Innovative Additive for Bitumen Based on Processed Fats

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Abstract. Various additives, admixtures and modifiers are used to improve technical properties and strength characteristics of building materials. Manufacturers of waterproofing materials, concrete, ceramics and bitumen have to use innovative, increasingly complex and costly additives, admixtures or modifiers. As a result, simple and inexpensive substances have been replaced by complex, long chain polymers, multi component resins or plastics. For economic and ecological reasons waste materials are more frequently used as additives, admixtures and modifiers. Nowadays the most commonly used physical modifiers of bitumen belong to the group of polymers - large molecular organic compounds of natural origin or being the result of planned chemical synthesis. Polymers are substances that do not chemically react with bitumen, they act as fillers or create a spatial network within bitumen (the so called physical cross-linking). The development of organic chemistry has allowed the synthesis of a number of substances chemically modifying bitumen. The most promising are heterocyclic organic compounds belonging to the group of imidazolines. The aim of the study presented in this paper was to demonstrate the suitability of processed natural and post-refining fat waste (diamidoamine dehydrate) as bitumen modifier. This paper discusses the impact of adding technical imidazoline on selected bitumen characteristics. Samples of bitumen 160/220, which is most commonly used for the production of waterproofing products, were analysed. For base bitumen and bitumen modified with technical imidazoline the following measurements were taken: measurement of the softening point by Ball and Ring method, determination of the breaking point by Fraass method and needle penetration measurement at 25°C. Later the samples were aged using TFOT laboratory method and the basic characteristics were determined again. The results showed that a small amount of imidazoline improved bitumen thermoplastic parameters at low temperatures and had a significant impact on weakening bitumen oxidation and ageing. The addition of technical imidazoline prevents bitumen from hardening, thus increasing its flexibility and its resistance to mechanical damage. Due to many difficulties in the production of polymer bitumens and in order to find cheaper, more environment friendly solutions, the authors proposed an ecological bituminous modifier which, due to chemical reaction with binders, creates a stable and firm in time product. Imidazolines have a negative impact on bitumen softening point, which makes them impossible to use as an independent modifier. Therefore, at a later stage of the research, the authors will attempt to create a hybrid bitumen modifier which will combine the beneficial effect of polymers and imidazoline on the characteristics of bituminous binders.
1. Introduction
Various additives, admixtures and modifiers are used to improve technical properties and strength characteristics of building materials. As a result of operation of these substances, the life of the products is prolonged and strength, water resistance and frost resistance of the products increase. With the development of technology, the demand for materials with special properties develops. Manufacturers of waterproofing materials, concrete, ceramics and bitumen have to use innovative, increasingly complex and costly additives, admixtures or modifiers. As a result, simple and inexpensive substances have been replaced by complex, long chain polymers, multi component resins or plastics. Polymer and resin compounds considerably improve technical characteristics of selected materials. However, artificial additives, admixtures and modifiers do not react chemically with most building materials. This is due to a different chemical structure, different density and molecular weight, different elemental and group composition and different intermolecular bonds of building materials produced mostly from natural and mineral raw materials. Polymers create independent, spatial networks or chains between particles of modified material and take a role of fillers or sealants. The lack of chemical reaction lasting in time can lead to accelerated material wear and the loss of desired technical characteristics and properties. For economic and ecological reasons waste materials are more frequently used as additives, admixtures and modifiers. Many research centres around the world are working on the development of waste recycling technologies. Processed waste is used in numerous branches of industry. The sector with the highest potential for waste utilization is the sector of construction and production of building materials. The aim of the study presented in this paper was to demonstrate the suitability of processed natural and post-refining fat waste (diamidoamine dehydrate) as bitumen modifier. This paper discusses the impact of adding technical imidazoline on selected bitumen characteristics.

2. Bitumen modification
The characteristics of bitumen mix have a decisive influence on the quality of finished product - waterproofing material or road surface [1] [2]. During storage, transport, production and installation of waterproofing materials bitumen is subject to ageing [3] [4] [5]. This term specifies the changes that take place over time in the structure and chemical composition of bitumen. The impact of external factors such as water, air or high temperature, leads to changes in the in-use performance of bitumen and bituminous products. Bitumen ageing is a complex issue, difficult to assess and not fully recognized [3] [6] [7] [8]. It depends on the chemical structure of bitumen and external factors. The main purpose of most research described in literature [6] [7] is the analysis of the effect of ageing on the performance characteristics of bituminous paving. However, the literature practically does not provide any information about the impact of ageing processes on the characteristics of waterproofing products. Due to the ageing process the characteristics of bituminous waterproofing materials deteriorate, roofing membrane becomes more rigid and cracks, it does not protect bulkheads from water penetration. In winter conditions, the water accumulated in the cracks freezes, which leads to the destruction of the waterproofing layer. Numerous temperature transitions through 0 degrees (up to 120 times a year), characteristic for the climate in Poland, shorten the life of roofing membranes and force investors to carry out costly repairs. The damaged roofing membrane is not a biodegradable material, which makes it a hazardous waste for the environment.

