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Innovative Methods of Bitumen Modification Used in Waterproofing

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***Abstract*—Due to rapid development of the building materials market, it is necessary to constantly improve the products offered by suppliers by optimizing production processes and improving the quality of finished product. The paper presents the most popular methods of bitumen modification used in waterproofing products. At present the most commonly used bitumen modifiers are compounds from the group of polymers (e.g. SBS). The advantages and disadvantages of this kind of modification, which mainly consists in physical interaction, are described in this paper. In addition to this, an innovative bitumen modification agent is presented. These are imidazolines which enter into chemical reaction with modified bitumen. The impact of both modifiers on the changes of selected bitumen characteristics are presented, i.e. on penetration, softening point, breaking point, flexural stiffness modulus, dynamic viscosity and adhesion to aggregate. The results obtained allow us to assume that the development of a hybrid modifier based on SBS polymer and technical imidazolines will eliminate the existing weaknesses of modified bitumen containing only SBS. This, in turn, will improve the quality and durability of finished waterproofing products and their production process will become faster and cheaper.**[1]

***Index Terms*—Bitumen, modification, polymers, imidazolines, waterproofing products.**

I. INTRODUCTION

Currently used waterproofing materials, consisting primarily of bituminous binders, are being pushed out of the market by mineral waterproofing products, plastic films or resin coatings. Many Research and Development centers do research of admixtures which improve the waterproofing properties of cement materials, which will eliminate the need to apply waterproofing coatings onto concrete surface. In the light of these events, in order to increase their competitiveness, manufacturers of traditional waterproofing materials are forced to seek new, better and cheaper solutions, both at the stage of material solutions as well as at the stage of manufacture of waterproofing products.

It is estimated that new generation roofing membranes in approx. 70% consist of modified bitumen (bitumen with fillers and modifiers). The remaining 30% are reinforcement (glass fleece, glass fibre) and mineral granules (Fig. 1). As a consequence, modified bitumen parameters have a decisive impact on the quality of the final product. Bitumen, whether natural or obtained by processing crude oil, primarily demonstrates waterproofing properties. However, its greatest disadvantages are: susceptibility to heat impact, oxidation and changes in in-use characteristics due to rheological changes, particularly ageing processes. To expand the temperature range in which bitumen is in viscoelastic state and to minimize the negative impact of ageing processes, various bitumen modifiers are used [1]-[4].

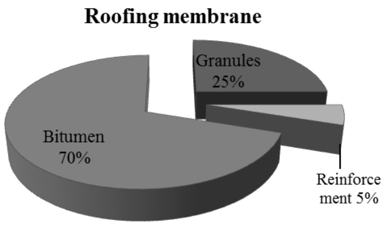

Fig. 1. Composition of waterproofing membranes currently in use.

One of the first chemical modifications of bitumen (in the early 20th century) was the formation of bitumen and sulphur emulsion. This is the so-called sulphur bitumen, also referred to as Dubbs asphaltic bitumen. It was obtained by heating bitumen with 25% addition of sulphur. The effect of such modification was an increase in bitumen softening temperature, increased ageing resistance and reduced ductility [4]–[6].

Most of the currently used methods of bitumen modification have physical character. They consist in, among other things, mixing of bitumen with a substance modifying the structure of bitumen by creating a spatial network of polymer bonds. For more than 25 years, SBS copolymer has been the basic modifier of bitumen used for the production of waterproofing materials (Fig. 2 and Fig. 3) . It modifies bitumen characteristics in a physical way - it slows down bitumen ageing process, increases its softening point and reduces its susceptibility to temperature changes [2], [4], [7], [8].

The process of production of modified bitumen consists of three phases [4], [6]:

1) phase I - swelling of SBS - application of an adequate amount of elastomer to bitumen at the temperature of approximately 180-190 ℃; at such a high temperature SBS begins to gradually expand as bitumen (its oil fraction) begins to penetrate into the polymer which gradually becomes softer;
2) phase II - shearing - soft SBS is passed through a shear mixer where the final fragmentation of polymer takes place; passing bitumen with SBS through the mixer can be repeated until a homogeneous mixture is obtained, without visible lumps or polymer grains;
3) phase III - maturation and crosslinking - after leaving

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the shear mixer, modified bitumen with fragmented SBS is stored in heated containers where product maturation takes place. In hot bitumen, particles of SBS polymer in which polystyrene endings are soft and polybutadiene chain is swollen remain unconnected; only when the temperature decreases a physical spatial SBS network is gradually formed: styrene endings join together to form styrenic domains, i.e. network nodes connected by butadiene chains.

