Paweł Mieczkowski
dr hab. inż.
Zachodniopomorski Uniwersytet Technologiczny w Szczecinie, Katedra Dróg i Mostów
Pawel.Mieczkowski@zut.edu.pl

Robert Jurczak
dr inż.
Zachodniopomorski Uniwersytet Technologiczny w Szczecinie, Katedra Dróg i Mostów
Robert.Jurczak@zut.edu.pl

Bartosz Budziński
mgr inż.
Zachodniopomorski Uniwersytet Technologiczny w Szczecinie, Katedra Dróg i Mostów
bbudzinski@zut.edu.pl

DOI: 10.35117/A_ENG_18_11_09

Asphalt concretes with metal-organic frameworks for highways and expressway road surfaces

Abstract: The aim of performed research and analysis is the evaluation of the influence of metal-organic catalyst (MOC) on the properties of asphalt concretes designed for KR5-7 traffic load. The anhydrous iron (III) chloride was added as a metal-organic catalyst in the amount of 2,5% of asphalt mass. The study determined the properties of asphalt concrete with modified binder (70/100+2,5% $FeCl3$) and referential asphalt concrete with typical binder 35/50. The test included determination of water and freeze-thaw resistance (ITSR) and resistance to permanent deformation. Additional basic tests were performed to compare the properties of modifies, the 70/100 and 35/50 asphalt. The research was performed for three binder conditions: before aging, short-term aging in accordance with RTFOT and PAV long-term aging. The test results allowed to determine the IP penetration index. Additionally, for 35/50 asphalt and modified binder the dynamic viscosity was determined before and after aging in accordance with RTFOT. The addition of metal-organic catalyst increased the resistance of the asphalt concrete to permanent deformation without changing its water and freeze-thaw resistance. In case of the 70/100 asphalt the addition of MOC improved the hardness (especially after short- and long-term aging) and influenced the rheology.

Keywords: Asphalt concret; Metal-organic catalyst (MOC)

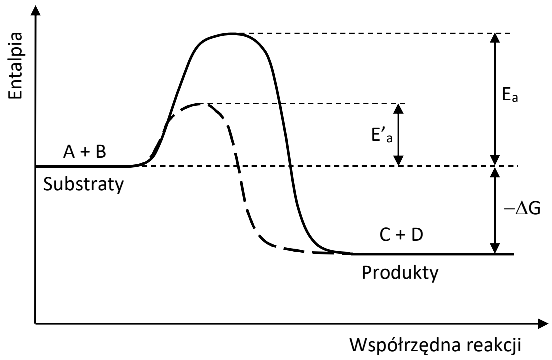
Introduction

The continuous increase of loads from motor vehicles (and above all increasing the share of heavy goods vehicles) forces to search for solutions that guarantee the achievement of proper functional features of the surface. Taking into account additional factors, i.e. climatic and weather impacts, the directions of undertaken actions must take into account the behavior of asphalt mixtures both in low (negative) and high operating temperatures. Possibilities of improving the properties of MMA through the appropriate selection of aggregates or their refinement (grain size, type of rock, cubic grains, etc.) are quite limited. In the case of a binder, the reservoir of changes is much wider. This is particularly important in the aspect of the accumulation of external influences, i.e. from car traffic and atmospheric factors. One of the ways to improve the characteristics of binders is the use of various modifiers, which in addition to changes in asphalt properties increase the strength parameters of mixtures at high temperatures (susceptibility to permanent deformation) and increase their resistance to low temperatures (low-temperature cracks). The most popular bitumen modifiers include thermoplastic polymers (SBS, SIS, EVA, APP, etc.), rubber from used car tires (natural and artificial rubber), synthetic resins, etc. [4, 5, 6, 9, 10]

Another type of asphalt binder's modifier may be organometallic catalysts. Their operation depends mainly on the stiffening of the bitumen as a result of oxidative polymerization [1, 2, 3, 7, 11, 12]. The obtained effects depend on the type of organometallic salt used and the course of the oxidation reaction [1, 2, 7, 11]. An additional benefit of their use may be a reduction in the temperature of MMA production and incorporation, thus reducing the emission of toxic and greenhouse gases into the atmosphere [6, 11, 12].