From the point of view of a user and in the interest of the environment protection it is very important to extend the life of waterproofing materials. For this purpose, various types of bitumen modifiers are used. These are substances that improve the in–use performance of waterproofing materials, increasing their durability and improving their resistance to high and low temperatures.

Nowadays the most commonly used physical modifiers of bitumen belong to the group of polymers - large molecular organic compounds of natural origin or being the result of planned chemical synthesis. They are produced by modification of natural compounds (e.g. rubber) or by polymerization of low molecular weight compounds [9] [10]. The production of polymers is harmful to the environment and it is an energy consuming process. The resulting waste is toxic and is not
biodegradable. Polymers are substances which do not chemically react with bitumen - they act as fillers or create a spatial network within the bitumen (the so-called physical cross-linking) [9]. At present the most commonly used bitumen modifier is SBS (styrene-butadiene-styrene). It has a significant effect on the improvement of rheological properties of bitumen, both at low and high temperatures [6] [7] [9] [10] [11]. This method, however, has a number of disadvantages. It is an energy and time consuming process. To achieve a desired effect, it is necessary to modify bitumen with the addition of 12% SBS (by weight). A large amount of polymer negatively affects the adhesion of bitumen to substrate. High viscosity of polymer-bitumen leads to technological problems - obtaining a homogeneous, easy to pump mix requires high temperature and long-lasting continuous mixing of products.

The development of organic chemistry has allowed the synthesis of a number of substances which chemically modify bitumen. The most promising are heterocyclic organic compounds belonging to the group of imidazolines. These substances have dispersing properties; they change thermoplastic characteristics 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 asphaltenes, significantly improving the resistance of bitumen to ageing [12].

The paper presents the results of laboratory tests of bitumen modified with technical imidazoline produced from processed fatty compounds.

3. Materials and methods

The study comprised the analysis of bitumen 160/220 samples as the most commonly used bitumen for the production of waterproofing products.

The basic physical characteristics of the used bitumen are as follows:

- softening temperature by Ring and Ball method: 42.1°C;
- Fraass breaking point: -14.5 °C;
- penetration P25°C/100g/5s.

As bitumen modifier, processed derivatives of diamidoamine (imidazoline) were used. These are chemical substances produced as a result of the aminolysis of fats. In addition to fatty amines synthesized from nitrile or fatty alcohols, they form a basic group of compounds produced world-wide and used for obtaining cationic and amphoteric surfactants.

Imidazolines are classified as 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 (figure 1):

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

The structure which does not contain double bond in the ring is called imidazolidine. Imidazolines belong to a wide range of surfactants, among which we can distinguish cationic and amphoteric imidazolines.
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, referred to as ICSO. This compound includes:

- up to 90% of imidazoline mixture (chemical structure presented in figure 2 and figure 3),
- up to 10% of amidoamines,
- up to 1% alkyltriamine

The modifiers used are the substances obtained as a result of diamidoamine cyclisation. This reaction occurs at higher temperatures and its products are: imidazoline D2R and water. The diagram of this reaction is presented in figure 4 and figure 5.
Bitumen was modified with technical imidazoline, the volume of which reached 2% of bitumen weight. The optimum amount of modifier was determined at the preliminary phase of the study. The compounds used in the tests were produced on the basis of the following fats: oleine, rapeseed oil, stearic acid, palmitic acid, lauric acid and lard.

The following characteristics were determined for the base bitumen and bitumen modified with technical imidazoline:

- measurement of softening temperature by Ring and Ball method in accordance with [13];
- measurement of breaking point by Fraass method in accordance with [14],
- needle penetration measurement according to [15].

To simulate bitumen ageing, TFOT laboratory method was used according to [16]. This method was selected because, according to the authors, it is the best method available which simulates ageing processes occurring during the production of roofing membrane by intense surface oxidation and the impact of high temperature [17]. In order to determine the susceptibility to ageing and the increase of bitumen stiffness, the remaining penetration was calculated.

4. Results and discussions

Table 1 shows the results of determination of bitumen softening point by Ring and Ball method before and after laboratory ageing. The measurements were made for binders modified with imidazoline and the results obtained were compared with the characteristics of base bitumen. The analysis of the results was made for bitumen samples separately before and after ageing.