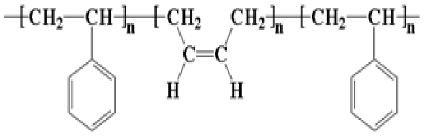
Fig. 2. Structural formula of SBS [9].


Fig. 3. Kraton D1101 – SBS in industrial form [10].

Apart from its undoubted advantages, SBS has also many disadvantages: it is expensive, bitumen modification with SBS is quite troublesome, it significantly reduces the adhesion of modified bitumen to substrate, which imposes the use of only selected bitumen for modification [4]. Due to this a lot of research and development centers are working on new types of polymers, which would help accelerate the production of modified bitumen with special characteristics. It seems that an alternative solution would be the use of SBS-based hybrid modifiers, which, due to additional components, would eliminate the disadvantages of this copolymer.

The intensive development of organic chemistry in recent years has allowed the synthesis of substances improving the characteristics of modified bitumen. Imidazolines can be an example of such substances. Imidazolines belong to heterocyclic compounds. They consist of a five-membered ring in which two nitrogen atoms are located. Imidazolines contain in their structure a ring of 4,5-dihydro-1H-imidazole. Depending on substituent in position 2 of the ring tautomeric forms are distinguished (Fig. 4) [11], [12].

1) hydrogen or hydrocarbon substituent,
2) substituent containing a ring-attached group -SH, -OH, - NH4 or substituted -NHR amine group.

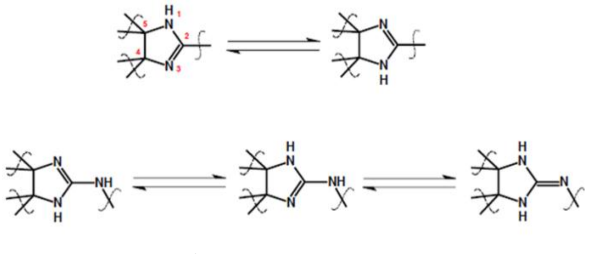
Fig. 4. Tautomerism of imidazoline and 2-iminoimidazolidine ring [11].

Technical imidazolines are a mixture of two different imidazolines with an admixture of amidoamines and alkylamines. The exact composition and proportions are protected by patent and are owned by the Institute of Heavy Organic Synthesis “Blachownia” in Kędzierzyn Koźle, further referred to as ICSO. This compound includes:

1) up to 90% of imidazoline mixture (chemical structure presented in Fig.5 and Fig. 6),
2) up to 10% of amidoamines,
3) up to 1% alkyltriamine

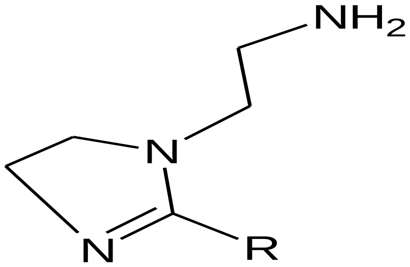
Fig. 5. Structural formula of imidazoline type I [11].

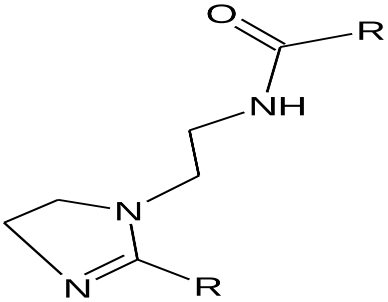
Fig. 6. Structural formula of imidazoline type II [11].

The structure which does not contain a double bond in the ring is called imidazoline. Imidazolines belong to a wide range of surfactants, among which we can distinguish cationic imidazolines and amphoteric imidazolines.

Imidazolines have dispersing properties. This results in a change of viscoelastic properties of bitumen. The reaction of imidazoline with bitumen leads to blocking of cyclisation of aromatic compounds and blocking the conversion of naphthenoaromatic fractions to resins and resins to asphaltens [11]–[13]. It is therefore expected that imidazoline will have a significant impact on the change of in-use characteristics of bitumen and on the increase of bitumen resistance to ageing.

