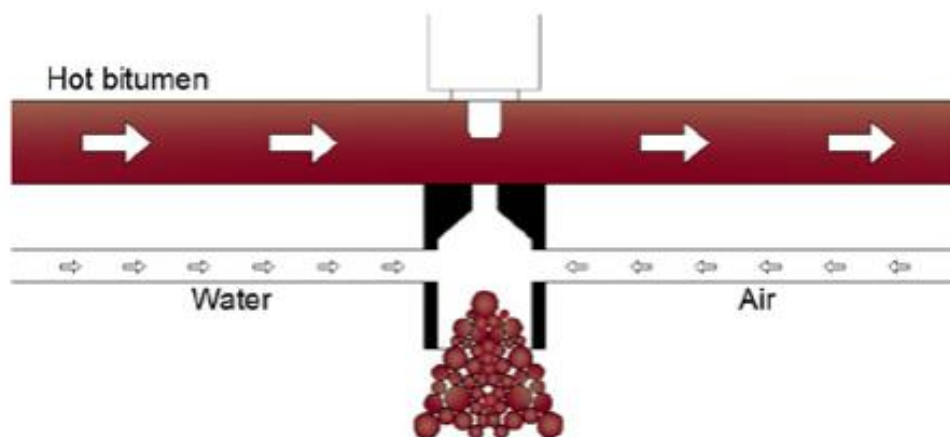


Fig. 1. Schematic procedure of producing foamed bitumen

The use of bitumen in the foamed state is one of the promising areas for improving the quality and efficiency of ACM production. Foaming reduces the surface tension of bitumen and therefore facilitates the process of mixing the mixture, promotes better coverage and uniform distribution of bitumen on the surface of mineral grains. This allows to reduce the cooking temperature of the ACM and, thus, to provide significant energy savings. Lower technological temperatures cause less thermal aging of bitumen, which, in turn, leads to improved quality of asphalt concrete and increased durability of the road surface. The formation of thinner bitumen films on the mineral surface reduces the required amount of bituminous binder and thus reduces the cost of ACM.^{6,7}

In addition, the quality of the bituminous binder used for ACM is important as well. It is known that the use of high molecular weight polymers in the bituminous binder helps to ensure the necessary physical and mechanical properties of coatings and their durability in conditions of heavy and intense traffic. Therefore, for many years, various additives have been used as modifiers of bituminous binders, which do not react with the components of bitumen (physical modification of bitumen) and additives that react with components of bitumen (chemical modification of bitumen). Physical modifiers of bitumen include thermoplastic polymers (polyethylene,¹³ polypropylene¹⁴), thermoplastic elastomers

(styrene-butadiene-styrene triblock copolymers (SBS)^{15,16}), polycondensation resins (phenol-cresol-formaldehyde resins and phenol-formaldehyde resins with labile peroxy bonds or methacrylic components¹⁷⁻²¹), petroleum resins with epoxy, hydroxy or carboxy groups,²² and also sulfur and sulfur-organic copolymers.²²⁻²³ Chemical modifiers of bitumen include polyphosphoric acid,²⁴ dodecylbenzene sulfonic acid (DBSA),²⁵ silane coupling agent (SCA),²⁶ thiourea dioxide (ThD)²⁷ or low-molecular organic compounds (formaldehyde and maleic anhydride).²⁸⁻³²

However, during studying the chemical modification of bitumens by MA, in addition to the chemical interaction of MA and bitumen components, active foaming of modified bitumens³⁰ was also observed. So, it was decided to investigate the possibility of using MA to obtain FB from which WMA was later made.

2. Experimental

2.1. Materials

The following materials were used for the modification of petroleum residues with maleic anhydride:

- paving bitumen BND 70/100 (oxidized bitumen) produced at JSC Ukrtatnafta (Kremenchuk, Ukraine). Its characteristics are given in Table 1, designated as BND 70/100;
- MA, white crystalline powder (used as a process modifier / chemical reagent);

To determine the preparation of gravel-mastic mixtures, the following materials were used:

- Crushed stone parts and crushed stone from natural stone, fr. 0–5, 5–10, 10–15 mm from LLC Novograd-Volyn Stone Crushing Plant;

- MP produced by “Skala-Podilskii Spetscarier (Special Quarry)”;
- stabilizing cellulose additive Celbit in the form of granules treated with bitumen in quantity 15 wt %. The humidity of Celbit was 1.8 wt %.

