BULLETIN OF THE POLISH ACADEMY OF SCIENCES
TECHNICAL SCIENCES, Vol. 74(1), 2026, Article number: e156767
DOI: 10.24425/bpasts.2025.156767

CIVIL ENGINEERING

Synergistic effect of additives on reducing asphalt binder aging

Mateusz M. Iwański*, Małgorzata Durlej, and Karolina Janus

Kielce University of Technology, Faculty of Civil Engineering and Architecture, Al. Tysiąclecia P.P. 7, 25-314 Kielce, Poland

Abstract. As an organic material, asphalt binder undergoes a aging process, the intensity of which depends on the stage of its technological use. The binder is exposed to high temperatures, which cause its oxidation. The viscoelastic properties of the binder deteriorate. Research is being conducted to limit the effects of asphalt aging. One of the directions is individually dosed chemical additives to be used in the binder. In the article, a combination of synthetic wax (SW_{LC}) and tall oil amidopolyamine (TOA) was used for the first time in the binder, in concentrations of 1.0%, 1.5%, 2.0% and 2.5% and in the amounts of 0.0%, 0.2%, 0.4% and 0.6% by weight in relation to asphalt. The function of these additives is to act as aging inhibitors and to improve the basic properties of the binder. The resulting binders containing combinations of SW_{LC} and TOA were then subjected to short-term and long-term aging. The effects of aging on penetration at 25°C, softening point and dynamic viscosity were analyzed, and their aging indices were determined. The penetration index and plasticity range of the modified asphalt were also determined. A synergistic effect of SW_{LC} and TOA was observed at the recommended amounts of 2.0% and 0.4% relative to the asphalt, which ensured a favorable change in the analyzed binder parameters. The results obtained are therefore of significant importance for road engineering practice in the design and construction of durable and sustainable road pavements and the possibility of using this type of binder in the environmentally friendly Warm Mix Asphalt technology.

Keywords: Warm Mix Asphalt (WMA); aging inhibitors; sustainable pavements; bio-based additives; rheological properties; aging process.

1. INTRODUCTION

The durability of asphalt pavement structures is contingent on the quality of the asphalt mixture utilized and its resistance to deterioration. Asphalt plays a decisive role in ensuring the required quality of the asphalt mix and guaranteeing the long-term service life of asphalt pavements. At the same time, the environmental aspects of its use must be taken into account. For this reason, innovative asphalt mixtures have been developed, which are produced and used at lower manufacturing temperatures. They are referred to as warm mix asphalt (WMA) or half-warm mix asphalt (HWMA), as opposed to conventional hot mixes. Lowering the technological temperature of asphalt reduces greenhouse gas emissions, especially CO_2, by about 20–30%, nitrogen oxides by 60–70%, while energy consumption during production drops by about 20–35% [1], which has a significant impact on mitigating climate change on the Earth. This type of action is aligned with global sustainable development frameworks such as the UN Sustainable Development Goals and the European Green Deal.

Asphalt plays a pivotal role in ensuring the required quality of the asphalt mixture and guaranteeing its long service life. Consequently, it is imperative that asphalt exhibits the most favorable physical and mechanical properties.

For this purpose, modifying additives are used, such as synthetic wax, which increases the asphalt mixture's resistance to permanent deformation [2], natural and waste plastics, which improve the rheological characteristics of the binder [3], and various chemical compounds, as demonstrated by Leng *et al.* [4], which improve the basic and rheological properties of the binder. At the same time, these additives aim to lower the technological temperatures required for the production and installation of the asphalt mixture. To this end, Van De Ven *et al.* [5] have also developed a technology for foaming asphalt with water.

During the transportation of the asphalt from the petrochemical plant to the mixing plant, its storage and subsequent production of the asphalt mixture, the material is exposed to elevated temperatures of up to 180°C. Subsequent exposure to solar radiation, oxygen in the atmosphere and prevailing climatic conditions during pavement operation further contributes to the deterioration of the asphalt. These factors cause unfavorable changes in asphalt properties as presented in the study by Malinowski *et al.* [6], which result in degradation of the asphalt pavement. These factors cause adverse changes in the properties of asphalt [6].

As asphalt is an organic material, the processes it undergoes are referred to as technological and operational aging, which is defined as the occurrence of physical and chemical changes leading to deterioration in its performance properties, as demonstrated in analyses carried out by Tauste *et al.* [7]. The physical and chemical changes associated with asphalt aging mainly concern the oxidation of its components, in particular the volatilization of low-molecular-weight fractions, as demonstrated by studies conducted by Pei *et al.* [8]. These processes cause an increase in the stiffness and brittleness of the binder and a reduction in its adhesion to the aggregate. As a result,

*e-mail: matiwanski@tu.kielce.pl

Manuscript submitted 2025-06-20, revised 2025-10-06, initially accepted for publication 2025-10-07, published in January 2026.

the quality of the asphalt mixture embedded in the pavement structure deteriorates, which is the result of the oxidation of asphalt components by atmospheric oxygen, as shown by research conducted by Gamarra and Ossa [9]. In order to limit this adverse aging process of the binder, research is being conducted on the use of various types of agents. The purpose of these agents is twofold: firstly, to improve the physical and mechanical properties of the binder, as discussed earlier; and secondly, to increase the resistance of asphalt to aging. This objective is achieved through the development of modern additives or modifiers for asphalt. Much of the recent research has focused on the use of various substances as aging retardants. This is achieved through the use of a range of organic and inorganic chemical compounds or inhibitors. Mineral-based materials, whose effectiveness was demonstrated in the studies by Zhang *et al.* [10], and nanomaterials, as presented in the studies by Zhou *et al.* [11], were used, which effectively slow down the aging process of asphalt. It is worth noting that in the field of organic compounds, the anti-aging effectiveness of SBS (styrene-butadiene-styrene) copolymer was identified based on the research of Xu *et al.* [12], a compound often used as an asphalt modifier to improve its physical and rheological properties.

Unfortunately, it is only used in traditional hot mix asphalt technology. At the same time, in addition to the beneficial effect of delaying asphalt aging, the additives used may have a less favorable effect on reducing the technological temperatures and the compaction process of the asphalt mixture. The studies conducted have generally focused on the use of only one WMA additive to asphalt. Yet preliminary studies conducted on the simultaneous use of two additives, namely F-T (Fischer-Tropsch) synthetic wax and a surfactant derived from tall oil amidopolyamine, have yielded intriguing results. It was found that the effect of these additives on the binder is complementary, with one additive compensating for the adverse effects of the other, thereby enhancing their beneficial effects [13].

The work herein was based on the following hypotheses:

1. The addition of low carbon footprint synthetic wax (SW_{LC}) and tall oil amidopolyamine (TOA) has a positive effect on the performance properties of asphalt.
2. The synergy between SW_{LC} and TOA slows down the aging process of asphalt.

