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ANALYSIS OF RHEOLOGICAL STATE OF SBS MODIFIED BITUMENS BASED ON VISCOSITY MEASUREMENTS

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Each bitumen has a slightly different group composition, thus bitumen modification with the SBS copolymer gives slightly different results in each case. Both in the industry and construction practice there is still no simple method available which would allow the evaluation of the impact of SBS content and the group composition of bitumen on the structural and rheological properties of the polymer bitumen mix. The article presents the results of the dynamic viscosity tests of three bitumen types. Based on the analysis of the results obtained, it was found that changes in the rheological properties caused by SBS additive are characteristic for each of the bitumens tested and their chemical and group composition. They are also proportionate to the amount of the modifier added. In order to have a possibility to measure this impact, three coefficients rheologically characterizing polymer and bitumen mixes were applied.

Key words: bitumen for roofing membrane, bitumen group composition, styrene-butadiene-styrene, dynamic viscosity

1. Introduction

For over twenty years, styrene-butadiene-styrene co-polymer (SBS) has been the most commonly used modifier in waterproofing building materials. In waterproofing industry, both the quantity and type of SBS used for modification of bitumen are most frequently determined through practical observation or cost considerations. Each bitumen has slightly different group composition, thus in each case the modification with SBS copolymer may give slightly different results. There is a noticeable lack of scientific tools allowing unequivocal and comprehensive assessment of the impact of bitumen chemical and group composition on the structural and rheological properties of the polymer and bitumen mix.

Based on the analysis of the tests on dynamic viscosity of SBS modified bitumen, the author defined the coefficients allowing the description of their rheological condition. The study presents the analysis of rheological condition of bitumens made with the use of these coefficients. Conclusions resulting from this analysis allow for optimization

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of SBS content in bitumen and determine the optimum conditions for the use of polymer and bitumen mix in production of waterproofing materials.

2. Methodology of the study

Tests were performed in the laboratory of the Institute of Structural Engineering at Poznań University of Technology [1]. Three types of bitumen were used:
- Soft bitumen 160/220,
- Soft bitumen 40/175,
- Hard bitumen 95/35.

Bitumen 40/175 is an oxidized variety of bitumen 160/220 [5, 6]. Both bitumens are characterized by a similar softening point $T_{(PiK)}$ and penetration $P_{(5s/25oC/100g)}$. The bitumens were obtained from the same crude oil from Ural deposits.

The bitumens tested are currently most common types of bitumens used for production of waterproofing materials. Bitumen 160/220 is used for membrane production, mainly modified types, while bitumen 40/175 is used for production of membranes and bitumen liquids. Bitumen 95/35 is mostly used to produce certain types of standard and semi-modified membranes.

The bitumens were modified with the linear type of thermoplastic elastomer SBS. Samples containing 3, 6, 9, and 12% of SBS were prepared for soft bitumens (40/175, 160/220), and samples with 3 and 6% SBS content were made for hard bitumen 95/35. The upper limit of SBS content in the prepared samples was determined by SBS absorption into bitumen.

The prepared samples were tested for group composition of bitumen and dynamic viscosity depending on temperature. The group composition tests were made using thin layer chromatography method (TLC) and dynamic viscosity tests were made using Höppler Consistometer at temperatures ranging from 10 to 70°C.

3. Test results

3.1. Group composition of bitumen

The test results are presented in Table 1. To assess the ratio between hydrocarbons contained in bitumen, the so called index of colloidal instability I_c was used. It was calculated according to the following formula [2,3]:

$$I_c = \frac{A + N}{S + C}$$

where:
S – resins (%)
C – ring hydrocarbons (%),

A – asphaltens (%),
N – saturated hydrocarbons (%).

Based on the test results concerning the determination of group composition of bitumens, the index of colloidal instability I_c (table 1) was calculated for each bitumen type.

Table 1

Group composition of bitumens and their index of colloidal instability (I_c)

Components	40/175	95/35	160/220
	Share of component in tested bitumen (%)		
Saturated compounds	7,0	11,6	16,5
Aromatic compounds	20,5	8,2	43,4
Resins	46,5	39,7	22,6
Asphaltens	17,9	31,1	9,1
I_c	0,37	0,90	0,39

The tested soft bitumen contain a relatively low amount of asphaltens (9.1 for bitumen 160/220 and 17.9 for bitumen 40/175). Micelles do not create three-dimensional network, they exist separately and are stabilized by a thick envelope of resins. These are the zol type bitumens. Bitumen 95/35 has the characteristics of zol-gel bitumen. This is an intermediate system. Bitumens of this type have a not very densely developed network structure of asphaltens which are stabilized by thick resin coating.

