

# Synergistic effect of additives on reducing asphalt binder aging

Mateusz M. Iwański<sup>1\*</sup>, Małgorzata Durlej<sup>2</sup>, Karolina Janus<sup>3</sup>

<sup>1</sup> Kielce University of Technology, Faculty of Civil and Architecture Engineering, Al. Tysiąclecia P.P. 7, 25-314 Kielce, Poland, e-mail: [miwanski@tu.kielce.pl](mailto:miwanski@tu.kielce.pl),

<sup>2</sup> Kielce University of Technology, Faculty of Civil and Architecture Engineering, Al. Tysiąclecia P.P. 7, 25-314 Kielce, Poland, e-mail: [mdurlej@tu.kielce.pl](mailto:mdurlej@tu.kielce.pl)

<sup>3</sup> Kielce University of Technology, Faculty of Civil and Architecture Engineering, Al. Tysiąclecia P.P. 7, 25-314 Kielce, Poland, e-mail: [kjanus@tu.kielce.pl](mailto:kjanus@tu.kielce.pl)

**Abstract.** As an organic material, asphalt binder undergoes an ageing 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 ageing. One of the directions is individually dosed chemical additives to binder. In the article, a combination of synthetic wax (SW<sub>LC</sub>) and tall oil amide polyamine (TOA) was used for the first time in the binder, in concentrations of 1.0%, 1.5%, 2.0% and 2.5% and in 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 ageing inhibitors and improve the basic properties of the binder. The resulting binders containing combinations of SW<sub>LC</sub> and TOA were then subjected to short-term and long-term ageing. The effects of ageing on penetration at 25°C, softening point and dynamic viscosity were analyzed, and their ageing indices were determined. The penetration index and plasticity range of the modified asphalt were also determined. A synergistic effect of SW<sub>LC</sub> and TOA was observed at the recommended amounts of 2.0% and 0.4% relative to 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.

**Key words:** Warm Mix Asphalt (WMA), ageing 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<sub>2</sub>, by about 20-30%, nitrogen oxides by 60-70%, as well as energy consumption during production by about 20-35% [1], which has a significant impact on mitigating climate change on 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 should exhibit 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.

\*e-mail: [miwanski@tu.kielce.pl](mailto:miwanski@tu.kielce.pl)

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 cause 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 ageing, which is defined as the occurrence of physical and chemical changes leading to a deterioration in its performance properties, as demonstrated in analyses carried out by Tauste et al. [7]. The physical and chemical changes associated with asphalt ageing mainly concern the oxidation of its components, in particular the volatilisation 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, 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 ageing 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 ageing. 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 ageing 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 studies by Zhang et al. [10], and nanomaterials, as presented in 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-ageing 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 ageing, 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. 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 was based on the following hypotheses:

1. The addition of low carbon footprint synthetic wax (SW<sub>LC</sub>) and tall oil amide polyamine (TOA) has a positive effect on the performance properties of asphalt.
2. The synergy between SW<sub>LC</sub> and TOA slows down the ageing process of asphalt.

In order to verify the above hypotheses, research was conducted on the use of both WMA additives to modify asphalt, taking into account the ageing process. These studies also aim to recommend additives for use in WMA technology. The use of the developed binder should ensure long-term durability of the asphalt pavement, taking into account 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 Asphalt 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 ageing 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<sub>LC</sub>) was utilized as an additive for 50/70 asphalt, distinguished by its diminished "carbon footprint" in comparison to 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<sub>LC</sub> 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 <sup>3</sup>	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 (H<sub>2</sub>). 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 crystallise at higher temperatures, while the short chains crystallise 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 <sup>3</sup>	0.98
Pour point	°C	< 20
Flash point	°C	>218

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

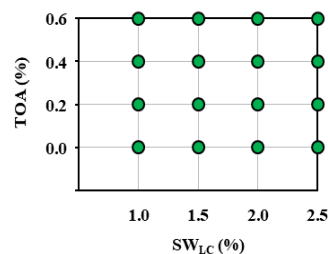
Two asphalt binders additives were utilized in the study, and particular emphasis was placed on achieving homogeneity in the modified binder. In pursuit of this objective, 1000 g of 50/70 asphalt was incorporated with TOA. The resulting binder was then subjected to a heating process at approximately 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<sub>LC</sub> 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<sub>LC</sub> 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 ageing RTFOT (Rolling Thin Film Oven Test)) according to EN 12607-1;
- long-term testing (operational ageing PAV (Pressure Ageing 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<sub>LC</sub> and TOA were determined on the basis of the assumed 4x4 factorial plan, according to the adopted test programme (Fig. 1).