In order to verify the above hypotheses, research was conducted on the use of both the WMA additives to modify asphalt, taking into account the aging process. These studies also aim to recommend additives for use in the WMA technology. The use of the developed binder should ensure long-term durability of the asphalt pavement, taking account of the beneficial environmental effect.

2. MATERIALS AND METHODS

2.1. Materials

The asphalt employed in the present study was asphalt binder 50/70, derived from the Orlen Asfalt S.A. petrochemical plant in Płock. This particular asphalt is widely utilized as a fundamental component in the composition of asphalt mixtures, which are commonly employed in the construction of the upper layers of pavement structures within Central European countries. However, asphalts with similar properties are used in other regions of the world.

In contrast, WMA (Warm Mix Asphalt) additives were utilized to modify the asphalt properties. The additives employed included synthetic wax with a reduced carbon footprint and tall oil amidopolyamine. The synergy of these additives is such that they regulate the aging process of the asphalt and counteract unfavorable changes in its physical-mechanical properties.

2.2. Synthetic wax LC

A novel generation of synthetic wax F-T (WS_{LC}) was utilized as an additive for the 50/70 asphalt, distinguished by its diminished "carbon footprint" in comparison with conventional additives employed in contemporary road practices. The material was introduced into road practice in 2023 as a material that meets the current high environmental requirements (Table 1).

Table 1
Basic properties of WS_{LC} synthetic wax [14]

Property	Unit	Value
Appearance	–	Solid, white or yellowish
Flash point	°C	285
Solidification point	°C	95
Density at 25°C	Mg/m^3	0.9
Molecular weight	g/mol	ca. 1000

Synthetic F-T wax differs significantly from natural paraffin, which is found in petroleum. It is a long-chain hydrocarbon (with hydrocarbon chains comprising between 40 and 115 carbon atoms) that is obtained via the Fischer-Tropsch synthesis process from carbon monoxide (CO) and hydrogen (H2). In comparison to natural paraffin, which contains hydrocarbon chains comprising between 15 and 50 carbon atoms, synthetic F-T wax exhibits a more finely crystalline structure. Its molecular weight is approximately 40% higher than that of the natural waxes found in asphaltene. The long hydrocarbon chains of synthetic F-T wax crystallize at higher temperatures, while the short chains crystallize at lower temperatures [1].

2.3. Tall oil amidopolyamines

Tall oil amidopolyamines (TOA) are insoluble in water but soluble in certain organic solvents (e.g. toluene, paraffin, trichloroethylene). It has been demonstrated that TOA can reduce the surface tension of the asphalt binder, thereby enhancing the efficacy of aggregate grain wrapping with asphalt during the production of asphalt mixtures. It is used as a surface-active agent SAA. The primary properties of the TOA employed in the present study are outlined in Table 2.

Table 2
Properties of TOA [15]

Property	Unit	Value
Appearance	–	Liquid, brown
Density 20°C	Mg/m^3	0.98
Pour point	°C	< 20
Flash point	°C	> 218

2.4. Synthetic wax LC and tall oil amidopolyamines TOA – modified bitumen preparation

Two asphalt binders additives were utilized in the study, and particular emphasis was placed on achieving homogeneity in the modified binder. In pursuit of this objective, 1000 g of 50/70 asphalt was incorporated with TOA. The resulting binder was then subjected to a heating process at approximately 160°C, followed by blending in a blender at 150 rpm for 30 seconds and subsequently at 600 rpm for 270 seconds. Subsequently, analytical samples were prepared for testing in accordance with EN 12594. Subsequently, SW_{LC} in liquid form was added to the binder, which had been prepared through the heating process. The binder was then subjected to a second round of mixing, in accordance with the previously outlined procedure. Following the acquisition of the binder modified with SW_{LC} and TOA, a macroscopic evaluation of the surface of the obtained binder samples was conducted to assess their homogeneity. Binder samples that satisfied the specified requirements were selected for further testing:

- short-term testing (technological aging RTFOT (rolling thin film oven test)) according to EN 12607-1;
- long-term testing (operational aging PAV (pressure aging vessel)) according to EN 14769.

Subsequently, the properties of the modified asphalt binder 50/70 were tested.

2.5. Design of experiment

The experimental plan was based on the assumptions of the factorial experimental plan algorithm [16]. The properties of the modified asphalt 50/70 with the addition of SW_{LC} and TOA were determined on the basis of the assumed 4x4 factorial plan, according to the adopted test program (Fig. 1).

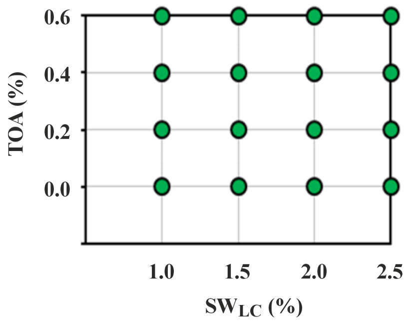


Fig. 1. Experimental plan for bitumen modification

The asphalt binder was modified with SW_{LC} and TOA prior to and following RTFOT and PAV aging simulations. The analysis was conducted in terms of penetration, softening temperature and dynamic viscosity. The experimental program involved the analysis of nine samples within a specified series of binder combinations. Penetration of the asphalt binder was determined in accordance with EN 1426:2009 at 25°C using a semi-automatic penetrometer. The softening point of the asphalt binder was determined using the "ring and ball" method in accordance with EN 1427:2009, while dynamic viscosity of the asphalt binder was determined using a DSR viscosity meter at $T = 135$°C in accordance with ASTM D 4402. Utilizing the results obtained for the aged and unaged binder, quantitative aging indices [6] were determined, i.e. PRR, SPI and VAI, which were calculated according to (1), (2) and (3):

$$\mathrm{PRR} = \frac{\mathrm{Penetration}_{\mathrm{RTFOT\ or\ RTFOT+PAV}}}{\mathrm{Penetration}_{\mathrm{unaged}}} \cdot 100\%, \tag{1}$$

$$\mathrm{SPI} = \mathrm{Softening\ point}_{\mathrm{RTFOT\ or\ RTFOT+PAV}} - \mathrm{Softening\ point}_{\mathrm{unaged}}, \tag{2}$$

$$\mathrm{VAI} = \frac{\mathrm{Viscosity}_{\mathrm{RTFOT\ or\ RTFOT+PAV}} - \mathrm{Viscosity}_{\mathrm{unaged}}}{\mathrm{Viscosity}_{\mathrm{unaged}}} \cdot 100\%. \tag{3}$$

During the tests, the penetration index PI values were found as in (4) by determining the asphalt temperature susceptibility taking into account its 25°C penetration grade (Pen) and softening point ($R_{\mathrm{R\&B}}$) and using the formula according to EN 12591:

$$\mathrm{PI} = \frac{20 \cdot T_{\mathrm{R\&B}} + 500 \cdot \log(\mathrm{Pen}) - 1952}{T_{\mathrm{R\&B}} + 50 \cdot \log(\mathrm{Pen}) - 120}. \tag{4}$$

The calculation was based on the assumption that the penetration of the asphalt is 800 (0.1 mm) at the softening point $T_{\mathrm{R\&B}}$, and the lower the PI value, the more easily the binder changes its consistency with temperature.