Table 1. Characteristics of bitumen BND 70/100

Index	Value	Standard or Ref.
Penetration at 298 K (0.1mm)	71	EN 1426:2018
Softening point (K)	319	EN 1427:2018
Ductility at 298 K (cm)	>100	EN 13398:2018
Adhesion to gravel (mark)	2.5	DSTU B V.2.7-81-98
Fraas breaking point (K)	263	EN 12593:2018
Plasticity interval (K)	329	PI = SP – FBP
Resistance to hardening at 436 K (RTFOT method):		EN 12607-1:2014
mass change (wt %)	0.03	
softening point after RTFOT (K)	325.2	
penetration at 298K after RTFOT (0.1 mm)	55	
softening point change (K)	6.2	
residual penetration (%)	77.5	

2.2. Experimental Procedure

Foaming of petroleum road bitumen was carried out in a metal cylindrical tank. The amount of bitumen was 500 g. Foaming agent – MA. It was added in one portion. Fig. 2 shows the process of foaming bitumen.

During foaming, the bitumen first expands to its maximum volume, remaining in this state for some time, and then slowly returns to its original volume.

Foamed bitumen is characterized by the following basic properties:

- degree of foaming (multiplicity of foaming) – is estimated by increase in volume of bitumen in the foamed state in comparison with an initial volume;
- stability (stability, survivability of the foamed state) – the ability of the foamed binder to maintain its volume over time.³³

These properties are interrelated and depend on the brand of the source bitumen and the laboratory or production conditions of the foam (foaming unit). Experience has shown that a sufficient degree of foaming is achieved by 10–15 times increase of the volume.

To determine the degree of foaming of bitumen, the rate of increase of its volume during the transition to

the foamed state is used, and the half-life of foam is applied as a criterion to assess the stability. The growth rate of the binder as a result of foaming is defined as the ratio of the maximum volume to its initial volume.

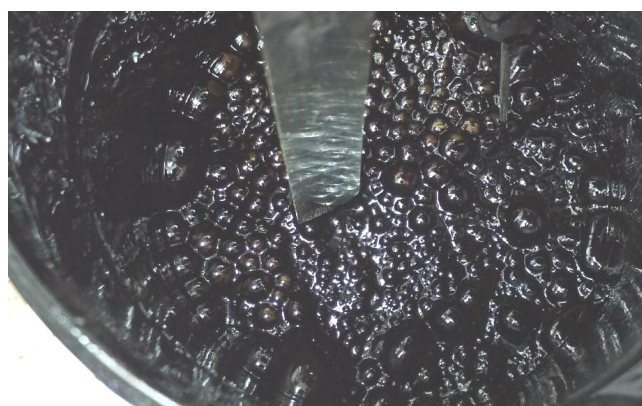


Fig. 2. The process of foaming bitumen by MA

The growth rate of the binder during foaming is calculated according to the formula:

$$\Delta V = V_{\max} / V_{\min}, \tag{1}$$

where V_{\max} – the maximum volume of the binder in the foamed state (cm^3); V_{\min} – the initial volume of the binder (cm^3).

The growth rate of the binder during foaming should be in the range from 10 to 20.

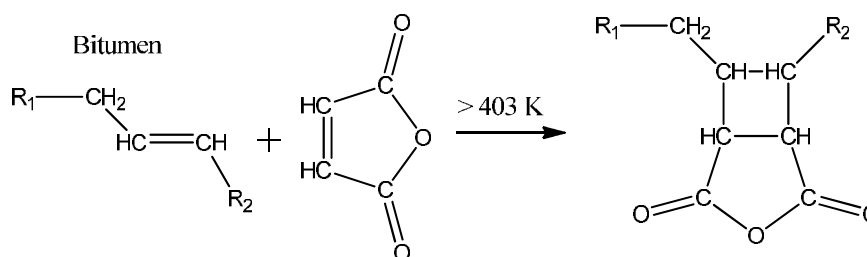
The half-life of the foam ($T_{1/2}$) is the time required to reduce the maximum volume of foamed bitumen by half. The half-life of the foam should be within 15–30 seconds.³⁴

The study of SMA in the form of cylindrical specimens (a diameter and a height of 71.4 mm and a weight of 655.0 g) was conducted according to the Ukrainian research methods. The average density of SMA was determined by hydrostatic weighing. Residual porosity was assessed by pore volume in SMA based on pre-set average density of cylindrical samples and the actual density of an SMA mix. Water-saturation was measured by the quantity of water absorbed by a sample at pre-set mode of saturation in a vacuum unit. The compression tensile 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 cylinder faces. Prior to measurements, the samples are thermostat-conditioned in a vessel with water during (60 ± 5) min at the temperature: (323 ± 1) K, (293 ± 1) K. The samples for testing compression tensile strength at 323 K are placed (before the thermostat-conditioning) into the tight polyethylene bags in order to prevent their contact with water. The compressive strength after water saturation at a temperature of 323 K was determined on samples after their saturation with water.