According to [4], bitumens with the colloidal instability index value Ic ranging from 0.08 to 0.36 are characterized by good compatibility with SBS elastomer. The calculations show that the Ic value for soft bitumens tested is close to the upper limit of compatibility with SBS. I_c index for bitumen 95/35 is 0.9 and is much higher than the upper limit of compatibility with SBS. This means that this bitumen type creates a typical two-phase system with SBS, which has a decisive impact on its structure as well as its thermo-mechanical properties.

3.2. Measurements of bitumen dynamic viscosity

As a result of viscosity measurements for each group of bitumens tested, a linear relationship was obtained between the natural logarithm of viscosity and temperature. In Figure 1 the results achieved for bitumen 160/220 and its SBS modified varieties are presented. Elastomeric modifier SBS added to the bitumen causes the increase of its viscosity, proportional to SBS content. Another characteristic observed in the bitumens after adding SBS is the gradual change of their susceptibility to temperature variations. It was observed that a change of bitumen susceptibility to temperature variations is a characteristic process, slightly different for each type of bitumen. Therefore, for each of the analyzed relation: the logarithm of bitumen viscosity and temperature, coeffi-

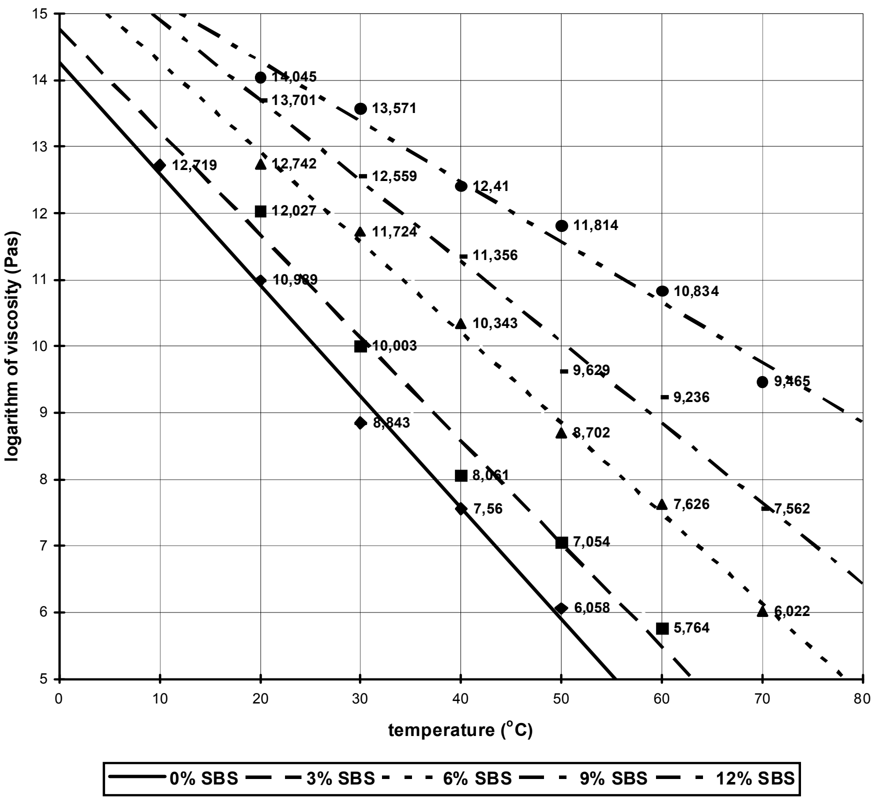

Figure 1. Graph presenting the relation between the logarithm of dynamic viscosity and temperature for bitumen 160/220 non-modified and modified with 3, 6, 9 and 12% SBS content.