Additionally, the designated temperature range of plasticity (plasticity range PR) of the asphalt, dependent on its softening point ($T_{\mathrm{R\&B}}$) and breaking point (T_{Fraass}), was determined by (5), according to the following formula:

$$\mathrm{PR} = T_{\mathrm{R\&B}} - T_{\mathrm{Fraass}}\ (°\mathrm{C}). \tag{5}$$

In order to comprehensively describe the change in the value of the parameter under investigation (y) in 50/70 asphalt binder as a function of SW_{LC} and TOA content, a statistical model using a second degree polynomial [16] was adopted according to (6):

$$y = b_0 + \sum_{i=1}^{n} b_i \cdot x_i + \sum_{i=j=1}^{n} b_{i=j} \cdot x_i \cdot x_j + \sum_{i=1}^{n} b_{ii} \cdot x_{ij}^2, \tag{6}$$

where: x_i = synthetic wax – SW_{LC} (%), x_j = tall oil amidopolyamines – TOA (%), $b_0 - b_5$ – regression coefficients.

Estimation of polynomial coefficients was based on ANOVA analysis of variance. Parameter approximation was based on the method of least squares [16]. Results were visualized using Statistica software [17].

To assess the significance of the effects of SW_{LC} and TOA on asphalt binder properties, Pareto analysis was used. This allows not only to determine whether a factor (SW_{LC} and TOA) was significant, but also to determine the strength of the influence of a given model parameter and the direction of the trend. The values in the Pareto plot correspond to the standardized values of the relative effect evaluation [18].

3. RESULTS AND DISCUSSION

The effects of short-term (RTFOT) and long-term (RTFOT + PAV) aging on the changes in penetration at temperature (Pen25), on softening temperature ($T_{R\,\&\,B}$) and on dynamic viscosity (η135) of 50/70 asphalt were carried out according to the test plan. Tests were carried out on nine specimens in a given series [16]. The change in penetration with temperature (Pen25) of asphalt 50/70 in terms of SW_{LC} and TOA was characterized by the aging indices PRR_{RTFOT} and $PRR_{RTFOT+PAV}$ using ANOVA analysis of variance. The parameters of the regression models using relationship (6) in the form of response plots were generated using Statistica [17] and are summarized in Table 3 and Table 4 and graphically presented in Fig. 2b, d.

Table 3
Fit function parameters for PRR_{RTFOT}

Model parameters	PRR_{RTFOT} (%); $R^2 = 0.56$; PE MS = 33.354				
	RC	SE	−95% C.Limit	+95% C.Limit	p_{value}
Intercept	34.617	5.938	22.875	46.358	< 0.001
(1) SW_{LC} (L)	42.195	6.890	28.571	55.819	< 0.001
SW_{LC} (Q)	−10.166	1.925	−13.972	−6.359	< 0.001
(2) TOA (L)	15.221	10.106	−4.762	35.206	0.134
TOA (Q)	−25.398	12.031	−49.189	−1.607	0.036
1Lx2L	7.285	3.850	−0.327	14.898	0.060

where Q – quadratic, L – linear, RC – regression coefficient, SE – std. error

Table 4
Fit function parameters for $PRR_{RTFOT+PAV}$

Model parameters	$PRR_{RTFOT+PAV}$ (%); $R^2 = 0.70$; PE MS = 11.023				
	RC	SE	−95% C.Limit	+95% C.Limit	p_{value}
Intercept	7.342	3.413	0.592	14.092	0.033
(1) SW_{LC} (L)	45.118	3.961	37.286	52.951	< 0.001
SW_{LC} (Q)	−10.894	1.106	−13.082	−8.706	< 0.001
(2) TOA (L)	13.983	5.810	2.495	25.472	0.017
TOA (Q)	−14.382	6.916	−28.059	−0.705	0.039
1Lx2L	0.034	2.213	−4.341	4.411	0.987

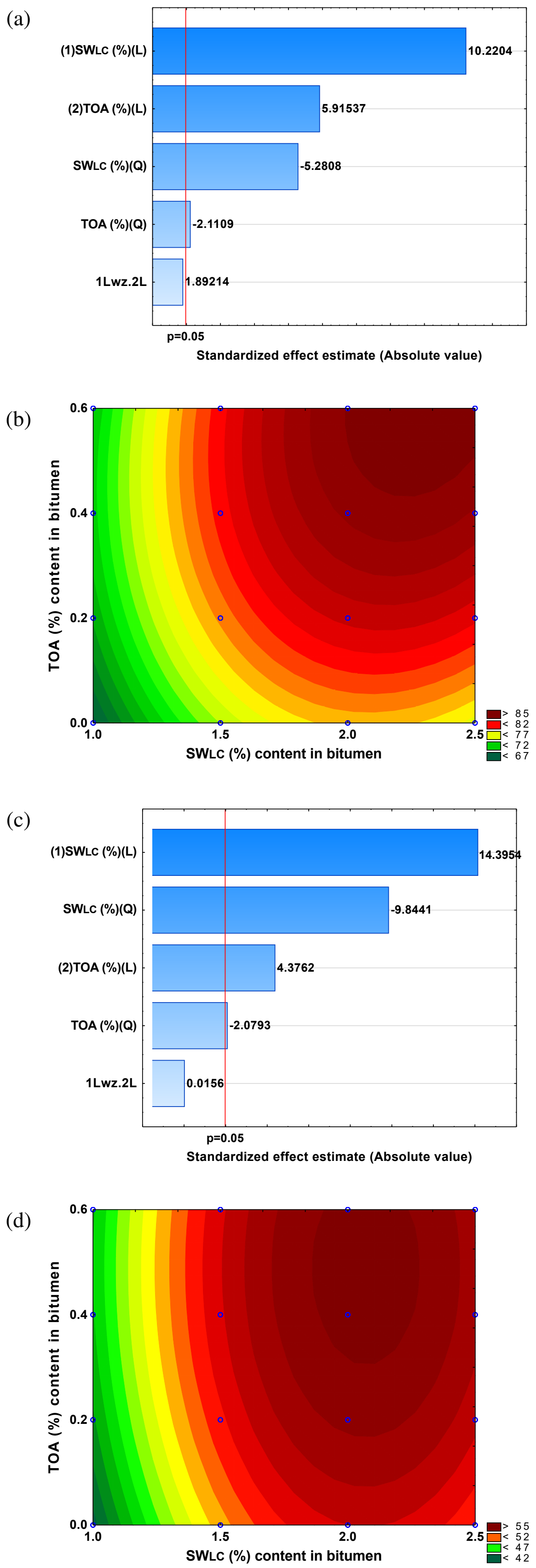


Fig. 2. Influence of WMA additives on asphalt binders characteristics: (a) Pareto relationship for PRR_{RTFOT}; (b) PRR after RTFOT; (c) Pareto relationship for $PRR_{RTFOT+PAV}$; (d) PRR after RTFOT+PAV

The analysis of the statistical parameters in Table 3 and Table 4 clearly shows that only SW_{LC} and TOA content had a significant effect on the PRR_{RTFOT} and $PRR_{RTFO+PAV}$ model parameters, as the associated p-value is lower than the selected significance level of $\alpha = 0.05$ (p-value < 0.05).