**Fig.1.** Experimental plan for bitumen modification

The asphalt binder was modified with SW<sub>LC</sub> and TOA prior to and following RTFOT and PAV ageing simulations. The analysis was conducted in terms of penetration, softening temperature and dynamic viscosity. The experimental programme 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 the 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 ageing indices [6] were determined, i.e. PRR, SPI and VAI, which were calculated according to Eq. (1), (2), (3):

$$PRR = \frac{Penetration_{RTFOT \text{ or } RTFOT+PAV}}{Penetration_{unaged}} \cdot 100\% \quad (1)$$

$$SPI = \frac{Softening\ point_{RTFOT \text{ or } RTFOT+PAV} - Softening\ point_{unaged}}{Softening\ point_{unaged}} \quad (2)$$

$$VAI = \frac{Viscosity_{RTFOT \text{ or } RTFOT+PAV} - Viscosity_{unaged}}{Viscosity_{unaged}} \cdot 100\% \quad (3)$$

During the tests, the penetration index PI values were found as in equation (4) by determining the asphalt temperature susceptibility taking into account its 25°C penetration grade (Pen) and softening point (T<sub>R&B</sub>) and using the formula according to EN 12591 Eq.(4):

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

The calculation was based on the assumption that the penetration of the asphalt is 800 (0.1 mm) at the softening point T<sub>R&B</sub>, and the lower the PI value, the more easily the binder changes its consistency with temperature.

Also designated the temperature range of plasticity (plasticity range PR) of the asphalt, dependent on its softening point (T<sub>R&B</sub>) and breaking point (T<sub>Fraass</sub>), was determined by Eq. (5) according to the following formula:

$$PR = T_{R\&B} - T_{Fraass} \text{ (°C)} \quad (5)$$

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 Eq. (6):

$$y = b_0 + \sum_{i=1}^n b_i \cdot x_i + \sum_{i=j=1}^n b_{ij} \cdot x_i \cdot x_j + \sum_{i=1}^n b_{ii} \cdot x_i^2 \quad (6)$$

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 visualised 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) ageing on the changes in penetration at temperature (Pen25), softening temperature ( $T_{R\&B}$ ) and dynamic viscosity ( $\eta_{135}$ ) 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 ageing 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 Figure 2b,d.

**Table 3.** Fit function parameters for the  $PRR_{RTFOT}$

Model parameters	$PRR_{RTFOT}$ (%); $R^2 = 0.56$ ; PE MS = 33.354				
	RC	SE	-95% C.Limit	+95% C.Limit	Pvalue
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

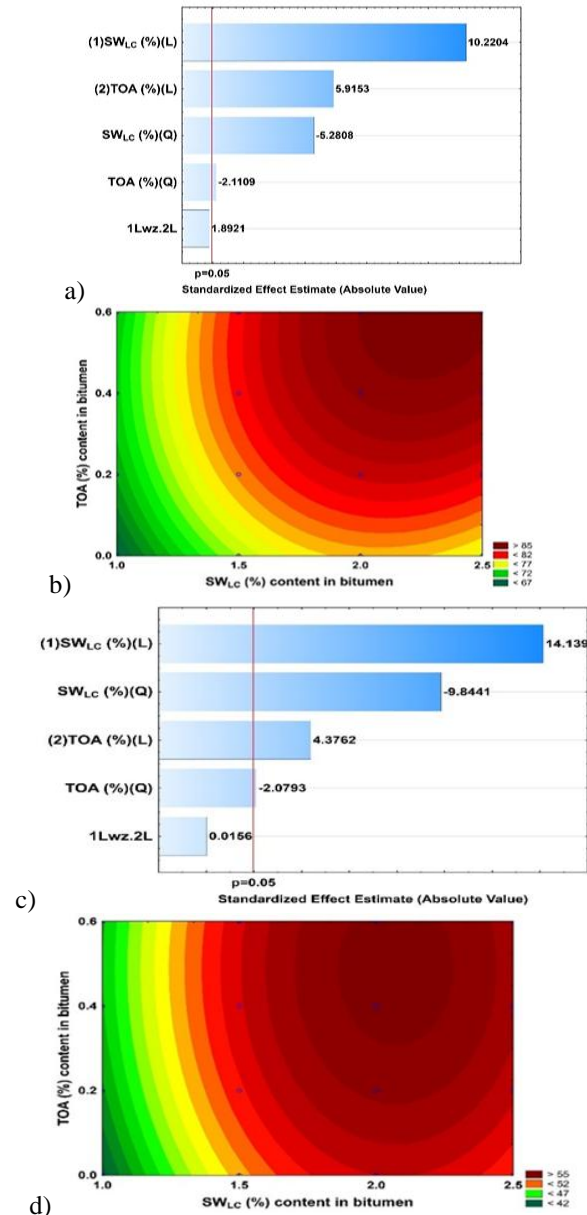
Where: Q – quadratic, L – linear, RC – Regression Coefficient, SE – Std. Error,