II. MATERIALS AND METHODS

A. Materials

For the purpose of the study the following materials were used: 160/220 penetration grade bitumen obtained by PKN Orlen refinery as a result of processing crude oil from Ural deposits. In the Polish market of bituminous waterproofing materials this is the most commonly used bitumen, which is due to widespread and easy access to this material and its relatively reasonable price. This bitumen was modified with two types of modifiers:

1) SBS (styrene-butadiene-styrene) elastomer: 3%, 6%, 9% and 12% content by weight
2) Technical imidazolines – oleic type I, oleic type II, rapeseed type I and rapeseed type II: 1% and 2%

content by weight

High degree of SBS modification (up to 12%) is due to the fact that such bitumen modification is necessary to obtain high quality waterproofing material. The amount of imidazoline added to bitumen was based on the preliminary results obtained during preliminary studies.

Kraton D1101, linear type SBS elastomer used for testing is white, coarse-grained powder. According to the manufacturer [10], the basic technical characteristics of the copolymer are as follows:

1) density: 0.94 kg/dm2,
2) ductility: 880/820%,
3) hardness according to Shore: A - 72/75,
4) styrene to rubber ratio by weight: 31 ÷69/30 ÷70%.

Imidazolines used in the studies were produced on the basis of such fats as olein and rapeseed oil. Modifiers used are dense liquids with pour point below -20 ℃; self-ignition temperature higher than 300 ℃; density at 20 ℃ from 0.900 to 0.960 g/cm3; and pH in the range of between 8 to 10. The exact composition and proportions of the ingredients are subject to patent protection and are the property of the Institute of Heavy Organic Synthesis Blachownia in Kędzierzyn Koźle.

B. Methods

For reference bitumen 160/220 and modified bitumen the following tests were made:

1) needle penetration at 25 ℃ according to [14],
2) determination of softening point by Ring and Ball method according to [15],
3) determination of breaking point by Fraass method in accordance with [16],
4) determination of stiffness modulus S in BBR rheometer at t = 60 s and temperature of –16 ℃ according to [17],
5) determination of dynamic viscosity at 60 ℃ in DSR rheometer according to [18],
6) determination of affinity between aggregate and bitumen according to [19].

The comprehensive studies conducted on bitumen show the influence of selected modifiers on viscoelastic and physico-chemical characteristics of bitumen. Determining the in-use characteristics of modified bitumens will help us specify the benefits or risks associated with the use of selected modifiers.

III. RESULTS AND DISCUSSON

Table I presents the results of needle penetration test at 25 ℃ according to [14]. Based on the results obtained, it can be concluded that even a small amount of SBS additive significantly reduces the value of bitumen penetration. For 12% SBS content we can observe that the penetration decreases by as much as approx. 70%. A different effect can be observed when bitumen is modified with imidazoline. The addition of this type of modifier in each case results in a significant increase in penetration, proportional to imidazoline content. The increases in penetration values range from 12% to 48%, depending on the type and amount of imidazoline. The increase in penetration value caused by the addition of technical imidazoline is a beneficial phenomenon from the perspective of the production process of waterproofing materials. Liquefaction of modified bitumen facilitates its pumping, application onto reinforcement of waterproofing membranes and the production process itself can take place at lower technological temperatures. Typically, the increase in bitumen penetration value is related to the decrease in the softening point of bitumen. The change in the value of the softening point of bitumen modified with the addition of imidazoline does not have a negative impact on its in-use performance. The impact of imidazoline as bitumen liquefier is perceived as a positive and desirable phenomenon by manufacturers of waterproofing materials.

TABLE I: DETERMINATION OF NEEDLE PENETRATION AT 25^0C

Item	Bitumen type	Penetration value [0.1 mm]	Increase (+) / decrease (–) of penetration value vs. reference bitumen [%]
1	160/220 – reference bitumen	156	–
2	160/220 + 3% SBS	122	-21.79%
3	160/220 + 6% SBS	87	-44.23%
4	160/220 + 9% SBS	71	-54.49%
5	160/220 + 12% SBS	48	-69.23%
6	160/220 + 1% oleic imidazoline type I	198	26.92%
7	160/220 + 2% oleic imidazoline type I	231	48.08%
8	160/220 + 1% oleic imidazoline type II	210	34.62%
9	160/220 + 2% oleic imidazoline type II	217	39.10%
10	160/220 + 1% rapeseed imidazoline type I	180	15.38%
11	160/220 + 2% rapeseed imidazoline type I	199	27.56%
12	160/220 + 1% rapeseed imidazoline type II	175	12.18%
13	160/220 + 2% rapeseed imidazoline type II	192	23.08%