3. Results and Discussion

In studies,^{30,35,36} it was found that when MA is added to bitumen, it interacts with it by the Diels-Alder reaction:



MA is known to be a hygroscopic compound, *i.e.* a crystalline compound contains water. During storage, the water content in MA can also increase. In our opinion, the water present in MA causes the foaming effect. That is, the addition of MA to road bitumen at temperatures above 403 K can achieve two positive effects, namely:

- 1) chemical modification of petroleum bitumen, which will improve the performance of the binder (heat resistance and adhesion to the surface of mineral fillers),^{30,35}
- 2) foaming of petroleum bitumens, the use of which will allow to obtain WMA, *i.e.* will reduce the temperature of manufacture, laying and compaction of ACM.

After research, it was found that the optimal growth rate of the binder ($\Delta V = 19$) and the half-life of the foam ($T_{1/2} = 27$ s) for foaming bitumen is reached by addition of 2 wt % MA of the mass of the bitumen at a bituminous binder temperature of 418 K. It should be noted that a difference in the size and number of foam bubbles was revealed while

comparing the foaming of bitumen with MA and water. Using the anhydride, we observed a larger number of bubbles, but their size was smaller in comparison with the foaming with water.

During the application of foamed bitumens, the technological process of SMAM preparation did not change significantly and was carried out in accordance with the standard sequence and content of technological operations in accordance with DSTU B V.2.7-127:2015 and DSTU B V.2.7-319. When using foamed bitumens, the preparation of mineral materials (sand, gravel and mineral powder), their drying, fractionation, dosing and feeding into the mixer were performed in the same sequence as in the conventional SMAM preparation technology. The only difference in the technology was the change in the processes of preparation and supply of a binder, which ensure its introduction into the mixer in the foamed state. The process of foaming bitumen consisted of such technological operations:

- heating the source bitumen to the appropriate temperature;
- addition of MA to the hot bitumen;

• mixing the bituminous binder until appearing of a foam and dosing and mixing it with mineral materials.

Due to the foaming effect, the bitumen turned into a relatively stable fine heterogeneous system, which consisted of a binder, air, water and steam. Remarkably, SMAM itself was characterized by plasticity, the facilitated mixing, and a more uniform distribution of bitumen on the surface of the mineral materials, accompanied by coating all mineral particles with a

thin bituminous film. Due to the above-mentioned characteristics and a relatively low temperature of the original bituminous binder, the technological temperatures of preparation and compaction of the mixture were reduced (Table 2).

The effect of modification of oxidized bitumen with MA, *i.e.* the comparison of the performance properties of BND 70/100 and modified, is given in Table 3.

Table 2. Temperature technological mode of production and consolidation of SMAM-15

Sample		Temperature (K)			
		mineral material	bitumen	SMAM	SMAM when compacted
Non-foamed bitumen	BND 70/100	453	428	438	428
	BND 70/100 + 2 wt % MA*		428	438	428
Foamed bitumen	FB1 foaming agent – 2 wt %; BND70/100		418	428	418
	FB2 foaming agent – 2 wt %; BND70/100	423	403	413	408

Note: conditions of the modification process: temperature – 403 K and time – 30 min.

Table 3. Characteristics of non-foamed bitumen

Index	BND 70/100	BND 70/100 + 2 wt % MA*	Standard or Ref.
Penetration at 298 K (0.1mm)	71	27	EN 1426:2018
Softening point (K)	319	333	EN 1427:2018
Ductility at 298 K (cm)	>100	–	EN 13398:2018
Adhesion to gravel (mark)	2.5	4.0	DSTU B V.2.7-81-98
Fraas breaking point (K)	263	263	EN 12593:2018
Plasticity interval (K)	56	70	PI = SP – FBP
Resistance to hardening at 436 K (RTFOT method):			EN 12607-1:2014
mass change (wt %)	0.03	0.23	
softening point after RTFOT (K)	325.2	324.4	
penetration at 298K after RTFOT (0.1 mm)	55	38	
softening point change (K)	6.2	-7.6	
residual penetration (%)	77.5	140.7	

Note: * conditions of the modification process: temperature – 403 K and time – 30 min.

Table 3 shows that the modification of MA bitumen significantly increases SP (from 319 to 333 K), but in during a short heating at 436 K, SP decreases to 324.4 K. This anomalous behavior of the binder modified MA will be studied in the following works. Also, modification of MA bitumen significantly increases PI and adhesion to the gravel surface.

The next stage of research was the design of SMAM-15 based on non-foamed (BND 70/100 and BND 70/100 + 2 wt % MA) or foamed bitumen (FB1 and FB2). The grain composition of SMAM-15 and SMA-15 based on it were designed to include a stabilizing additive for SMA (Celbit fiber treated with Celbit bitumen) and various binder variants (non-foamed or foamed bitumen BND 70/100).