cients of linear regression *a* and *b* were calculated. Table 2 shows the examples of values calculated for bitumen 160/220. The value of slope *a* is a parameter characterizing the susceptibility of given bitumen to temperature changes. The higher the *a* value, the faster the change of viscosity accompanied by temperature change. Low *a* value is very beneficial for bitumen. This indirectly leads to higher softening point temperature and lower brittleness temperature – bitumen maintains viscoelastic properties in a wider temperature range, which makes it a proper material to perform the waterproofing function. As a result of the calculations, five values of coefficient *a* were obtained for soft bitumen tested (160/220, 40/175), for SBS content reaching (0, 3, 6, 9, 12%) and for bitumen 95/35 three values were obtained (for 0, 3, 6% SBS content). These values were presented on a graph (Figure 2) showing a correlation of coefficient *a* and SBS content in bitumen. For each bitumen variety the points plotted on the graph created a characteristic sequence. It was approximated by calculating the regression line coefficients of second degree $y = a + bx + cx2$ (tab. 3). The function achieved was named thermal variation function and marked $W_{\Delta t}$. For bitumen 95/35 no correlation coefficient was calculated, since for one degree of freedom and the second degree equation it always equals 1.

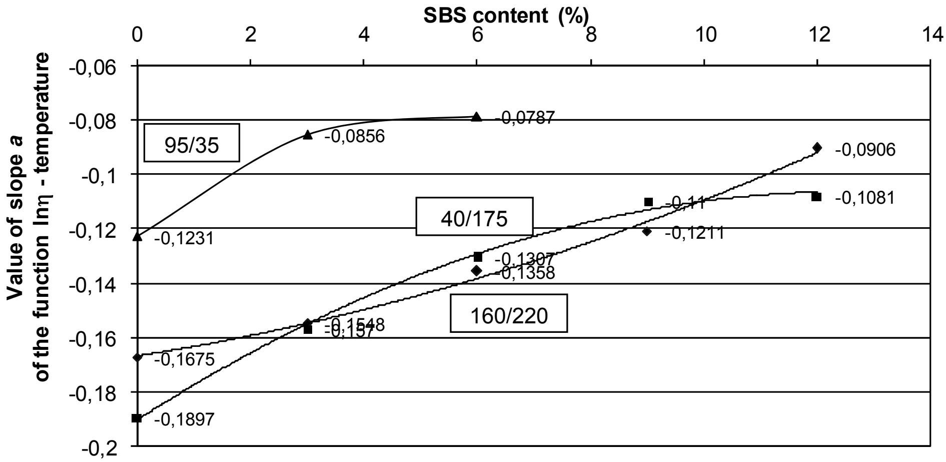

Figure 2. Relation between the value of slope *a* for the function: logarithm of bitumen viscosity – temperature and SBS content in bitumen

Table 2

Values of regression and correlation coefficients and confidence interval for the regression coefficient for the dependence of the logarithm of dynamic viscosity on temperature for bitumen 160/220 (and its SBS modified varieties)

Tested bitumen type and SBS content in bitumen	Linear regression coefficient: y = ax + b		Correlation coefficient (degrees of freedom)	Critical value of correlation coefficient	Confidence interval for regression coefficient *a* at the level of significance 0,05
	a	*b*	*k*	k_{kr}	
160/220	–0,1675	14,2591	0,9963 (3)	0,8783	±0,0265
160/220 +3% SBS	–0,1548	14,7720	0,9900 (3)	0,8783	±0,0405
160/220 +6% SBS	–0,1358	15,6380	0,9980 (4)	0,8114	±0,0119
160/220 +9% SBS	–0,1211	16,1241	0,9932 (4)	0,8114	±0,0235
160/220 +12% SBS	–0,0906	16,0990	0,9906 (4)	0,8114	±0,0174

Table 3

Value of regression coefficients and function correlation $y = a + bx + cx^2$ for the relation between the value of slope *a* for function ln η (*y*) and SBS content in bitumens tested (*x*)

Tested bitumen type	Regression curve coefficient: $y = a+bx+cx^2$			Correlation coefficient (degrees of freedom)	Critical value of correlation coefficient
	a	*b*	*c*	*k*	k_{kr}
160/220	–0,1670	0,0033	0,00025	0,9969 (3)	0,8783
40/175	–0,1907	0,0134	–0,00053	0,9981 (3)	0,8783
95/35	–0,1231	0,0176	–0,00170	–	–

Minor differences in thermal variations of soft bitumens (40/175, 160/220) are due to their similar colloidal structure. The chemical and group composition of bitumens makes their dissipative environment create favorable conditions for swelling and next for dissolving the polymer. The value of bitumen colloidal instability index suggests the possibility of creating a single-phase system, unlike in the hard bitumen tested (95/35). In this case, despite of the far lower content of SBS, the colloidal system probably adopts a two-phase state. Increments of the function values in the tested range of SBS content (0-12% for soft bitumen and 0-6% for hard bitumen) are following for the bitumens tested are following:

– 160/220: 0.756,
– 40/175: 0.845,
– 95/35: 0.444.