However, then analysis of the significance of the effect of SW_{LC} and TOA on the PRR_{RTFO} and $PRR_{RTFOT+PAV}$ of the modified asphalt was performed using the Pareto relationship [18] shown in Fig. 2a, c.

From the Pareto analysis presented in Fig. 2a, c, results show that both SW_{LC} and TOA have a significant effect on the penetration aging rates of PPR_{RTFOT} and $PPR_{RTFOT+PAP}$ asphalt binder. It is important to note that both WMA additive intensities show an increasing trend. As a result of the synergy, with increasing amounts of SW_{LC} in the range of 2.0% to 2.5% and TOA in the range of 0.4% to 0.6%, the most favorable effect on reducing RTFOT aging of the binder is observed. On the other hand, with a lower amount of SW_{LC}, it has a stiffening effect on the penetration at 25°C and the RTFOT process further enhances this tendency, which was also confirmed in another study [19]. On the other hand, the addition of TOA alone has a negative effect on penetration at 25°C during RTFOT aging, as confirmed by studies [19]. By analyzing the results presented in Fig. 2d, results show that the RTFOT+PAV process causes a further change in the penetration. The trends of the effects of SW_{LC} and TOA on penetration are similar in nature to those of the RTFOT process. However, due to the synergistic effects of SW_{LC} and TOA, the least detrimental effect of RTFOT+PAV aging occurs at a SW_{LC} concentration of 2.0% and a TOA concentration of 0.4% by weight of binder. The observed beneficial changes consisting in a reduction in the rate of aging of the binder as a result of its modification with WMA additives may be the result of beneficial changes in its chemical composition. They result from a slowdown in the aging of the carbonyl index $I_{C=0}$, sulfoxide index $I_{S=0}$ and aromaticity index $I_{C=C}$, which has also been demonstrated in other studies [20].

The change in softening temperature ($T_{R\,\&\,B}$) of the 50/70 asphalt binder in terms of SW_{LC} and TOA was characterized by the aging indices SPI_{RTFO} and $SPI_{RTFOT+PAV}$ using ANOVA analysis of variance. The parameters of the regression models using relation (6) in the form of response plots are summarized in Table 5 and Table 6 and shown graphically in Fig. 3b, d.

The analysis of the statistical parameters in Table 5 and Table 6 clearly shows that SW_{LC} and TOA content had a significant effect on the SPI_{RTFOR} and $SPI_{RTFOT+PAV}$ model parameters, as the associated p-value is lower than the selected significance level of $\alpha = 0.05$ (p-value < 0.05).

An analysis of the significance of the effect of SW_{LC} and TOA on SPI_{RTFO} and $SPI_{RTFOT+PAV}$ of the modified asphalt binder was performed using the Pareto relationship [18] (Fig. 3a, c).

From the Pareto characteristics shown in Fig. 3a, c, results show that the beneficial effects of WMA additives on slowing down the aging rates of SPI_{RTFOT} and $SPI_{RTFOT+PAV}$ binders are characterized by a similar intensity of their effects. At the same time, the influence of TOA is the most significant one, although it shows a decreasing trend, which most probably results from its role as an adhesion agent lowering the bitumen viscos-

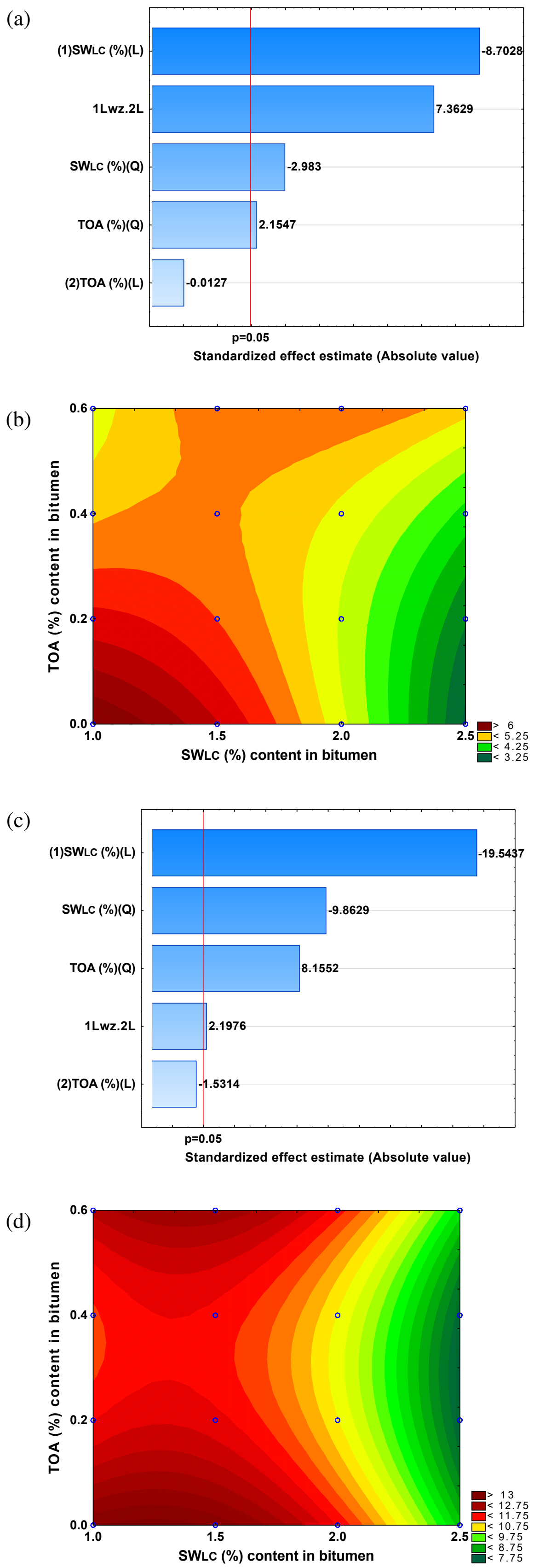


Fig. 3. Influence of WMA additives on asphalt binders characteristics: (a) Pareto relationship for SPI RTFOT; (b) SPI after RTFOT; (c) Pareto relationship for SPI RTFOT+PAV; (d) SPI after RTFOT+PAV