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

Model parameters	$PRR_{RTFOT+PAV}$ (%); $R^2 = 0.70$ ; PE MS = 11.023				
	RC	SE	-95% C.Limit	+95% C.Limit	Pvalue
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

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

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



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

From the Pareto analysis presented in Figure 2a,c, results show that both  $SW_{LC}$  and TOA have a significant effect on the penetration ageing rates of  $PRR_{RTOT}$  and  $PRR_{RTOT+PAV}$  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 ageing 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 ageing, 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 ageing 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 ageing 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 ageing of the carbonyl index  $I_{C=O}$ , sulfoxide index  $I_{S=O}$  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 ageing indices  $SPI_{RTFOT}$  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.

**Table 5.** Fit function parameters for the  $SPI_{RTFOT}$

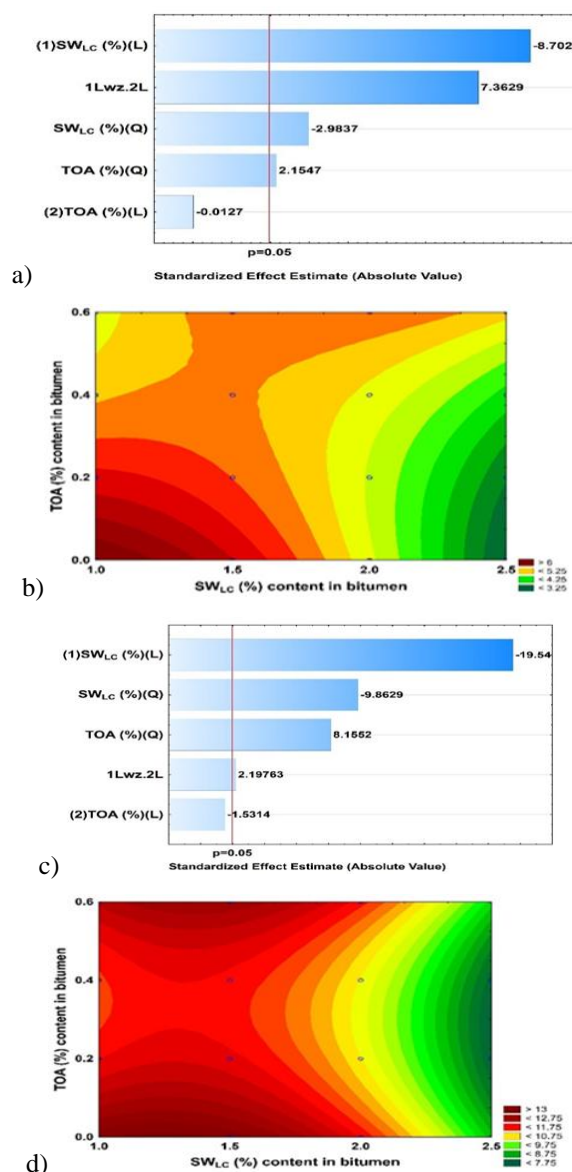
Model parameters	$SPI_{RTFOT}$ (%); $R^2 = 0.501$ ; PE MS = 0.741				
	RC	SE	-95% C.Limit	+95% C.Limit	Pvalue
Intercept	7.026	0.886	5.273	8.778	<0.001
(1) $SW_{LC}$ (L)	0.612	1.028	-1.420	2.646	0.552
$SW_{LC}$ (Q)	-0.857	0.287	-1.425	-0.28	0.003
(2) TOA (L)	-9.731	1.508	-12.714	-6.74	<0.001
TOA (Q)	3.869	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 the  $SPI_{RTFOT+PAV}$