They identify the susceptibility of the individual bitumen type to SBS modification. The course of thermal variation function ($W_{\Delta t}$) describing the dependence between coefficient *a* and SBS content in bitumen tested is characteristic for each bitumen type. It describes its susceptibility to SBS modification.

Another parameter characteristic for each of the bitumens tested, possible to determine on the basis of viscosity studies, is SBS effect which leads to bitumen curing and increase of viscosity at a given temperature (Figure 1). In order to determine the degree of intensity of this change, for each of the bitumen variety tested, viscosity values were calculated at temperatures: 20, 40 and 60°C, i.e. at the extreme and average temperature of measurements. Calculated values of the logarithm of viscosity were plotted on the graph to show the dependence on SBS content. In Fig 3, for instance, the dependence for bitumen 160/220 is presented. For each bitumen tested and for each temperature mentioned above, the coefficients *a* and *b* of the regression line y = ax + b and correlation coefficients were calculated (Table 4).

Analyzing the values of slope *a* coefficients of regression lines contained in Table 4, it can be observed that they increase together with the temperature rise. Thus the angle of lines showing the dependence between the logarithm of viscosity and SBS content in bitumen increases while the temperature at which the viscosity was measured rises.

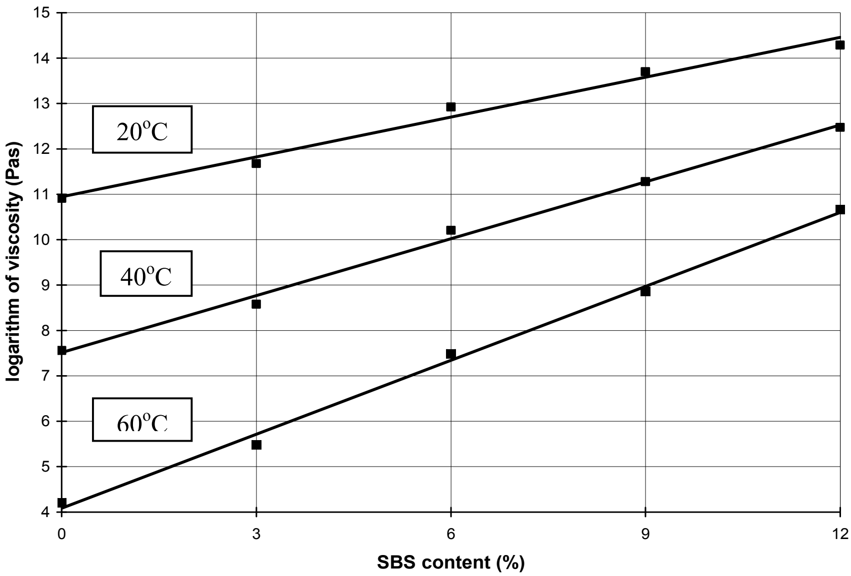

Figure 3. Relation between the logarithm of viscosity and SBS content for bitumen 160/220 at temperatures: 20, 40 and 60°C

Table 4

Values of regression coefficients and correlation for the relation between logarithm of viscosity and SBS content in bitumens tested at temperatures of 20, 40 and 60°C

Tested bitumen type	Temperature (°C)	Linear regression coefficient: $y = ax + b$		Correlation coefficient (degree of freedom)	Critical value of correlation coefficient
		a	b	k	k_{kr}
160/220	20	0,2927	10,9429	0,9926 (3)	>0,8783
	40	0,4177	7,5137	0,9976 (3)	
	60	0,5427	4,0845	0,9980 (3)	
40/175	20	0,2821	11,2479	0,9961 (3)	
	40	0,4222	7,6251	0,9913 (3)	
	60	0,5624	4,0023	0,9865 (3)	
95/35	20	0,1716	13,6845	0,9961 (1)*	–
	40	0,3196	11,3245	0,9742 (1)	
	60	0,4676	8,9645	0,9618 (1)	

* Statistics analysis was not made for one degree of freedom. The values obtained are treated as approximate.