Table 5
Fit function parameters for SPI_{RTFOT}

Model parameters	SPI_{RTFOT} (%); $R^2 = 0.501$; PE MS = 0.741				
	RC	SE	−95% C.Limit	+95% C.Limit	p_{value}
Intercept	7.026	0.886	5.273	8.778	< 0.001
(1) SW_{LC} (L)	0.612	1.028	−1.420	2.646	0.552
SW_{LC} (Q)	−0.857	0.287	−1.425	−0.28	0.003
(2) TOA (L)	−9.731	1.508	−12.714	−6.74	< 0.001
TOA (Q)	3.869	1.795	0.318	7.421	0.032
1Lx2L	4.231	0.574	3.095	5.368	< 0.001

Table 6
Fit function parameters for $SPI_{RTFOT+PAV}$

Model parameters	$SPI_{RTFOT+PAV}$ (%); $R^2 = 0.801$; PE MS = 0.743				
	RC	SE	−95% C.Limit	+95% C.Limit	p_{value}
Intercept	9.005	0.886	7.252	10.757	< 0.001
(1) SW_{LC} (L)	7.027	1.028	4.994	9.060	< 0.001
SW_{LC} (Q)	−2.833	0.287	−3.406	−2.265	< 0.001
(2) TOA (L)	−11.487	1.508	−14.462	−8.505	< 0.001
TOA (Q)	14.643	1.795	11.092	18.193	< 0.001
1Lx2L	1.2627	0.574	0.126	2.398	0.029

ity [5]. A significant synergistic effect of the two additives on the SPI_{RTFOT} and $SPI_{RTFOT+PAV}$ aging rates is observed (Fig. 3a, c), which most probably results from the slowing down of the chemical changes in bitumen during the aging process [20]. The most favorable synergistic effect of SW_{LC} and TOA is observed at a compactness of 2.0% SW_{LC} and TOA at 0.4% for the RTFOT process and in the entire SW_{LC} dosage range and from 0.4% TOA for the RTFOT+PAV aging process. In contrast, in the remaining range of SW_{LC} dosage to the asphalt, its unfavorable stiffening role becomes apparent [19].

The change in viscosity at 135°C (η135) of the 50/70 bitumen in terms of SW_{LC} and TOA was characterized by the aging indices VAI_{RTFO} and $VAI_{RTFOT+PAV}$ using ANOVA analysis of variance. The parameters of the regression models using (6) are summarized in Table 7 and Table 8 and presented in Fig. 4b, d.

The analysis of the statistical parameters in Table 7 and Table 8 clearly shows that TOA content had a significant effect on the VAI_{RTFOR} and $VAI_{RTFOT+PAV}$ model parameters, as the associated p-value is lower than the selected significance level of $\alpha = 0.05$ (p-value < 0.05).

However, the analysis of the significance of the effects of SW_{LC} and TOA on the VAI_{RTFOT} and the $VAI_{RTFOT+PAV}$ of the modified asphalt binder was carried out using the Pareto relationship [18], as shown in Fig. 4a, c.

From the Pareto characteristics presented in Fig. 4a, c, results show that the beneficial effect of WMA additives on slowing

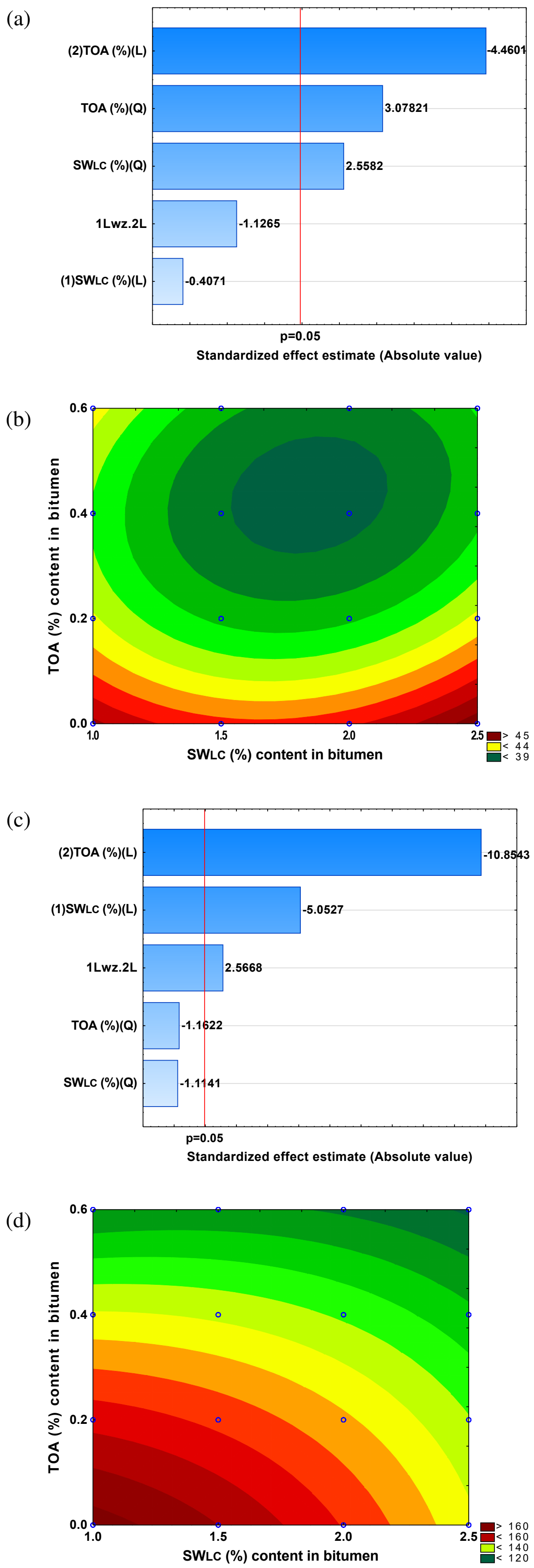


Fig. 4. Influence of WMA additives on asphalt binders characteristics: (a) Pareto relationship for VAI_{RTFOT}; (b) VAI after RTFOT; (c) Pareto relationship for $VAI_{RTFOT+PAV}$; (d) SPI after RTFOT+PAV

Table 7
Fit function parameters for VAI_{RTFOT}

Model parameters	VAI_{RTFOT} (%); $R^2 = 0.413$; PE MS = 31.817				
	RC	SE	−95% C.Limit	+95% C.Limit	p_{value}
Intercept	58.374	5.799	46.906	69.842	0.001
(1) SW_{LC} (L)	−15.906	6.729	−29.212	−2.600	0.019
SW_{LC} (Q)	4.810	1.880	1.092	8.527	0.011
(2) TOA (L)	−23.668	9.871	−43.186	−4.149	0.017
TOA (Q)	36.173	11.751	12.937	59.408	0.002
1Lx2L	−4.236	3.760	−11.671	3.199	0.261