Samples before ageing: The addition of technical imidazoline causes a change in the softening point of bitumen. The lowest value of the parameter was obtained for the bitumen samples with the addition of oleic imidazoline - a decrease by 3.1° C (which is a change of 7.4% compared to the base bitumen). The smallest decrease in the softening point versus "pure" bitumen was obtained for palmitic imidazoline, i.e. by 2.4° C. Intermediate values were recorded for the remaining samples.
Table 1. Softening point $T_{R&B}$ of bitumen modified with technical imidazoline

| Type of sample                  | $T_{R&B}$ before TFOT ageing $[^\circ C]$ | $T_{R&B}$ after TFOT ageing $[^\circ C]$ | Increase of softening point as a result of TFOT ageing $[%]$ |
|---------------------------------|------------------------------------------|------------------------------------------|----------------------------------------------------------|
| 1 160/220 – base bitumen        | 42.1                                     | 44.1                                     | 4.75                                                     |
| 2 160/220 + oleic imidazoline   | 39.0                                     | 40.0                                     | 2.56                                                     |
| 3 160/220 + rapeseed imidazoline| 39.4                                     | 44.0                                     | 11.68                                                    |
| 4 160/220 + lauric imidazoline  | 39.2                                     | 41.0                                     | 4.59                                                     |
| 5 160/220 + palmitic imidazoline| 39.7                                     | 40.3                                     | 1.51                                                     |
| 6 160/220 + lard imidazoline    | 39.4                                     | 44.0                                     | 11.68                                                    |

Samples after ageing: For all the samples subjected to ageing the value of the parameter increased compared to the samples before ageing - the phenomenon of bitumen stiffening was observed (which is in accordance to the literature of the subject). The increase of the parameter for the base bitumen was 2.0 $^\circ$C (which is a change of 4.75% compared to bitumen before ageing). The addition of imidazoline in most cases resulted in lower increase of the value of the parameter than for non-modified bitumen. For the samples of bitumen with the addition of palmitic imidazoline the value increased by 0.6 $^\circ$C (which is a change of 1.51% compared to bitumen before ageing). However, the addition of rapeseed and lard imidazoline resulted in an increase of the parameter by 4.6 $^\circ$C (which is a change of 11.68% compared to bitumen before ageing).

Table 2. Breaking point $T_{Fr}$ for bitumen modified with technical imidazoline

| Type of sample                  | $T_{Fr}$ before TFOT ageing $[^\circ C]$ | $T_{Fr}$ after TFOT ageing $[^\circ C]$ | Increase of breaking point as a result of TFOT ageing $[%]$ |
|---------------------------------|------------------------------------------|------------------------------------------|----------------------------------------------------------|
| 1 160/220 – base bitumen        | -14.5                                    | -9.5                                     | 34.48                                                    |
| 2 160/220 + oleic imidazoline   | -21.5                                    | -18                                      | 16.28                                                    |
| 3 160/220 + rapeseed imidazoline| -21.5                                    | -20.5                                    | 4.65                                                     |
| 4 160/220 + lauric imidazoline  | -20.0                                    | -19.5                                    | 2.50                                                     |
| 5 160/220 + palmitic imidazoline| -21.5                                    | -19.5                                    | 9.30                                                     |
| 6 160/220 + lard imidazoline    | -22.5                                    | -20.5                                    | 8.89                                                     |

Table 2 shows the results of the Fraass breaking point for bitumen before and after ageing. The Fraass breaking point was determined for binders modified with imidazoline. The results obtained were compared to the characteristics of base bitumen. The analysis of the results was made separately for bitumen samples before and after ageing.

Samples before ageing: The addition of technical imidazoline to bitumen causes a significant decrease in the breaking point. The lowest value of the parameter was obtained for bitumen samples with the addition of lard imidazoline - a decrease by 8 $^\circ$C (which is a change of 55.2% compared to the base bitumen). The smallest decrease in the parameter was obtained for bitumen samples with the addition of lauric imidazoline, i.e. by 5.5 $^\circ$C (which is a decrease of 37.9% compared to the base bitumen). Intermediate values were recorded for the remaining samples.

Samples after ageing: As a result of the laboratory ageing of bitumen, the value of the parameter increased compared to the samples before ageing – the bitumen stiffened, became less flexible and less resistant to low temperatures (which is in accordance to the literature of the subject). High (unfavourable) increase of the parameter equalling 5 $^\circ$C was recorded for the base bitumen (a change of 34.5% compared to bitumen before ageing). The best results were obtained for lauric imidazoline as the softening point of bitumen before laboratory ageing significantly decreased (from -14.5 $^\circ$C for
"pure" bitumen to -20°C for bitumen with imidazoline), while the breaking point slightly increased after laboratory ageing (an increase of 2.5%).