The selected composition of SMAM-15 is given in Table 4.

Physico-mechanical properties of the molded samples of SMA-15 using different types of binder (non-foamed or foamed bitumen) are given in Table 5. The flow rate of the binder from SMAM-15 for all compositions

did not exceed 0.20 wt % according to requirement DSTU B V.2.7-127:2015.

Table 4. Composition of SMAM-15

Name of material	Content of material in asphalt concrete (wt %)
1 Aggregates	85
including fractions	
10/15 mm	50
5/10 mm	20
0.071/5 mm	15
2 MP(≤0,071 mm)	15
3 Celbit	0.4
4 Bitumen (non-foamed or foamed bitumen)	6.5

Table 5. Physical and mechanical properties of SMA-15

№	Index	SMA-15				Requirements for SMA-15 according to DSTU B V.2.7-127:2015
		non-foamed bitumen		foamed bitumen		
		BND 70/100	BND 70/100 + wt 2 %*	FB1	FB2	
1	Average density (g/cm ³)	2.41	2.37	2.41	2.39	–
2	Water-saturation (% vol)	1.7	2.4	1.5	2.2	1.0/3.0
3	Compressive strength (MPa): 293 K 323 K	3.7	2.8	3.8	2.9	≥ 2.1
		1.4	1.4	1.4	1.1	≥ 0.6
4	Compressive strength after water-saturation for 323 K (MPa)	1.2	1.3	1.2	0.9	–

Note: *conditions of the modification process: temperature – 403 K and time – 30 min.

The analysis of Table 5 reveals that the foaming of MA at low process temperatures (samples FB1 and FB2) enables manufacturing SMA-15, which according to certain indicators meets the requirements of DSTU B V.2.7-127: 2015. In addition, due to foaming, the physical and mechanical properties of SMA-15 at low process temperatures are similar to those of SMA-15 made at standard non-foaming process temperatures for hot SMA-15 using oxidized bitumen

(FB1). Nevertheless, a critical reduction in process temperatures, as in the case of FB2 temperature regimes, requires an increase in the mixing time of the mixture to cover the binder grains of the stone material. Even after doubling this time, not all grains of stone material remained coated with the binder that resulted in lower physical and mechanical properties of SMA-15 on binder FB2 as compared with other SMA-15s listed in Table 5.

4. Conclusions

The expediency of using maleic anhydride as a foaming agent for the production of so-called foamed bitumens was studied. The application of the foamed bitumens allows to reduce the temperature of production, laying and compaction of crushed-mastic asphalt concrete, which can significantly reduce the cost of road construction. It was found that, when used as a foaming agent, maleic anhydride in the amount of 2 % of the bitumen mass allows to decrease the production temperature of SMA-15 by at least 20 K. It was shown that foaming of bitumen with maleic anhydride at significantly lower technological temperatures enables production of asphalt concrete mixtures that meet the physical and mechanical parameters of the regulatory requirements, whereas the physical and mechanical properties of the samples prepared at low process temperatures are similar to those of the samples made at standard process temperatures without foaming.

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ОДЕРЖАННЯ БІТУМУ, МОДИФІКОВАНОГО НИЗЬКОМОЛЕКУЛЯРНИМИ ОРГАНІЧНИМИ СПОЛУКАМИ ІЗ НАФТОВИХ ЗАЛИШКІВ. 5. ВИКОРИСТАННЯ МАЛЕЙНОВОГО АНГІДРИДУ ДЛЯ ОДЕРЖАННЯ СПІНЕНИХ БІТУМІВ

Анотація. В роботі досліджено можливість використання малеїнового ангідриду, як спінюючого агенту, для одержання спінених бітумів. За показниками збільшення об'єму в'язучого та періоду розкладу піни встановлено оптимальний вміст малеїнового ангідриду. Із використанням малеїнового ангідриду, як спінюючого агенту, одержано спінений бітум, який використовувався для одержання двох зразків щибенево-мастикових асфальтобетонів, які відрізнялися між собою температурами змішування та ущільнення щибенево-мастикових асфальтобетонних сумішей. Після чого проведено проектування складу щибенево-мастикових асфальтобетонних сумішей із використанням не спінених (БНД 70/100 та БНД 70/100 модифікованого малеїновим ангідридом) спінених бітумів (БНД 70/100 спіненого малеїновим за двох різних температурних режимів). Проведено формування зразків щибенево-мастикових асфальтобетонів та їх випробування.

Ключові слова: малеїновий ангідрид, модифікування бітуму, спінені бітуми, теплий асфальтобетон.