Model parameters	$SPI_{RTFOT+PAV}$ (%); $R^2 = 0.801$ ; PE MS = 0.743				
	RC	SE	-95% C.Limit	+95% C.Limit	Pvalue
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

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  $SPI_{RTFOT}$  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  $SPI_{RTFOT}$  and  $SPI_{RTFOT+PAV}$  of the modified asphalt binder was performed using the Pareto relationship [18] (Fig. 3a,c).



**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

From the Pareto characteristics shown in Fig. 3a,c results show that the beneficial effects of the WMA additives on slowing down the ageing 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, although it shows a decreasing trend, which most probably results from its role as an adhesion agent lowering the bitumen viscosity [5]. A significant synergistic effect of the two additives on the  $SPI_{RTFOT}$  and  $SPI_{RTFOT+PAV}$  ageing 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 ageing 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 ( $\eta_{135}$ ) of the 50/70 bitumen in terms of  $SW_{LC}$  and TOA was characterized by the ageing indices  $VAI_{RTFOT}$  and  $VAI_{RTFOT+PAV}$  using ANOVA analysis of variance. The parameters of the regression models using equation (6) are summarized in Table 7 and Table 8 and plotted in Fig. 4b, d

**Table 7.** Fit function parameters for the  $VAI_{RTFOT}$

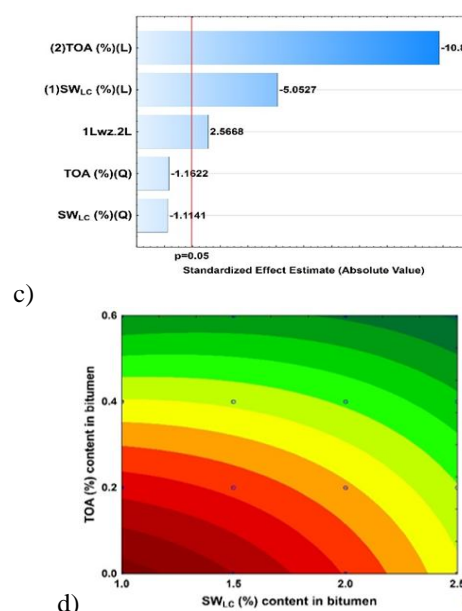
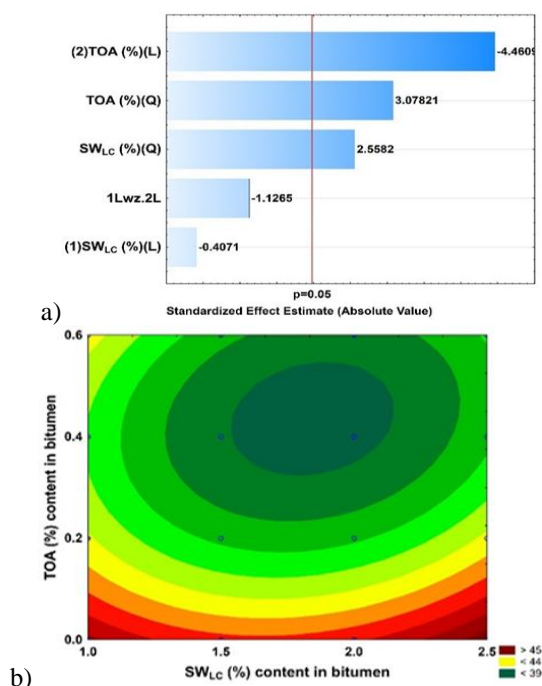
Model parameters	$VAI_{RTFOT} (\%); R^2 = 0.413; PE MS = 31.817$				
	RC	SE	-95% C.Limit	+95% C.Limit	Pvalue
Intercept	58.374	5.799	46.906	69.842	0.001
(1) $SW_{LC}$ (L)	-15.906	6.729	-29.212	-2.600	0.019
$SW_{LC}$ (Q)	4.810	1.880	1.092	8.527	0.011
(2) TOA (L)	-23.668	9.871	-43.186	-4.149	0.017
TOA (Q)	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 the  $VAI_{RTFOT+PAV}$