Mechanism of the interaction of organometallic catalysts on asphalts

Organometallic catalysts are compounds in which the carbon atoms of organic groups are bonded to metal atoms. They affect the quicker reaction of the chemical equilibrium by the reaction, reduce the energy needed to initiate the reaction and accelerate its course (Figure 1). The catalyst does not cause a reaction which theoretically cannot occur. Its effect is limited to changing the reaction rate without changing the chemical composition after its completion [1, 2].



1. The course of free enthalpy for the reactions without (continuous line) and with the participation of the catalyst (dashed line)

On the basis of the enthalpy changes (Fig. 1) it can be stated that during the collision of particles, their valence electrons are rearranged. It is connected with the increase of the energy of the system. In the first stage, an unstable active complex form, the energy of which is greater than the energy of the substrates for activation energy E. It undergoes immediate disintegration, creating a more stable reaction product. With the participation of the catalyst, the energy barrier, i.e. the activation energy E_a, decreases to E'_a, and thus the greater the number of molecules is able to react. The difference between the energy of substrates and products (−ΔG) is the energy that is released by the system as a result of the reaction.

Metal-organic catalyst may be road bitumen modifiers. When added to the asphalt, it reacts with the oxidation polymerization, resulting in curing of the binder. The reactions between metal-organic catalyst and asphalt can be divided into two parts. In the first stage, hydroxides are formed (at a high temperature in the presence of oxygen), followed by diaformones (in places of the most sensitive connections of aromatic and aliphatic asphalt). In the second, metal complexes are formed with ketones that cross-link the asphalt. The result is an increase in asphalt viscosity and the cohesion of asphalt mixtures.

The catalyst facilitates the formation of bonds between metal ions and asphalt particles. The polymerization process proceeds relatively quickly after mixing the binder with aggregate in the presence of active oxygen. The rate of oxidation and polymerization decreases from the moment of mixing the binder with the aggregate (especially during incorporation), mainly due to limited oxygen access and temperature drop. However, it can be assumed that oxidation polymerization reactions may also take place after the completion of the incorporation process (with the participation of oxygen from the air).

Metal-organic catalyst salt also affects the reduction of bitumen viscosity (in the range of technological temperatures), which is the result of the inert hydrocarbon part contained in it. The effect of this may be a decrease in the temperature of MMA production and incorporation even by 30ºC (in relation to the standard technology), and thus reduction of toxic gas emissions (SO_2, NO_2, NO etc.) and greenhouse gases (CO_2, CO) to the atmosphere.

Materials for research

Two road asphalts (distilled): 35/50 and 70/100 were used for the tests. Their choice was dictated by the need to obtain:

- suitable strength parameters of asphalt mixtures (35/50)
- low viscosity at the stage of their manufacture and incorporation (70/100).

As a metal - organic catalyst, anhydrous iron (III) chloride FeCl3 was used. It should be noted that this compound is characterized by high hygroscopicity, which requires special precautions for its use. From this, among others A mixture of a metal - organic catalyst with naphthenic acids in a 5: 1 ratio (iron chloride: naphthenic acids) was prepared for the study. Naphthenic acids constituted a conglomerate of various hydrocarbon substances, including toxic acids, alcohols, esters and others (similar in structure to those contained in asphalt). Their use allowed for an additional reduction in the viscosity of the 70/100 asphalt.

Research methodology

The tests were carried out in two stages. The first concerned asphalt binders, in the second one parameters of asphalt concrete were determined.

Binder tests concerned road asphalt 35/50 and 70/100 and asphalt 70/100 modified with iron (III) chloride in an amount of 2.5%. The samples of bituminous binders were prepared both for the study of asphalts themselves and for the preparation of asphalt mixtures with their participation. This consisted in each time heating the asphalt (weighing 2.5 kg) in a container with a volume of approx. 3.5 dm3 (protected against the air supply) to 160ºC. This process was carried out in an oil bath, ensuring uniform heating of the container and the asphalt in it. After obtaining the required temperature, a modifier was added to the binder. After being distributed in the binder, the whole was mixed for 10 minutes using a stirrer at a constant speed of 240 rpm. At the end of this step, the heating was turned off and a mixing process of 120 rpm was carried out for a further 10 minutes. Samples prepared in this way constituted research material. 35/50 and 70/100 base asphalt were prepared in an identical manner (without modifier), i.e. they were heated to 160°C and stirred for 20 minutes.