Table II shows the results of the determination of softening point by Ring and Ball method according to [15]. SBS modification of bitumen results in a significant increase in softening point and it is proportional to the content of modifier. This has a positive effect on the characteristics of modified bitumen - its viscoelastic range is expanded and it is resistant to high temperatures. The addition of 12% of SBS results in an increase in the softening point by approximately 160%. The modification of bitumen with imidazoline results in a slight but noticeable decrease in softening point and it is proportional to the amount of the modifier added. The largest decrease in softening point was observed for bitumen modification with 2% amount of rapeseed imidazoline type I, i.e. the decrease reached 8.31% as compared to the reference bitumen. The lowest decrease in softening point occurred in the case of bitumen modification with 1% amount of rapeseed imidazoline type II, i.e. it decreased by 0.7% as compared to the reference bitumen. Intermediate values were recorded for the remaining samples. A decrease in the softening point deteriorates heat resistance of bitumen, that is why the use of technical imidazoline is only possible in small quantities (maximum 1% -2% so that the effect of the change of the softening point of bitumen would not have a decisive impact on the quality of the finished waterproofing product.

TABLE II: DETERMINATION OF SOFTENING POINT BY RING AND BALL METHOD

Item	Bitumen type	Softening point [^{0}C]	Increase (+) / decrease (–) of softening point vs. reference bitumen [%]
1	160/220 – reference bitumen	42.1	–
2	160/220 + 3% SBS	47.8	13.54%
3	160/220 + 6% SBS	97.2	130.88%
4	160/220 + 9% SBS	103.2	145.13%
5	160/220 + 12% SBS	110.2	161.76%
6	160/220 + 1% oleic imidazoline type I	41.2	-2.14%
7	160/220 + 2% oleic imidazoline type I	39.6	-5.94%
8	160/220 + 1% oleic imidazoline type II	41.5	-1.43%
9	160/220 + 2% oleic imidazoline type II	38.7	-8.08%
10	160/220 + 1% rapeseed imidazoline type I	41.0	-2.61%
11	160/220 + 2% rapeseed imidazoline type I	38.6	-8.31%
12	160/220 + 1% rapeseed imidazoline type II	41.8	-0.71%
13	160/220 + 2% rapeseed imidazoline type II	39.4	-6.41%

TABLE III: DETERMINATION OF BREAKING POINT BY FRAASS

Item	Bitumen type	Breaking point [^{0}C]	Increase (+) / decrease (–) of the value of breaking point vs. reference bitumen [%]
1	160/220 – reference bitumen	-14.6	–
2	160/220 + 3% SBS	-16.0	-9.59%
3	160/220 + 6% SBS	-24.0	-64.38%
4	160/220 + 9% SBS	-38.0	-160.27%
5	160/220 + 12% SBS	-43.0	-194.52%
6	160/220 + 1% oleic imidazoline type I	-19.5	-33.56%
7	160/220 + 2% oleic imidazoline type I	-21.5	-47.26%
8	160/220 + 1% oleic imidazoline type II	-18.0	-23.29%
9	160/220 + 2% oleic imidazoline type II	-19.0	-30.14%
10	160/220 + 1% rapeseed imidazoline type I	-18.0	-23.29%
11	160/220 + 2% rapeseed imidazoline type I	-21.5	-47.26%
12	160/220 + 1% rapeseed imidazoline type II	-18.5	-26.71%
13	160/220 + 2% rapeseed imidazoline type II	-21.5	-47.26%

Table III shows the results of the determination of breaking point by Fraass, according to [16]. Based on the results obtained, it can be concluded that bitumen modification with SBS leads to a significant decrease in breaking point, proportional to SBS content. The modification of bitumen with 12% SBS results in a decrease in the breaking point by approx. 195%. A similar effect can be observed for bitumen modified with imidazoline. In each case, a decrease in breaking point proportional to imidazoline content could be observed. The most beneficial effect was observed for oleic imidazoline type I, rapeseed imidazoline type I and rapeseed imidazoline type II – decrease in breaking point by approx. 47% when 2% modifying additive was used. The smallest decrease in breaking point was recorded for oleic imidazoline type II - decrease by 23% for 1% additive and decrease by 30% for 2% of technical imidazoline addition. Intermediate values were recorded for the other types of imidazoline. Both the modification with SBS additive and by imidazoline gives a beneficial effect - a significant decrease in the breaking point can be observed, bitumen viscoelastic range is expanded in its lower range, modified bitumen is characterized by higher resistance to low temperatures, which is a very important aspect in the climatic conditions of Poland.