Model parameters	$VAI_{RTFOT+PAV} (\%); R^2 = 0.525; PE MS = 171.46$				
	RC	SE	-95% C.Limit	+95% C.Limit	Pvalue
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

The analysis of the statistical parameters in Table 7 and Table 8 clearly shows that TOA content had a significant effect on the  $VAI_{RTFOT}$  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).

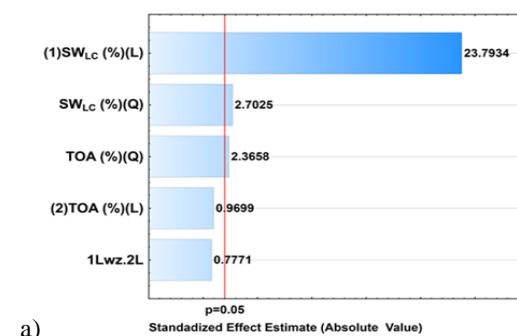
However, the analysis of the significance of the effects of the  $SW_{LC}$  and the TOA on the  $VAI_{RTFOT}$  and the  $VAI_{RTFOT+PAV}$  of the modified asphalt binder was carried out using the Pareto relationship [18], as shown in Fig. 4a,c.

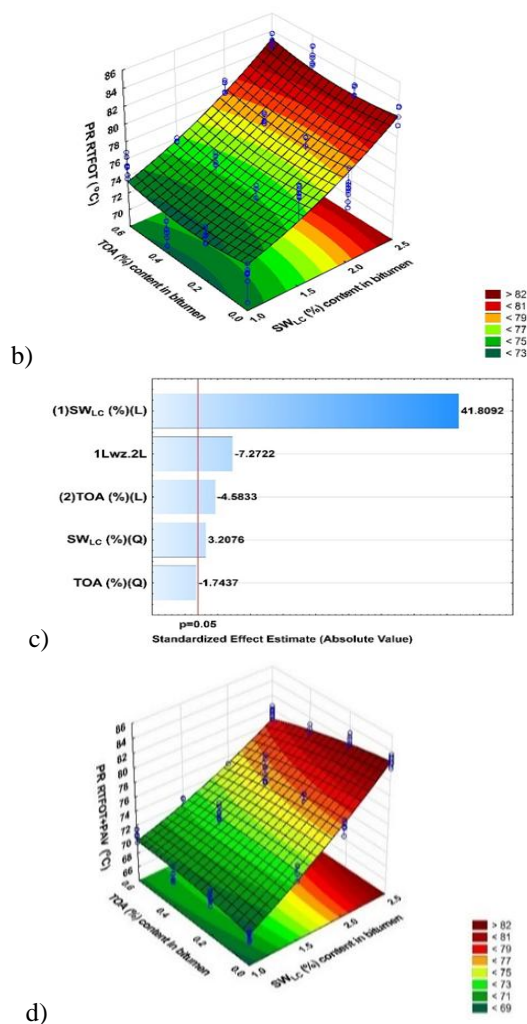


**Fig. 4.** Influence of WMA additives on asphalt binders characteristics: a) Pareto relationship for  $VAI_{RTFOT}$ ; b)  $VAI$  after RTFOT; c) Pareto relationship for  $VAI_{RTFOT+PAV}$ ; d) SPI after RTFOT+PAV

From the Pareto characteristics presented in Fig. 4 a, c, results show that the beneficial effect of WMA additives on slowing down the ageing 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, 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 ageing rate of  $VAI_{RTFOT+PAV}$  is observed (Fig. 4c), resulting in a slowdown in the ageing 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 ageing 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 ageing was characterized using ANOVA analysis of variance. The parameters of the regression models using equation (6) in the form of response plots are shown graphically in Figure 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).