The effect of the modifier on the properties of bituminous binders (before and after the technological and operational aging processes) was determined on the basis of research:

- penetration at 25ºC in accordance with PN-EN 1426,
- softening temperatures according to PiK in accordance with PN-EN 1427,
- Fraass breaking point according to PN-EN 12593.

In addition, for asphalt 35/50 and 70/100 with 2.5% FeCl3 not aged and after technological aging (short-term), the dynamic viscosity determination was performed in the temperature range from 100 to 170ºC using a rotational viscometer according to PN-EN 13302.

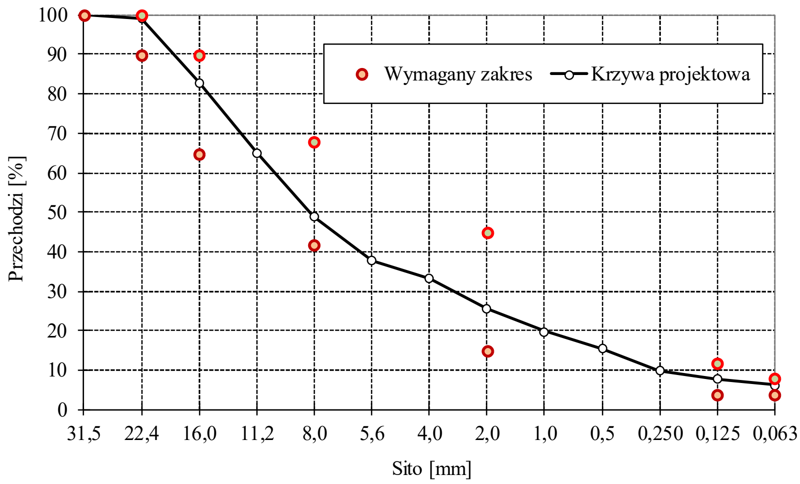
The process of technological aging (short-term) in laboratory conditions was simulated based on the RTFOT (Rolling Thin Film Oven Test) method according to PN-EN 12607-1. In the case of operational aging, the PAV (Pressure Aging Vessel) method was applied in accordance with the PN-EN 14769 standard.

In the case of asphalt mixtures, the tests were carried out on three samples of asphalt concrete intended for the foundation layer with granulation up to 22 mm (AC 22 P). In terms of grain size, the content of binder and voids, they corresponded to the requirements for the KR5-7 movement in accordance with WT-2: 2014 [13]. The differences concerned only the type of binder used (35/50, 70/100 and modified 70/100).

Asphalt concrete (grit) and fine (broken sand) greywacke (Koschenberg), as well as limestone filler (Nordkalk), were used for asphalt concrete. The composition of the asphalt mixture is presented in Tab. 1 and Fig. 3. The free space on Marshall samples formed with 35/50 reference asphalt was 5.2%.

Tab. 1. Composition of mineral-asphalt mixture for the foundation layer AC 22 P

Material name	Mixture	
	mineral [%]	mineral-asphalt [%]
Grit16/22 (Koschenberg)	18,0	17,3
Grit 11/16 (Koschenberg)	18,0	17,3
Grit 8/11 (Koschenberg)	18,0	17,3
Grit 5/8 (Koschenberg)	10,5	10,0
Grit 2/5 (Koschenberg)	10,0	9,6
Broken sand 0/2 (Koschenberg)	20,0	19,2
Calcium filler (Nordkalk)	5,5	5,3
Asphalt binder	–	4,0
Adhesive agent	–	0,3[1)]
1) in relation to the weight of the asphalt binder		



2. The graining curve of asphalt concrete AC 22 P for traffic KR5-7 in accordance with WT-2: 2014

In the field of concrete concretes tests, the term was:

- resistance to permanent deformation (WTSAIR, PRDAIR) according to PN-EN 12697-22, method B in air (60°C, 10,000 cycles);

- sensitivity to water in accordance with PN-EN 12697-12 at 25 ° C (compaction: 2 × 35 strokes, storage at 40 ° C with one freezing cycle).