Table 3. Penetration of bitumen modified with technical imidazoline

| Type of sample                          | Penetration before TFOT ageing [0.1mm] | Penetration after TFOT ageing [0.1mm] | Remaining penetration after TFOT ageing [%] |
|----------------------------------------|---------------------------------------|---------------------------------------|--------------------------------------------|
| 1 160/220 – base bitumen              | 157                                   | 74                                    | 52.87                                      |
| 2 160/220 + oleic imidazoline          | 231                                   | 155                                   | 32.90                                      |
| 3 160/220 + rapeseed imidazoline       | 192                                   | 106                                   | 44.79                                      |
| 4 160/220 + lauric imidazoline         | 178                                   | 137                                   | 23.03                                      |
| 5 160/220 + palmitic imidazoline       | 191                                   | 147                                   | 23.04                                      |
| 6 160/220 + lard imidazoline           | 206                                   | 146                                   | 29.13                                      |

Table 3 shows the results of the determination of bitumen penetration before and after ageing. The bitumen penetration was determined for binders modified with imidazoline. The results obtained were compared to the parameters of base bitumen. The analysis of the results was made separately for bitumen samples before and after ageing.

Samples before ageing: The addition of technical imidazoline causes a significant increase in the bitumen penetration. The highest value of the parameter was obtained for bitumen samples with the addition of oleic imidazoline - an increase of 74.0 [0.1mm] (an increase of 47.1% as compared to the base bitumen). The smallest increase of the parameter was obtained for the bitumen with the addition of lauric imidazoline, i.e. by 21.0 [0.1mm] (13.4% as compared to the base bitumen). Intermediate values were recorded for the remaining samples.

Samples after ageing: For all the samples of bitumen subject to the ageing process, the value of the parameter decreased compared to the samples before ageing. Based on the results obtained, the remaining penetration was calculated as a percentage decrease in the value of penetration after laboratory ageing by TFOT method in relation to the bitumen which had not undergone the ageing process. Figure 6 shows the values of the remaining penetration for the tested samples of imidazoline modified bitumen. The addition of technical imidazoline resulted in a significant decrease in the value of the remaining penetration of modified bitumen compared to the "pure" bitumen. This dependence was observed for all the types of imidazoline used. The lowest (most favourable) values of the remaining penetration were recorded for bitumen modified with lauric and palmitic imidazoline.

The paper presents the results of laboratory tests of a new generation of substances modifying bitumen. These are organic chemical compounds belonging to the group of imidazolines, heterocyclic compounds which are partially hydrogenated derivative of imidazole. The presented results show that a small amount of imidazoline improves thermoplastic properties of bitumen at low temperatures and has a significant impact on weakening of bitumen oxidation and ageing. The addition of technical imidazoline prevents hardening of bitumen, increases its flexibility and thus improves its resistance to mechanical damage.
Figure 6. Remaining penetration of bitumen modified with technical imidazoline

Soft high penetration bitumen is easy to pump and mix. Its processing does not require the use of high temperatures, which protects the bitumen against overheating and strong oxidation. The reduction of technological temperature increases the profitability of production. The authors would like to point out that the addition of technical imidazoline provides the parameters desired by roofing membrane manufacturers (at the stage of material production) such as: increase of the bitumen penetration, decrease of the breaking point and decrease of the remaining bitumen penetration.

Roofing membranes made of bitumen modified with imidazoline will be resistant to cracks and mechanical damage occurring during membrane installation on a roof (rolling out of membrane) and during the use of the roof (e.g. during maintenance work on the roof). This is particularly important in the climate in Poland, where water penetrating through cracks freezes cyclically and damages the roofing.

5. Conclusions
Increasing requirements as to bitumen waterproofing materials have led to the focus on the technology using soft bitumen which is easy to pump and mix (this makes the market of roofing membrane manufacturers independent of price volatility and availability of hard paving grade bitumen). Bitumen from this group is characterized by high breaking point and low softening point. In order to obtain a finished product (roofing membrane) resistant to a full temperature range, thermoplastic polymers are used as modifiers of soft bitumen. Unfortunately, these methods are not fully effective, both due to technical or ecological reasons. Polymers are not fully compatible with bitumen (too high viscosity), require high technological temperatures and long-lasting homogenisation. This technology is inefficient and harmful to the environment.

Due to numerous difficulties in the production of polymer bitumen and in order to find cheaper, more environmentally friendly solutions, the authors proposed an ecological bitumen modifier which, thanks to a chemical reaction with binders, creates a stable and firm in time product. Imidazolines have a slightly negative effect on the softening point of bitumen, due to which they cannot be used as an independent modifier. Therefore, at a later stage of the research, the authors will attempt to develop a hybrid bitumen modifier which will combine the beneficial effects of polymers and imidazoline on the properties of bituminous binders.
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