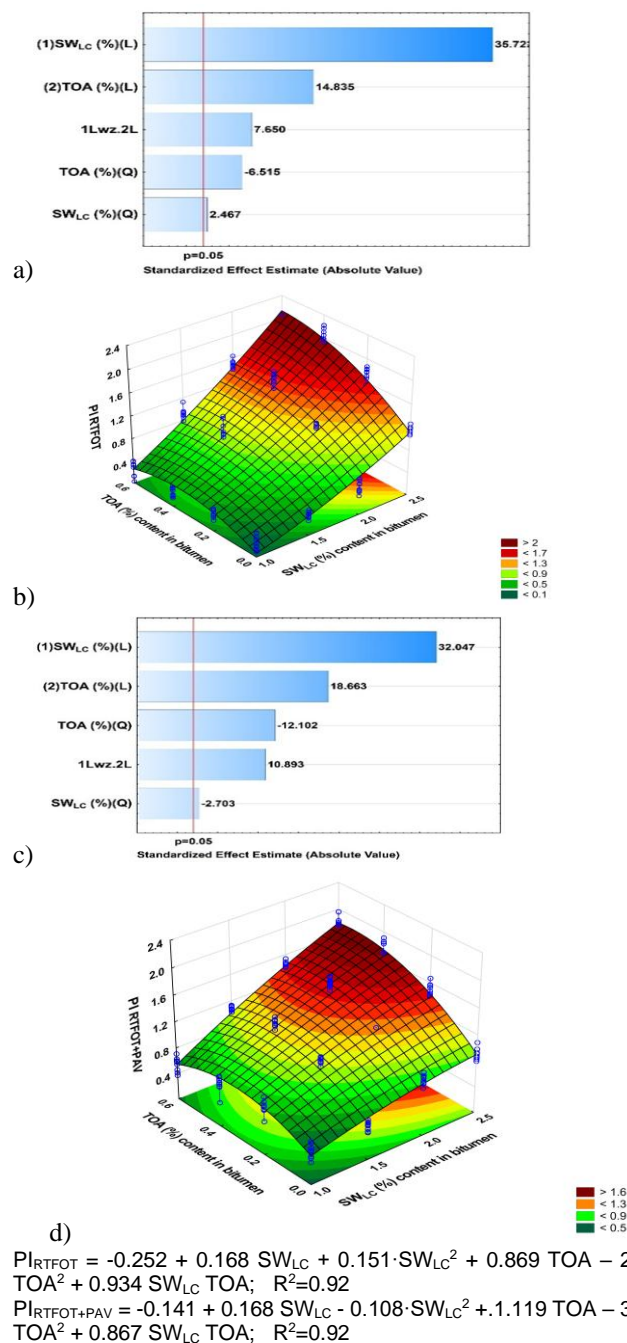
$$PR_{RTFOT} = 71.353 + 0.419 SW_{LC} + 1.584 \cdot SW_{LC}^2 - 6.158 TOA + 8.666 TOA^2 + 0.911 SW_{LC} TOA; R^2=0.81$$

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

**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

The thermal yield range of PR is determined computationally based on temper softening and Fraass temperature. Consequently, the intensity characteristics of the effects of WMA additives during RTFOT and RTFOT+PAV ageing are a consequence of their effects on these binder properties. Thus, a significant effect of both  $SW_{LC}$  and TOA on the change in PR during binder ageing and the synergistic effect of WMA additives during RTFOT+PAV ageing are observed. The PR range after RTFOT+PAV ageing is reduced compared to RTFOT ageing. 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 ageing was characterized using ANOVA analysis of variance. Regression models using relationship (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  $PI_{RTFOT}$  and  $PI_{RTFOT+PAV}$  of modified asphalt was performed using the Pareto relationship [18] (Fig. 6a,c).