Procedures for sample preparation, conditioning and testing were in accordance with the provisions of technical document WT-2: 2014 [13].

Test results and analysis

Needle penetration allows you to determine the consistency of asphalts. The test was carried out at 25 ° C, in accordance with PN-EN 1426. The preparation of the samples consisted of filling the penetration vessel with an asphalt binder to a height of at least 10 mm greater than the anticipated depth of the needle. The sample was then cooled at ambient temperature (15-30 ° C) in 60-90 minutes and then placed in a water bath at a fixed test temperature. After the thermostatic period, the sample was placed on the test bench and the measurement was performed in accordance with the requirements of the standard, i.e. with a needle load of 100 g, during 5 s. The results of the aging and post-aging tests according to RTFOT and PAV are presented in Tab. 2. The test result was determined as the average of four determinations.

Tab. 2. Results of penetration tests of asphalt binders before and after aging by RTFOT and PAV

Sample type	Value from the research [×0,1 mm]		
	BEFORE	RTFOT	RTFOT+PAV
Asphalt 35/50	42,1±0,8	34,1±0,5	31,5±0,4
Asphalt70/100	82,6±1,3	69,1±0,9	65,2±0,6
Asphalt70/100+2,5%$FeCl_3$	73,1±1,1	60,6±0,6	45,6±0,6

The research shows that the largest decrease in penetration was obtained for asphalt modified with iron (III) chloride and the lowest for asphalt 35/50. In the case of unmodified asphalts (35/50 and 70/100), the largest decreases in penetration were observed after aging by RTFOT (about 8-12 × 0.1 mm), much lower after PAV (about 2.5-4 × 0.1 mm). In the case of modified asphalt, penetration drops were at a similar level, both after aging by RTFOT and after PAV (13-15 × 0.1 mm). Bitumen modified after aging RTFOT + PAV in terms of penetration meets the requirements as for road asphalt 35/50 before aging.

The PiK softening temperature was determined in an automatic apparatus in accordance with the PN-EN 1427 standard. Sample preparation consisted of heating them to temperatures of about 140-150 ° C, and then filling the rings arranged on a plate lubricated with anti-adhesive. After cooling, excess weight was cut with a knife. Samples prepared in this way together with steel balls and guides were placed in a beaker of water. After 15 minutes of thermostatting (at 5ºC), the liquid heating was started at 5ºC/min. The result was the average temperature of three determinations, at which the steel ball covered a distance of 25.0-4.4 mm. The results of examinations before aging and after aging according to RTFOT and PAV are presented in Tab. 3.

Tab. 3. Results of testing softening temperature of asphalt binders before and after aging according to RTFOT and PAV

Sample type	Value from the study [°C]		
	BEFORE	RTFOT	RTFOT+PAV
Asphalt35/50	55,2±0,5	60,1±0,6	61,9±0,3
Asphalt 70/100	44,8±0,8	51,4±0,8	53,2±0,5
Asphalt70/100+2,5%$FeCl_3$	50,1±0,7	58,3±0,5	65,4±0,6

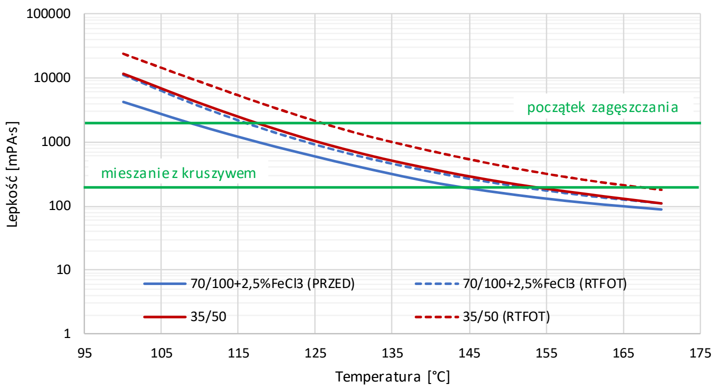
The results of the research indicate that the aging processes (both RTFOT and PAV) cause an increase in the softening temperature. In the case of 35/50 and 70/100 road asphalt, the increments are at a similar level - after aging RTFOT TPiK increased by approx. 4.9-6.6°C, while after PAV in both cases the increase was 1.8 ° C. The changes taking place in asphalt 70/100 with 2.5% FeCl3 were much higher. Both after aging by RTFOT and PAV, an increase in temperature of approx. 8.1-8.2°C was found each time. The softening temperature of bitumen modified after aging with RTFOT was on a similar level as for asphalt 35/50 (also after RTFOT), whereas after PAV it was already higher than the temperature obtained for asphalt 35/50. This shows that the asphalt is firmly stiffened.