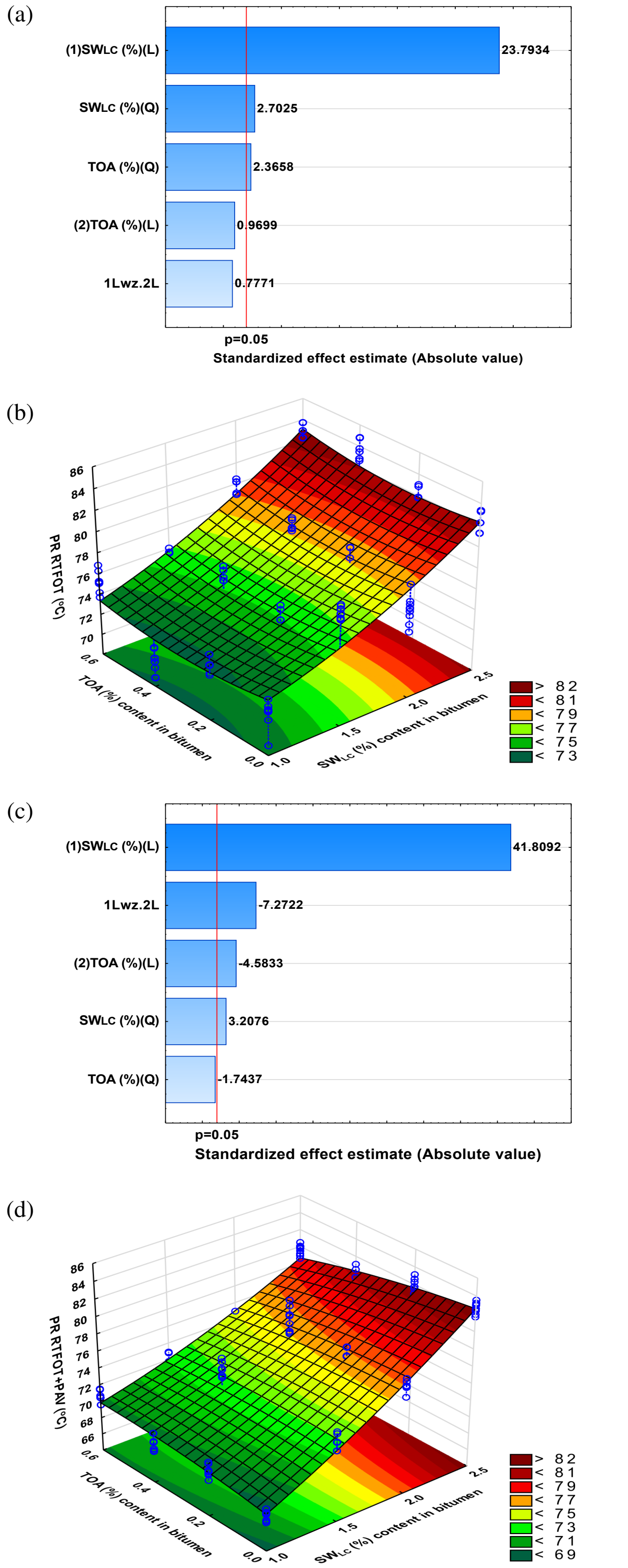
Table 8
Fit function parameters for $VAI_{RTFOT+PAV}$

Model parameters	$VAI_{RTFOT+PAV}$ (%); $R^2 = 0.525$; PE MS = 171.46				
	RC	SE	−95% C.Limit	+95% C.Limit	p_{value}
Intercept	170.289	13.464	143.667	196.911	0.001
(1) SW_{LC} (L)	0.434	15.622	−30.455	31.3247	0.977
SW_{LC} (Q)	−4.862	4.364	−13.494	3.7677	0.267
(2) TOA (L)	−73.160	22.915	−118.471	−27.8491	0.001
TOA (Q)	−31.706	27.280	−85.648	22.235	0.247
1Lx2L	22.408	8.729	5.147	39.669	0.011

down the aging rate of VAI_{RTFOT} and $VAI_{RTFOT+PAV}$ binders is characterized by a similar intensity of their effects. At the same time, the effect of TOA is the most significant one, although it shows a downward trend, which, as mentioned earlier, is most likely a consequence of its role as an adhesive agent. A significant synergistic effect of both additives on the aging rate of $VAI_{RTFOT+PAV}$ is observed (Fig. 4c), resulting in a slowdown in the aging process of the binder. The most beneficial synergistic effect of SW_{LC} and TOA is observed at a content of 2.0% SW_{LC} and 0.4% TOA for the RTFOT process and across the entire SW_{LC} dosage range and from 0.4% TOA for the RTFOT+PAV aging process. However, in the remaining SW_{LC} dosage range for asphalt, its unfavorable stiffening effect is evident [19], which may result in cracks forming on the asphalt surface during winter [19].

The change in PR of the asphalt in terms of SW_{LC} and TOA after RTFOT and RTFOT+PAV aging was characterized using ANOVA analysis of variance. The parameters of the regression models using (6) in the form of response plots are shown graphically in Fig. 5b, d. On the other hand, the significance analysis of the effect of SW_{LC} and TOA on PR_{RTFOT} and $PR_{RTFOT+PAV}$ of the binder was performed using the Pareto relation [18] (Fig. 5a, c).