TABLE IV: DETERMINATION OF STIFFNESS MODULUS AT $t = 60$ S AT TEMPERATURE OF –16 ℃

Item	Bitumen type	Stiffness modulus S(60s) [MPa]	Increase (+) / decrease (–) of the value of stiffness modulus vs. reference bitumen [%]
1	160/220 – reference bitumen	102.7	–
2	160/220 + 3% SBS	94.3	-8.18%
3	160/220 + 6% SBS	68.9	-32.91%
4	160/220 + 9% SBS	35.4	-65.53%
5	160/220 + 12% SBS	–	–
6	160/220 + 1% oleic imidazoline type I	99.3	-3.31%
7	160/220 + 2% oleic imidazoline type I	88.3	-14.02%
8	160/220 + 1% oleic imidazoline type II	83.9	-18.31%
9	160/220 + 2% oleic imidazoline type II	77.2	-24.83%
10	160/220 + 1% rapeseed imidazoline type I	93.1	-9.35%
11	160/220 + 2% rapeseed imidazoline type I	82.1	-20.06%
12	160/220 + 1% rapeseed imidazoline type II	91.1	-11.30%
13	160/220 + 2% rapeseed imidazoline type II	82.2	-19.96%

TABLE V: DETERMINATION OF DYNAMIC VISCOSITY AT TEMP OF 60 ℃

Item	Bitumen type	Dynamic viscosity at temp of 60 ℃ [Pa·s]	Increase (+) / decrease (–) of the value of dynamic viscosity vs. reference bitumen [%]
1	160/220 – reference bitumen	74.2	–
2	160/220 + 3% SBS	272.8	267.65%
3	160/220 + 6% SBS	1061.6	1330.73%
4	160/220 + 9% SBS	3409.7	4495.28%
5	160/220 + 12% SBS	7196.1	9598.25%
6	160/220 + 1% oleic imidazoline type I	75.54	1.81%
7	160/220 + 2% oleic imidazoline type I	52.49	-29.26%
8	160/220 + 1% oleic imidazoline type II	38.08	-48.68%
9	160/220 + 2% oleic imidazoline type II	34.79	-53.11%
10	160/220 + 1% rapeseed imidazoline type I	37.76	-49.11%
11	160/220 + 2% rapeseed imidazoline type I	37.78	-49.08%
12	160/220 + 1% rapeseed imidazoline type II	55.40	-25.34%
13	160/220 + 2% rapeseed imidazoline type II	38.09	-48.67%

Table IV shows the results of the determination of stiffness modulus S in BBR rheometer at t = 60s, at temperature of -16 ℃, according to [17]. The tests were conducted at -16 ˚C due to the requirements for bitumen modified with polymers included in Annex B of the standard [20]. Based on the results obtained it can be observed that both the modification with SBS and with imidazoline results in a decrease in stiffness modulus $S(t$ = 60s). In both cases this decrease is proportional to the amount of modifier used. Bitumen modification with 9% SBS resulted in a decrease in stiffness modulus $S(t$ = 60s) by approximately 66%. For 12% SBS content modified bitumen is characterized with very good flexibility characteristics at low temperatures, which results in exceeding the maximum deflection of the sample during the test in BBR rheometer and termination of the test before the set time limit. In the case of imidazoline, the largest decrease in stiffness modulus $S(t$ = 60s) was achieved for modification with 2% oleic imidazoline type II - the stiffness modulus decreased by approx. 25%. The smallest decrease in stiffness modulus of modified bitumen was recorded for modification with oleic imidazoline type I, which reached 14% for 2% of imidazoline content vs. reference bitumen. Intermediate values were recorded for other imidazoline types. In the case of bitumen used in waterproofing products, the decrease in stiffness modulus $S(t$ = 60s) should be considered as beneficial effect of modification as it prevents bitumen stiffening, due to which its flexibility and thus resistance of waterproofing products to mechanical damages increases.