Determination of TFraass brittleness temperature was made in accordance with PN-EN 12593. This is the highest temperature at which a 0,5 mm thick asphalt layer applied to a thin steel plate, during cooling at a constant speed (1 ° C/min), scratches or breaks her bending. Plate bending is performed every 1ºC from a temperature of 10 ± 2ºC above the expected breaking point. The average of three determinations was taken as the result of the test. Values obtained from aging and post-aging tests according to RTFOT and PAV are presented in Tab. 4.

Tab. 4. Results of testing the brittleness temperature of asphalt binders before and after aging according to RTFOT and PAV

Sample type	**Value from the research [°C]**		
	BEFORE	RTFOT	RTFOT+PAV
Asphalt 35/50	-9,2±1,1	-8,3±0,7	-7,8±0,6
Asphalt 70/100	-19,1±1,6	-17,3±0,9	-16,1±0,8
Asphalt70/100+2,5%$FeCl_3$	-17,4±1,7	-14,6±1,2	-11,2±0,7

It can be concluded on the basis of research that the aging processes (both RTFOT and PAV) cause an increase in brittle temperature. In the case of 35/50 and 70/100 road asphalts, the increments are small - after aging RTFOT $T_{Fraassa}$ increased by approx. 0.9-1.8°C, whereas after PAV the temperature increase was from 0.5 to 1.2°C. The changes taking place in asphalt 70/100 with 2.5% FeCl3 were much higher. After aging by RTFOT, the temperature of brittleness increased by 2.8°C, whereas after PAV by 3.4°C. The brittleness temperature of asphalt modified after aging with RTFOT and PAV was lower than that of road asphalt 35/50 before aging. This may indicate that the asphalt modified after aging with RTFOT and PAV will be characterized by higher resistance to thermal cracking (both low temperature and fatigue from temperature fluctuations). The dynamic viscosity in the temperature range 100-170ºC was performed using the rotational viscometer according to PN-EN 13302. The determination consists in measuring the relative resistance (torque) to the rotation of the spindle, immersed in a container filled with asphalt. Test results for 35/50 asphalt and modified before and after aging according to RTFOT are shown in Fig. 3.



3. Viscosity of asphalt 35/50 and 70/100 modified with anhydrous iron (III) chloride before and after aging by RTFOT

The results of dynamic viscosity tests indicate that 70/100 asphalt modified with anhydrous iron (III) chloride has a viscosity similar to that of 35/50 asphalt before aging. When using it for asphalt mixtures (instead of 35/50 asphalt), it is possible to lower the enclosure temperature by almost 20 ° C. However, due to the specificity of this type of modifier, this requires further research, including due to the course of oxidation polymerization processes. They run much more intensively in thin layers of binder on the surface of the aggregate in relation to the laboratory conditions of RTFOT aging.

In order to determine the rheological type of asphalt and changes occurring due to the addition of an organometallic catalyst and aging processes, Ip penetration index was determined before and after aging by RTFOT and PAV. I_p values were determined based on the penetration value at 25 ° C and the softening point according to PiK from formula (1). The results of calculations are presented in Tab. 5.

$$I_p = \frac{20 \cdot T_{PiK} + 500 \cdot \log P - 1952}{T_{PiK} - 50 \cdot \log P + 120} \quad (1)$$

where:

T_{PIK} – softening temperature, °C;

P – penetration in 25°C, ×0,1mm.