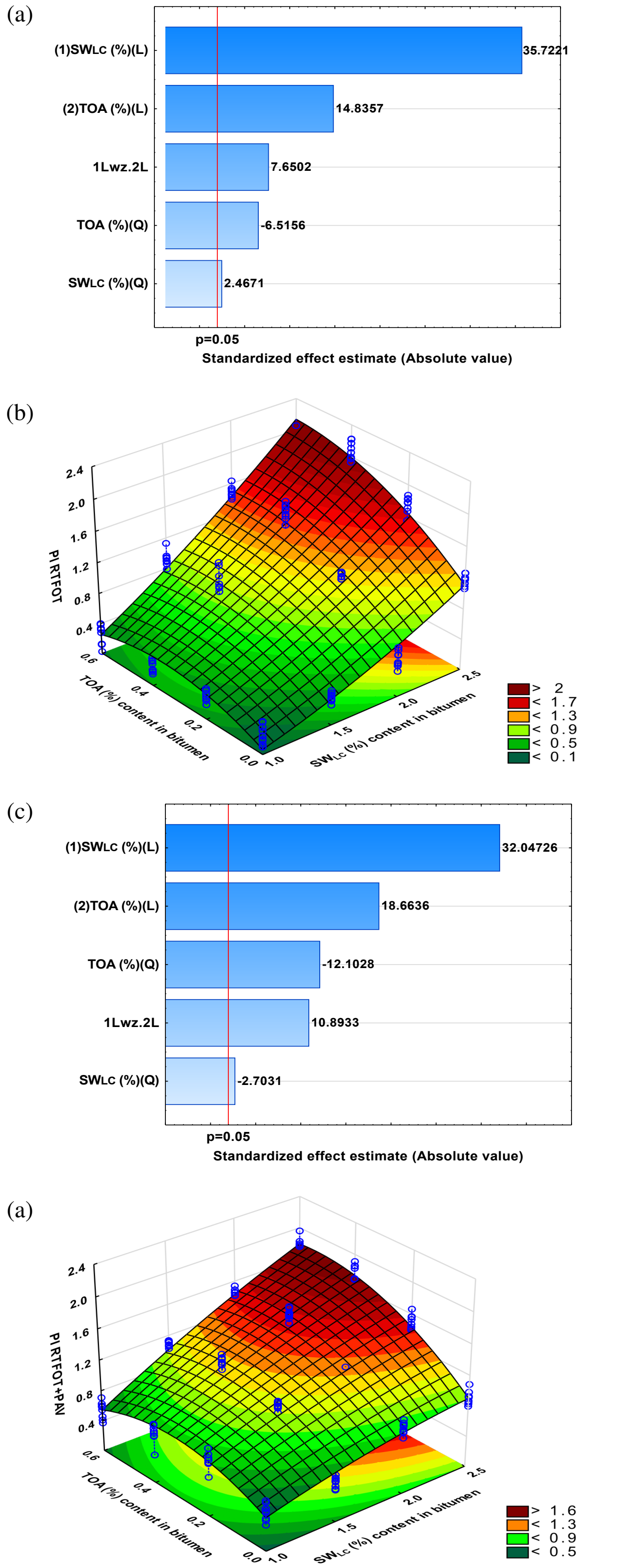
The thermal yield range of PR is determined computationally based on softening temperature and Fraass temperature. Consequently, the intensity characteristics of the effects of WMA additives during RTFOT and RTFOT+PAV aging are a con-



$$PR_{RTFOT} = 71.353 + 0.419SW_{LC} + 1.584 \cdot SW_{LC}^2 - 6.158TOA + 8.666TOA^2 + 0.911 SW_{LC} TOA;\ R^2 = 0.81$$

$$PR_{RTFOT+PAV} = 62.181 + 4.864SW_{LC} + 1.318 \cdot SW_{LC}^2 + 11.043TOA - 4.479 TOA^2 - 5.978 SW_{LC} TOA;\ R^2 = 0.93$$

Fig. 5. Influence of WMA additives on asphalt binder characteristics: (a) Pareto relationship for PR_{RTFOT}; (b) PR after RTFOT; (c) Pareto relationship for $PR_{RTFOT+PAV}$; (d) PR after RTFOT+PAV together with the representation of the models describing the relationship



$$PI_{RTFOT} = -0.252 + 0.168SW_{LC} + 0.151 \cdot SW_{LC}^2 + 0.869TOA - 2.486TOA^2 + 0.934SW_{LC}TOA;\ R^2 = 0.92$$

$$PI_{RTFOT+PAV} = -0.141 + 0.168SW_{LC} - 0.108 \cdot SW_{LC}^2 + 1.119TOA - 3.011TOA^2 + 0.867SW_{LC}TOA;\ R^2 = 0.92$$

Fig. 6. Influence of WMA additives on asphalt binder characteristics: (a) Pareto relationship for PI_{RTFOT}; (b) PI after RTFOT; (c) Pareto relationship for $PI_{RTFOT+PAV}$; (d) PI after RTFOT+PAV together with the representation of the models describing the relationship

sequence of their effects on these binder properties. Thus, a significant effect of both SW_{LC} and TOA on the change in PR during binder aging and the synergistic effect of WMA additives during RTFOT+PAV aging are observed. The PR range after RTFOT+PAV aging is reduced as compared to RTFOT aging. This proves the stiffening role of SW_{LC}, primarily in terms of Fraass brittleness temperature, which is the result of the formation of synthetic wax crystals in the binder [19]. The most beneficial effect of SW_{LC} and TOA on the change in PR during aging is observed in the range of doses from 1.0% to 1.5% and from 0% to 0.6%, respectively. This is because an increase in SW_{LC} content causes the binder to stiffen due to the formation of wax crystals [19].

The change in PI of asphalt binder in terms of SW_{LC} and TOA after RTFOT and RTFOT+PAV aging was characterized using ANOVA analysis of variance. Regression models using (6) are shown graphically as response plots in Fig. 6b, d. On the other hand, the significance analysis of the effect of SW_{LC} and TOA on PI_{RTFO} and $PI_{RTFOT+PAV}$ of modified asphalt was performed using the Pareto relationship [18] (Fig. 6a, c).

From the analysis of the Pareto plot (Fig. 6a, c), results show that there is a significant beneficial effect of both SW_{LC} and TOA with an increasing trend and that there is an initial synergy of these two additives in terms of PI in both RTFOT and RTFOT+PAV aging. It can be clearly stated that as a result of the use of SW_{LC} and TOA, 50/70 asphalt meets the criteria for modified asphalt for which PI > 1. Therefore, it can be used in asphalt pavements subjected to heavy traffic. The change in PI during aging is most favorably influenced by SW_{LC} content in the range of 1.0% to 1.5% and TOA in the range of 0.0% to 0.6% of the binder mass. This is most likely a consequence of the slowing down of chemical changes in asphalt as a result of such additive content [20].

In summary, from the evaluation of the bitumen properties analyzed, the SW_{LC} and TOA contents of 2.0% and 0.4%, respectively, contribute most favorably to reducing the effects of RTOT and RTFOT+PAV aging on the binder properties. This is most likely the result of beneficial changes in the chemical composition of the modified asphalt. It is related to the reduction in the rate of change of the carbonyl index, sulfoxide index and aromaticity index. The model developed, showing the effect of SW_{LC} and TOA on the analyzed properties of asphalt after aging, can also be used to obtain the required binder compositions. The binder developed in this manner can be used, for example, in the construction of asphalt pavements with increased resistance to permanent deformation or with greater resistance to low temperatures and moisture.