Table V shows the results of dynamic viscosity at 60 ℃, according to [18]. Based on the test results obtained, it can be concluded that a small addition of SBS causes a significant increase in viscosity. The increase in dynamic viscosity of bitumen makes the production of waterproofing materials more difficult. Bitumen is harder to pump, higher technological temperatures are required, which increases the costs of production. A favourable phenomenon of viscosity reduction can be observed in the case of bitumen modification with technical imidazoline. The most beneficial results were obtained for bitumen modified with oleic imidazoline type II - dynamic viscosity decreased by 48% for 1% of imidazoline content and by 53% for 2% of imidazoline addition. The lowest decrease in viscosity of bitumen modified with technical imidazoline was observed for oleic imidazoline type I - dynamic viscosity decreased respectively by approximately 2% for 1% of imidazoline content and about 29% for 2% of imidazoline content. Intermediate values were recorded for the other technical imidazolines. It can be assumed that, by reducing bitumen viscosity, the addition of technical imidazoline will facilitate and accelerate the production of waterproofing materials. It will be possible to apply lower technological temperatures, which will reduce the impact of technological ageing on the changes in bitumen characteristics.

TABLE VI: DETERMINATION OF AFFINITY BETWEEN AGGREGATE AND BITUMEN

Item	Bitumen type	Share of surface of basalt aggregate covered with bitumen [%]	Increase (+) / decrease (–) of share of basalt aggregate covered with bitumen vs. reference bitumen [%]
1	160/220 – reference bitumen	40.0	–

Item	Bitumen type	Share of surface of basalt aggregate covered with bitumen [%]	Increase (+) / decrease (–) of share of basalt aggregate covered with bitumen vs. reference bitumen [%]
2	160/220 + 3% SBS	30.0	-25.0%
3	160/220 + 6% SBS	25.0	-37.5%
4	160/220 + 9% SBS	20.0	-50.0%
5	160/220 + 12% SBS	15.0	-62.5%
6	160/220 + 1% oleic imidazoline type I	60.0	50.0%
7	160/220 + 2% oleic imidazoline type I	65.0	62.5%
8	160/220 + 1% oleic imidazoline type II	50.0	25.0%
9	160/220 + 2% oleic imidazoline type II	55.0	37.5%
10	160/220 + 1% rapeseed imidazoline type I	60.0	50.0%
11	160/220 + 2% rapeseed imidazoline type I	60.0	50.0%
12	160/220 + 1% rapeseed imidazoline type II	50.0	25.0%
13	160/220 + 2% rapeseed imidazoline type II	55.0	37.5%

Table VI shows the results of the adhesion of bitumen to the surface of basalt aggregate according to [19]. On the basis of the results obtained, it can be concluded that SBS additive significantly reduces the adhesion of modified bitumen to aggregate. The use of SBS additive in the amount of 12% results in an increase of the surface not covered with bitumen by over 60% compared to reference bitumen. Bitumen modified with technical imidazoline is characterized by higher adhesion to aggregate versus reference bitumen. The highest increase in the share of the surface of basalt aggregate covered with bitumen when compared to the reference bitumen was observed in bitumen modified with oleic imidazoline type I - respectively 50% increase for 1% imidazoline content and 65% for 2% additive content. For the remaining samples, intermediate values were obtained. In the case of bitumen used for waterproofing membranes, the improvement of the adhesion to aggregate surface (greater share of basalt aggregate surface covered with bitumen) should be considered a beneficial modification effect, as the adhesion of mineral granules to reinforcement coated with bitumen improves. It also facilitates application technology of waterproofing membranes (they are often adhered to concrete substrate).

IV. CONCLUSIONS

The results of the study presented in the paper confirm the positive effects of bitumen modification with SBS: an increase in softening point, decrease in breaking point, decrease in stiffness modulus. They also draw attention to any of the following disadvantages: reducing the adhesion of bitumen to aggregate surface, reducing the penetration value and an increase in viscosity, which in the case of bitumen used in waterproofing products makes the production process more difficult and deteriorates the characteristics of the finished product. In addition to this, attention should be paid to the fact that high degree of modification is necessary to achieve the desired characteristics of modified bitumen. This means higher costs, time consuming and energy consuming production process.

To counteract these disadvantages, the authors propose the use of additives liquefying bitumen - technical imidazolines. Bitumen modification with even a small amount of imidazoline leads to a significant increase in penetration, with only a slight decrease in softening point. Moreover, an improvement in the in-use performance of imidazoline modified bitumen can be observed. This is a result of: an increase in breaking point, reduced viscosity, reduced stiffness modulus and improvement of adhesion to aggregate. Developing the optimum proportion of SBS and imidazoline modifiers will allow obtaining modified bitumen without the disadvantages caused by the addition of SBS only. The proposed solution will simplify the production process and reduce the production costs while improving the quality and durability of the finished waterproofing product. Due to this, in the later stages of the research the authors will attempt to create a hybrid bitumen modifier which will combine the beneficial effects of polymers and imidazolines on bitumen characteristics.

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