This proves that together with the increase of bitumen temperature, bitumen modification with SBS elastomer becomes more efficient. The same amount of SBS leads to much higher bitumen viscosity. It was observed that the change of coefficient *a* related to the temperature changes is linear – it is a constant value for the given type of bitumen. The number indicating the value of change of coefficient *a,* resulting from the change of bitumen temperature by 1°C, was called bitumen stabilization coefficient and marked with a symbol $W_{\Delta}{}^{o}{}_{C}$. This is another parameter characteristic for the given type of bitumen. The value of stabilization coefficient is lowest for bitumen 160/220 ($W_{\Delta}{}^{o}{}_{C} = 6{,}25 \times 10^{-2}$). Oxidized bitumen subjected to these studies show clearly higher value $W_{\Delta}{}^{o}{}_{C}$: 40/175 – $7{,}01 \times 10^{-2}$ and 95/35 – $7{,}40 \times 10^{-2}$. The stabilization coefficient provides material information about individual bitumen types and determines their behaviour at different temperatures.

The increase of SBS effectiveness together with the temperature rise is due to the physical character of components (bitumen and polymer). As these are materials sensitive to temperature variations, after liquefaction they achieve favorable conditions for mutual dissolution and formation of a homogeneous colloidal system. The bitumen components most sensitive to temperature increase are resins and saturated hydrocarbons. Both act as good solvents for styrene-butadiene rubber.

In order to fully compare the stiffening effect of SBS elastomer on individual types of bitumen with differing softening point T_{PiK}, another coefficient was introduced. Regression line coefficients *a* and *b* were calculated for the relation: logarithm of viscosity and SBS content in bitumen for the softening point T_{PiK} for each bitumen tested. The results of calculations are presented in Table 5. Slope *a* was named the coefficient of rigidity W_s. It characterizes the modifying effectiveness of SBS on bitumen at its softening point. For soft bitumens (160/220 and 40/175) W_s values are similar and reach respectively 0.4177 and 0.4363. The stabilizing effect of SBS on hard bitumen (PS 95/35) is significantly higher.

Table 5

Stabilization coefficient $W_{\Delta}{}^{o}{}_{C}$ and coefficient of rigidity W_s

Tested bitumen type	Temperature T_{PiK} (°C)	Linear regression coefficient: $y = ax + b$		Correlation coefficient *k*
		a (W_s)	b	
160/220	40	0,4177	7,5137	0,9976
40/175	42	0,4362	7,2628	0,9907
95/35	86,5	0,6637	5,8375	0,9530

The value of W_s is 0.6637 and is approx. 60% higher than for soft bitumen. Hard bitumen, due to a high content of asphaltens and thus a high softening point, and at the same time relatively low content of oil (saturated compounds), has a relatively poor solvent properties in comparison with SBS. Under these circumstances, SBS is exposed to high temperatures for a longer period than in soft bitumen. This reinforces the uncoupling and polystyrene evaporation process. The coefficient of rigidity W_s and the notion of thermal variation function $W_{\Delta t}$ and stabilization coefficient $W_{\Delta}{}^{o}{}_{C}$ introduced earlier, allow the description of the effectiveness of SBS modifying impact on bitumen, both in terms of its susceptibility to temperature change and the intensity of viscosity increase.

Table 6 presents the summary of physical and chemical characteristics analyzed in this study. The example of rheological condition of bitumens tested with the use of coefficients is presented in Chapter 4.

Table 6

Total list of physical and mechanical characteristics of bitumens tested

Characteristic feature tested	Bitumen type		
	160/220	40/175	95/35
Group composition of bitumens			
Type of bitumen colloidal system	zol	zol	zol / zol– gel
Colloidal instability coefficient I_c	0,39	0,37	0,9
Bitumen compatibility with SBS	satisfactory	satisfactory	poor
Dynamic viscosity			
Thermal variation function $W_{\Delta t}$ – coefficient c	0,00025	–0,0134	–0,0170
Intensity of increase of thermal variation function value	increasing	decreasing	decreasing
Bitumen stabilization coefficient $W_{\Delta}{}^{o}{}_{C}$	$6,25 \times 10^{-2}$	$7,01 \times 10^{-2}$	$7,40 \times 10^{-2}$
Coefficient of rigidity W_s	0,4177	0,4362	0,6637

4. EXAMPLE OF ANALYSIS OF RHEOLOGICAL STATE OF BITUMENS TESTED WITH THE USE OF COEFFICIENTS

BITUMEN 160/220

The intensity of the increase of thermal variation function value $W_{\Delta t}$ becomes higher when SBS content in bitumen increases. The effects of modification are visible only when SBS content in bitumen becomes significant (> 6-9%). The value of coefficient $W_{\Delta}{}^{o}{}_{C}$ is 6.25 x 10^{-2}. This means that SBS modifying effect is quite stable regardless of the temperature of operation.