4. CONCLUSIONS

Based on the first-ever studies published on the influence of SW_{LC} synthetic wax and TOA tall oil amidopolyamines on the analyzed change in asphalt binder parameters during RTFOT and RTFOT+PAV aging, the following conclusions can be drawn:

1. The WMA additives used in the recommended quantities have a significant beneficial effect on the change in pene-

tration at 25°C, reducing its value by approximately 20%, causing an increase in softening temperature of up to 25% and a reduction of approximately 15% in dynamic viscosity at 135°C, as well as an increase in the penetration index and plasticity temperature range of the asphalt binder.
2. In terms of SW_{LC} and TOA content of 2.0% and 0.4% by weight of the asphalt binder, respectively, there is a significant beneficial synergistic effect of the WAM additives used in the binder in relation to their impact during RTFOT aging of approximately 26% and RTFOT+PAV of 27% on the analyzed parameters of the asphalt binder.
3. The WMA additives used slow down the RTFOT and RTFOT+PAV aging process as a result of their synergistic effect, thus acting as asphalt binder aging inhibitors.
4. The model developed, characterizing the effect of WMA additives on the properties of asphalt, taking into account the aging process, enables the development of a modified binder composition depending on its intended use in asphalt pavement.

Asphalt modified with optimal amounts of SW_{LC} and TOA, i.e. 2.0% and 0.4%, respectively, will have a significant impact on the technological process of asphalt mixture production. The use of modified binder will reduce the technological temperatures of asphalt mixture production to 30°C as compared with traditional methods, while maintaining its required properties. At the same time, it will meet the high requirements for use in sustainable road construction based on a circular economy. Slowing down the binder aging process will also ensure durability of the asphalt pavement. Reducing the technological temperatures of asphalt mixture production will contribute to improving environmental protection by reducing greenhouse gas emissions.

ACKNOWLEDGEMENTS

The research work was funded by National Centre for Research and Development of Poland, grant number LIDER XIII project No. 0068/L-13/2022.

REFERENCES

[1] M. Sukhija, N. Saboo, and E. Pani, ”Economic and environmental aspects of warm mix asphalt mixtures: A comparative analysis,” *Transp. Res. Part D Transp. Environ.*, vol. 109, p. 103355, 2022, doi: 10.1016/j.trd.2022.103355.

[2] M.R.D. Hugo Silva, J.R.M. Oliveira, J. Peralta, and S.E. Zooro, “Optimization of warm mix asphalt using different blends of binders and synthetic paraffin wax contents,” *Constr. Build. Mater.*, vol. 24, no. 9, pp. 1621–1631, 2010, doi: 10.1016/j.conbuildmat.2010.02.030.

[3] S. Nizamuddin, Y.J. Boom, and F. Giustozzi, “Sustainable polymers from recycled waste plastics and their virgin counterparts as bitumen modifiers: A comprehensive review,” *Polymers*, vol. 13, p. 3242, 2012, doi: 10.3390/polym13193242.

[4] Z. Leng, A. Gamez, and I.L. Al-Qadi, “Mechanical property characterization of warm-mix asphalt prepared with chemical additives,” *J. Mater. Civ. Eng.*, vol. 26, pp. 304–311, 2014, doi: 10.1061/(ASCE)MT.1943-5533.0000810.

[5] M.F.C. Van De Ven, K.J. Jenkins., JLM. Voskuilen, and R. Van Den Beemt, “Development of (half-) warm foamed bitumen mixes: State of the art,” *Int. J. Pavement Eng.*, vol. 8, no. 2, pp. 163–175, 2007, doi: 10.1080/10298430601149635.

[6] S. Malinowski, A. Woszuk, and W. Franus, “Modern two-component modifiers the aging process of road bitumen,” *Constr. Build. Mater.*, vol. 409, p. 133838, 2023, doi: 10.1016/j.conbuildmat.2023.133838.

[7] R. Tauste, F. Moreno-Navarro, M. Sol-Sanchez, and M.C. Rubio-Gamez, Understanding the bitumen ageing phenomenon: A review, *Constr. Build. Mater.*, vol 192, pp. 593–609, 2018, doi: 10.1016/j.conbuildmat.2018.10.169.

[8] Z. Pei *et al.*, “Analysis of the microcharacteristics of different kinds of asphalt based on different aging conditions,” *Mater. Struct.*, vol. 55, p. 250, 2022, doi: 10.1617/s11527-022-02088-3.

[9] A. Gamarra and E.A. Ossa, “Thermo-oxidative aging of bitumen,” *Int. J. Pavement Eng.*, vol. 19, no. 6 pp. 641–650, 2018, doi: 10.1080/10298436.2016.1199876.

[10] C. Zhang *et al.*, “Effect of different organic layered double hydroxides on the anti-aging property of bitumen,” *Constr. Build. Mater.*, vol. 367, p. 130316, 2023, doi: 10.1016/j.conbuildmat.2023.130316.

[11] S. Zhou, S. Li, and C. Yan, “Influence of fumed silica nanoparticles on the rheological and anti-aging properties of bitumen,” *Constr. Build. Mater.*, vol. 397, p. 132388, 2023, doi: 10.1016/j.conbuildmat.2023.132388.

[12] S. Xu *et al.*, “Anti-aging performance and mechanism analysis of styrene–butadiene–styrene modified bitumen containing antioxidant/cinnamic acid intercalated layered double hydroxides,” *Constr. Build. Mater.*, vol. 361, p. 129660, 2022, doi: 10.1016/j.conbuildmat.2022.129660.

[13] M.M. Iwański, M. Durlej, K. Janus, and R. Horodecka. “The effect of synthetic wax and surface-active agent on the aging and low-temperature properties of 50/70 bitumen before and after foaming,” *Roads Bridges*, vol. 23, pp. 311–329, 2024, doi: 10.7409/rabdim.024.015.

[14] Sasobit, [Online] Available at: https://sasobit.com/files/downloads/PDF_070722/Productflyer_SASOBIT_LC.pdf (accessed on 21 September 2023).

[15] Nouryon, AkzoNobel, [Online] Available at: https://www.izbudujemy.pl/produkty/18048/Srodek-adhezyjny-do-asfaltow-drogowych-WETFIX-BE (accessed on 21 September 2023).

[16] D.G. Montgomery, *Design and Analysis of Experiments*. Eighth edition, John Wiley & Son Inc. Hoboken: NJ, 2013.

[17] STATISTICA 13.3. Statsoft. [Online] Available at: https://www.statsoft.com (accessed on 20 August 2019).

[18] G.F. Piepel and J.A. Cornell, “Mixture Experiment Approaches: Examples, Discussion, and Recommendations,” *J. Qual. Technol.*, vol. 26, pp. 177–196, 1994, doi: 10.1080/00224065.1994.11979525.

[19] G. Mazurek and M. Iwański, “Analysis of selected properties of asphalt concrete with synthetic wax,” *Bull. Pol. Acad. Sci. Tech. Sci.*, vol. 66, no. 2, pp. 217–228, 2018, doi: 10.24425/122102.

[20] M. Feng *et al.*, “Analysis of rheological behavior and anti-aging properties of SBS modified asphalt incorporating UV absorbent and naphthenic oil (NPO),” *Constr. Build. Mater.*, vol. 377, p. 130958, 2023, doi: 10.1016/j.conbuildmat.2023.130958.