Tab. 5. Penetration index I_p values for bituminous binders before and after aging by RTFOT and PAV

Sample type	**Value from the research**		
	BEFORE	RTFOT	RTFOT+PAV
Asphalt35/50	-0,38	0,16	0,33
Asphalt70/100	-1,40	-0,05	0,24
Asfphalt70/100+2,5%$FeCl_3$	-0,23	1,18	1,81

Aging processes affect rheological changes in the binder. In all cases, IP increases, which makes the binderless temperature-sensitive. The use of a modifier in the form of iron (III) chloride contributed to a significant increase in the penetration index after aging processes, both RTFOT and PAV.

Investigations of asphalt mixtures concerned three AC 22 P asphalt concrete diversified due to the type of asphalt binder (35/50, 70/100, 70/100 + 2.5% FeCl3). They were produced in a laboratory mixer in 45 kg weights. In order to harmonize thermal conditions, the same temperatures of aggregates, binders, ingredients, and compaction were assumed for all three mixtures. They were respectively: aggregate (pre-mixed) - 170 ± 2°C, asphalt - 160 ± 2°C, enclosing - 165 ± 5°C, compaction - 135 ± 5°C (both samples for ITSR and rutting). Samples for the assessment of water and frost sensitivity were formed immediately after mixing. In the case of rutting, the asphalt mixture was subjected to short-term conditioning (aging) in accordance with the provisions of technical document WT-2: 2014 [13].14 samples were tested for sensitivity to water and frost, of which 10 volumetric densities were the closest to each other (5 samples of "dry set" and "wet set"). Samples for testing were conditioned in accordance with the provisions of technical document WT-2: 2014 [13]. The test results are presented in Tab. 6.

Tab. 6. The average values obtained in the ITSR sensitivity test for water and frost

Sample type	**Value from the research**

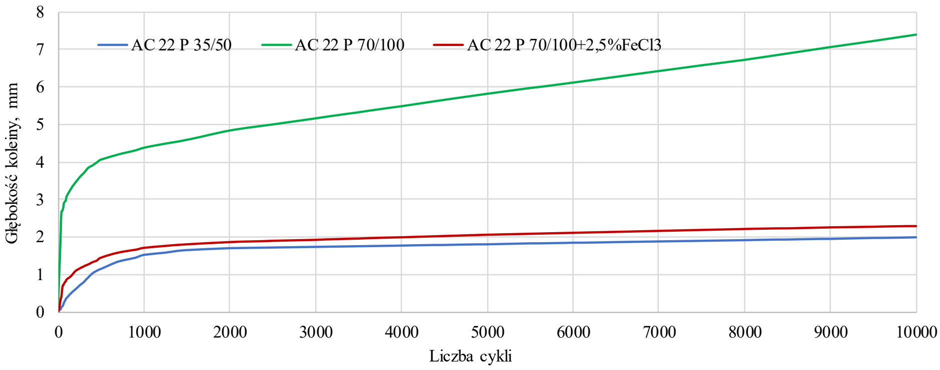
	ITS_w [kPa]	ITS_d [kPa]	ITSR [%]
AC 22 P 35/50	1354,7	1647,5	82,2
AC 22 P 70/100	951,6	1104,2	86,2
AC 22 P 70/100+2,5%FeCl3	1458,5	1781,1	81,9

The test results indicate that in all cases the requirement for water and frost sensitivity for asphalt concretes for traffic KR5-7 according to WT-2: 2014 (ITSR70) was met. It can be seen that the most favorable resistance to water and frost was achieved for concrete with 70/100 asphalt. On the other hand, bituminous concretes containing 35/50 and 70/100 modified FeCl3 asphalt have similar sensitivity.

The rutting resistance test was performed in a small rocker gauge (method B, in the air, 60°C, 10000 cycles) in accordance with PN-EN 12697-22 and the applicable provisions of the technical document WT-2: 2014 [13]. The determination for each of the asphalt mixtures was performed on two samples. The test results are presented in Tab. 7 and Fig. 4.