The effect of SBS addition on the increase of bitumen viscosity at softening point (W_s) is average, significantly smaller than the impact on industrial bitumen, which is consistent with its chemical and group composition expressed by bitumen colloidal instability coefficient I_c which equals 0.39.

Bitumen 40/175

The intensity of the increase of thermal variation function value $W_{\Delta t}$ significant at the beginning, decreases together with the increasing SBS content in bitumen. The modifying effects can be observed at a very low SBS content (0-6%). High SBS content (> 9%) used for bitumen modification is ineffective and economically not justified.

The value of $W_{\Delta}{}^{o}{}_{C}$ coefficient is 7.01 x 10^{-2}. This means less stable SBS modifying effect than in case of bitumen 160/220 at various temperatures of operation. The effect of SBS addition on the increase of viscosity at bitumen softening point (W_s) is average, but significantly higher than the effects of SBS on bitumen 160/220. In this case, the determining bitumen component versus SBS is resin content, which, especially at temperatures close to the softening point, undergo liquefaction and becomes a good solvent for polymer.

Bitumen 95/35

The pace of the value increment of the function $W_{\Delta t}$ is significant when SBS content in bitumen increases to 3% (noticeably higher than for soft bitumen), however, when SBS content is within the range of 3-6%, it significantly decreases. The biggest modifying effect of SBS addition to bitumen is achieved when SBS content is very low (0-3%). The increment of the function $W_{\Delta t}$ within the range of 0 to 6% SBS content (maximum amount possible to absorb by this bitumen) is 0.444 and is almost half lower than for soft bitumen. This means that the modification of this type of bitumen with SBS addition gives poor results and may be economically unjustified. The value of coefficient $W_{\Delta}{}^{o}{}_{C}$ is 7.40×10^{-2}. This may result in a very unstable behaviour of products manufactured with the use of this type of bitumen when temperature variations occur during the products use.

The effect of the SBS addition on the increase of viscosity at the softening point (W_s) is significant, much larger (by approx. 50%) than in the case of soft bitumens discussed above. However, this effect can be observed only in a small range of SBS content (up to 3%). The large increase of viscosity in bitumens with small SBS content (only approx. 3%) is the result of substantial amount of resin, which at a relatively high softening point shift into liquid state, creating good conditions for solubility of the polymer.

5. Conclusions

The analysis of the results of dynamic viscosity studies shows that the changes of rheological properties of bitumen caused by SBS elastomer addition are characteristic for each of the materials tested and for their chemical and group composition, as well as they are proportional to the amount of modifier added. In order to obtain the possibility of measurable evaluation of this impact, the following terms and coefficients were introduced, characterizing bitumen and polymer mixes rheologicaly tested:

– Thermal variation function $W_{\Delta t}$,
– Bitumen stabilization coefficient $W_{\Delta}{}^{o}{}_{C}$,
– Stiffness index W_s.

These coefficients allow the analysis of the rheological state of bitumens tested with focus on their practical use.

References

1. K. Zieliński, *The role of SBS co-polymer in determining the structure and thermomechanical properties of bitumen types used in waterproofing materials*, Publishing House of Poznań University of Technology, Dissertation No. 409, Poznań 2007.
2. G. Ramond, Ch. Such, *Bitumes et bitumes modifies. Relations structures, propriétés, composition*, Bull. Liaison Labo. P. et Ch., 1990, p. 65.
3. R.L. Hubbard, K.E. Stansfield, *Analytical Chemistry*, London 1948, 20.
4. I. Gaweł, M. Kalabińska, J. Piłat, *Road asphalts*, Transport and Communication Publishers, Warsaw 2001.
5. EN 12591:2004 Bitumen and bituminous binders – Specifications for paving grade bitumens.
6. PN-76/C-96178.02 Petroleum products – Asphalts for industrial uses for dampproofing and waterproofing PS.

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