**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

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 ageing. It can be clearly stated that as a result of the use of SW<sub>LC</sub> 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 ageing is most favorably influenced by SW<sub>LC</sub> 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<sub>LC</sub> and TOA contents of 2.0% and 0.4% respectively have the most favorable effect in reducing the effects of RTOT and RTFOT+PAV ageing 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 developed model showing the effect of SW<sub>LC</sub> and TOA on the analyzed properties of asphalt after ageing can also be used to obtain the required binder compositions. The binder developed in this way 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 out on the influence of SW<sub>LC</sub> synthetic wax and TOA tall oil amidopolyamines on the analyzed change in asphalt binder parameters during RTFOT and RTFOT+PAV ageing, the following conclusions can be drawn:

1. The WMA additives used in the recommended quantities have a significant beneficial effect on the change in penetration 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<sub>LC</sub> 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 WMA additives used in the binder in relation to their impact during RTFOT ageing to approximately 26% and RTFOT+PAV to 27% on the analyzed parameters of the asphalt binder.
3. The WMA additives used slow down the RTFOT and RTFOT+PAV ageing process as a result of their synergistic effect, thus acting as asphalt binder ageing inhibitors.
4. The developed models characterizing the effect of WMA additives on the properties of asphalt, taking into account the ageing process, enables the development of a modified binder composition depending on its intended use in asphalt pavement.

Asphalt modified with optimal amounts of SW<sub>LC</sub> and TOA, 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 compared to 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 the durability of the asphalt pavement. Reducing the technological temperatures of asphalt mixture production will contribute to improving environmental protection by reducing greenhouse gas emissions.

#### ACKNOWLEDGEMENT

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". *Transportation Research Part D: Transport and Environment*, vol. 109, 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.org/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, 3242, pp. 1-51, 2012, doi.org/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. Civil Engin.*, vol. 26, pp. 304-311, 2014, doi.org/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. Wozzuk and W. Franus, "Modern two-component modifiers the aging process of road bitumen". *Constr. Build. Mater.*, vol. 409, 133838, pp. 1-14, 2023, doi.org/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.org/10.1016/j.conbuildmat.2018.10.169.
- [8] Z. Pei, M. Xu, J. Cao, D. Feng, W. Hu, J. Ren, R. Jing and J. Yi, "Analysis of the microcharacteristics of different kinds of asphalt based on different aging conditions", *Materials and Structures/matériaux Et Constructions.*, vol. 55, 2022, doi.org/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.org/10.1080/10298436.2016.1199876.
- [10] C. Zhang, H. Dong, T. Wang, Y. Li, S. Xu, Y. Zheng, Y. Que and Y. Chen, "Effect of different organic layered double hydroxides on the anti-aging property of bitumen", *Constr. Build. Mater.*, vol. 367, 2023, doi.org/10.1016/j.conbuildmat.2023.130316.
- [11] S. Zhou, S. Li, C. Yan, "Influence of fumed silica nanoparticles on the rheological and anti-aging properties of bitumen", *Constr. Build. Mater.*, vol. 397, 2023, https://doi.org/10.1016/j.conbuildmat.2023.132388.
- [12] S. Xu, Y. Wang, X. Jia, C. Bian, S. Tighe, C. Zhang and H. Ma, "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, 2022, doi.org/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 and Bridges*, vol. 23, pp. 311 – 329, 2024, doi: 10.7409/rabdim.024.015.
- [14] Sasobit, Available online: [https://sasobit.com/files/downloads/PDF\\_070722/Productflyer\\_SASOBIT\\_LC.pdf](https://sasobit.com/files/downloads/PDF_070722/Productflyer_SASOBIT_LC.pdf) (accessed on 21 September 2023),
- [15] Nouryon, AkzoNobel, Available online: <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. Available online: [www.statsoft.com](http://www.statsoft.com) (accessed on 20 August 2019).
- [18] G.F. Piepel and J.A. Cornell, "Mixture Experiment Approaches: Examples, Discussion, and Recommendations". *Journal of Quality Technology*, vol. 26, pp. 177–196, 1994, doi.org/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. 2017–228, 2018, <https://doi.org/10.24425/122102>
- [20] M. Feng, Z. Chongxin, F. Zhen, L. Chen, H. Yingjie, J. Xinyen, and W. Meng. "Analysis of rheological behavior and anti-aging properties of SBS modified asphalt incorporating UV absorbent and naphthenic oil (NPO)". *Constr. Build. Mater.*, vol. 377, 130958, 2023, doi.org/10.1016/j.conbuildmat.2023.130958