Tab. 7. The average values obtained in the resistance to permanent deformation test

Sample type	**Value from the research**	
	PRD_{AIR} [%]	WTS_{AIR} [mm/10^3 cykli]
AC 22 P 35/50	3,3	0,036
AC 22 P 70/100	12,3	0,316
AC 22 P 70/100+2,5%$FeCl_3$	3,8	0,047



4. Rutting depth increase in samples of asphalt concrete AC 22 P with asphalts 35/50, 70/100 and 70/100+2,5%$FeCl_3$

The results of resistance to permanent deformation tests confirm the suitability of iron (III) chloride for the modification of bituminous binders. The amount of permanent deformation and its increase (in the range of 5000-10000 cycles) for blends with asphalt 35/50 and 70/100 + 2.5% FeCl3 are on a similar level and meet the requirements provided for in WT-2: 2014 for bituminous concretes for traffic KR5-7 [13]. In the case of 70/100 asphalt, both values are much higher and do not meet the requirements.

Conclusions

The conducted research allows to formulate the following conclusions:

- addition of an metal-organic catalyst (in the form of a mixture of anhydrous iron (III) chloride and naphthenic acids) to road asphalt results in an increase in

stiffness in the useful temperature range, characterized by a decrease in penetration, an increase in softening temperature and brittle temperature;
- aging according to RTFOT and PAV intensifies rheological changes in asphalt 70/100 modified with anhydrous iron (III) chloride, which leads to an increase in the hardness of the binder with a simultaneous decrease in resistance to low temperatures;
- 70/100 asphalt modified with iron (III) chloride can be an alternative to harder asphalt (e.g. 35/50) as a component of asphalt concrete for the heaviest traffic (KR5-7);
- asphalt concrete with the participation of 70/100 modified FeCl3 asphalt meets the requirements of the technical document WT-2: 2014 for mixtures for the KR5-7 movement, both in terms of sensitivity to water and frost as well as resistance to permanent deformation;
- further research should be directed to possible further polymerization processes occurring in the layer, which may affect the stiffness of the mixture and consequently increase the susceptibility to cracks.

Source materials

[1] Bielecka-Florjańczyk E., Włostowska J. Chemia organiczna. WN-T, Warszawa 2005
[2] Cotton A., Wilkinson G., Gaus P. Chemia nieorganiczna. Podstawy. PWN, Warszawa 1998
[3] Galarraga C.E., Scott C., Loria H., Pereira-Almao P. Kinetic Models for Upgrading Athabasca Bitumen Using Unsupported NiWMo Catalysts at Low Severity Conditions. Industrial & Engineering Chemistry Research, 2012, v. 51, str. 140-146
[4] Gaweł I., Piłat J., Radziszewski P., Kowalski K.J., Król J.B. Rubber modified bitumen. Polymer Modified Bitumen, 2011, str. 72-97
[5] Jew P., Shimizu J.A., Svazic M., Woodhams R.T. Polyethlene-modified bitumen for paving applications. Journal of Applied Polymer, 1986, v. 31, str. 2685-2704
[6] Mallick R., Bergendahl J. Reducing Greenhouse Gas Emissions from Asphalt Materials. Project Number: MQP-RBM-0601, Worcester Polytechnic Institute, 2007
[7] Moszew J. Chemia organiczna. PWN, Warszawa 1958
[8] Nejad F.M., Aghajani P., Modarres A., Firoozifar H. Investigating the properties of crumb rubber modified bitumen using classic and SHRP testing methods. Construction and Building Materials, 2012, v. 26, str. 481-489
[9] Pérez-Lepe A., Martinez-Boza F.J., Gallegos C., Gonzáles O., Muňoz M.E., Santamaria A. Influence of the processing conditions on the rheological behavior of polymer-modified bitumen. Fuel, 2003, v. 82, str. 1339-1348
[10] Segnoz B., Isikyakar G. Evaluation of the properties and microstructure of SBS and EVA polymer modified bitumen. Construction and Building Materials, 2008, v. 22, s. 1897-1905
[11] Stefańczyk B., Mieczkowski P. Dodatki, katalizatory i emulgatory w mieszankach mineralno-asfaltowych. WKiŁ, Warszawa 2010
[12] Stefańczyk B., Mieczkowski P. Mechanizmy oddziaływania katalizatorów metaloorganicznych na asfalty stosowane w technologii drogowej. Magazyn Autostrady, 2016, v. 5, str. 23-29
[13] WT-2 2014 – część I. Mieszanki mineral o-asfaltowe. Wymagania Techniczne. Nawierzchnie asfaltowe na drogach krajowych, GDDKiA, Warszawa 2014