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Identification of potential antioxidants for asphalt pavements using rheological and chemical testing

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ABSTRACT: Asphalt pavements are subjected to various environmental factors such as rainfall, sunlight, humidity and wind that causes oxidative aging of bitumen leading to reduced structural and functional performances in the longer run. Antioxidants are often added to asphalt binders to enhance their resistance to oxidative ageing. In the current study, two different antioxidants, Zinc Diethyldithiocarbamate and Lignin were evaluated for their effectiveness in improving the performance of asphalt binders. The laboratory mixing procedures were conducted at two different percentages and laboratory aging were performed. Rheological and chemical tests were then conducted to evaluate the performance of the binders at different temperatures. The current study provides valuable insights into the use of antioxidants for improving the performance and service life of asphalt pavements, which will help in the development of perpetual asphalt pavements in the future.

1 INTRODUCTION

The annual production of asphalt mixtures in EU-27 countries i estimated at approximately 220 million tonnes, as reported by the European Asphalt Pavement Association (2023). Enhancing the durability of bituminous binders and asphalt pavement holds significant promise for positive environmental impact. Therefore, the imperative to extend the lifespan of asphalt mixtures becomes evident.

One pivotal factor influencing the degradation of asphalt mixtures is the aging behavior of bitumen as elucidated by Abraham *et al.* (2023). The intricate chemical composition of bitumen renders the precise aging process still a subject of ongoing research. However it is widely acknowledged that environmental factors, namely oxygen, moisture UV radiation, and temperature, play pivotal roles in bitumen aging, as highlighted by Apostolidis *et al.* (2017). Among these factors, temperature serves as an accelerant, exacerbating the aging proce s induced by other variables. Aging manifests in the hardening of bitumen rendering the asphalt pavement more susceptible to cracking, consequently diminishing its operational lifespan.

In the realm of anti-aging additives, antioxidants and rejuvenators emerge as the two most employed substances, as discussed by Apostolidis *et al.* (2017). Rejuvenators serve as a remedial measure, particularly valuable for recycling asphalt pavement, while antioxidants function preventatively to mitigate aging and enhance the longevity of new asphalt mixtures. Antioxidants achieve this by impeding the oxidation of bitumen. Oxidation is a chemical reaction wherein oxygen molecules interact with reactive chemical constituents within bitumen, resulting in the formation of compounds such as carbonyl groups within the bitumen. This oxidation process is widely recognized as a paramount contributor to asphalt mi ture aging as noted by Apeagyei (2011).

However, a notable knowledge gap persists regarding antioxidants: their effects exhibit variations across different bitumen types, and comprehensive testing is lacking to fully grasp these nuances. The source of crude oil and the distillation proce s wield a substantial

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influence over the chemical properties of bitumen, thereby impacting their interaction with antioxidants. Research findings concerning the chemical and rheological propertie of bitumen in conjunction with various antioxidants reveal that certain antioxidants consistently exhibit a greater efficacy in reducing aging across divers bitumen types, a indicated by Adwani *et al.* (2023). Consequently it become imperative to subject antioxidants to rigorou testing across a pectrum of bitumen varieties worldwide.

Two specific antioxidants namely zinc diethyldithiocarbamate and kraft lignin, have been identified by Adwani *et al.* 2023) as effective in mitigating aging in specific bitumen samples. However the effects of these antioxidants warrant further investigation, encompassing a broader array of bitumen type . This study focu es on evaluating these two antioxidants in conjunction with a commonly u ed bitumen penetration grade in the Netherlands.

The primary objective of this paper is to address the question: Can the antioxidants zinc diethyldithiocarbamate (ZDC) and kraft lignin be considered promising additive for the reduction of bitumen aging? This overarching research question can be ubdivided into the following specific inquiries:

(1) What alterations in rheological and chemical properties of bitumen are induced by the introduction of ZDC and kraft lignin?
(2) To what extent do ZDC and kraft lignin mitigate short- and long-term oxidative aging in bitumen?

To address these inquiries, a series of laboratory experiments will be conducted u ing multiple bitumen samples containing zinc diethyldithiocarbamate and kraft lignin. The aim is to ascertain whether both antioxidants hold promise as additive for various bituminous materials. It is important to note that this research is confined to the laboratory aging of bitumen samples, and field-aged samples are not encompassed within the scope of this study.

2 MATERIALS AND METHODS

2.1 *Materials and sample preparation*

The bitumen employed in this investigation is a 70/100 penetration grade bitumen. The study incorporates two distinct antioxidants: zinc diethyldithiocarbamate, procured from Sigma Aldrich (CAS 14324-55-1), and kraft lignin from an unspecified origin.

To facilitate experimentation, a total of five bitumen samples each weighing 200 grams were meticulously prepared. This entailed the formulation of two samples wherein zinc diethyldithiocarbamate was blended with the bitumen, with concentrations of three and five weight percentages, respectively (named as ZDC3 and ZDC5). Additionally two other samples were composed by combining kraft lignin with the bitumen at identical weight percentages (named as KL3 and KL5). The fifth sample served as the control devoid of any antioxidant additives. Comprehensive details regarding these five samples are presented in Table 2.1.

The blending of antioxidants with bitumen was achi ved through a mixing proce s employing a mixer head. Considering the melting points of the chosen antioxidants, we used distinct blending methods for the two additives. Lignin, with a full melting point at 147°C and flow at 163°C was treated differently than Zinc Diethyldithiocarbamate, which melts between 178°C to 183°C. Zinc diethyldithiocarbamate wa intimately mixed with the bitumen at a temperature of 190°C for 20 minutes, followed by an additional 40 minutes of mixing at 165°C. Conversely, kraft lignin was incorporated into the bitumen matrix at a constant temperature of 165°C with mixing extending for a duration of one hour.

After the preparation phase, both short-term and long-term aging of the bitumen samples were conducted. This aging as essment involved the utilization of the Thin Film Oven Test (TFOT) and the Pressure Aging Vessel (PAV) test instrumental in evaluating the performance characteristics of the bitumen specimens.

2.2 *Fourier Transform Infrared (FTIR) spectroscopy*

In this study, the assessment of oxidative aging in bitumen is facilitated through Fourier Transform Infrared (FTIR) spectroscopy, which scrutinizes alterations in the chemical composition of the material. The Nicolet iS50 FTIR Spectrometer was used for this purpose, with the chosen spectroscopy technique being Attenuated Total Reflection (ATR). To initiate the FTIR tests, each bitumen sample underwent preliminary heating within the temperature range of 160-180°C for a duration of five minutes. Throughout this period, rigorous stirring with a metal spatula was intermittently performed to ensure uniformity among the samples. Following this heating phase, small drops of the samples were carefully collected on silicon paper for subsequent FTIR analysis after they had sufficiently cooled.

The absorption spectra of all samples were systematically recorded within the wavelength range of 600 to 4000 cm^{-1}. Each FTIR test comprised 24 scans conducted at a resolution of 4 cm^{-1}. Spectra that exhibited outliers were discerned and subsequently omitted from the dataset, ensuring data integrity. For each sample, four replicates of the FTIR tests were executed to enhance the reliability of the results.

To gauge the extent of oxidative aging, specific wavelengths associated with carbonyl and sulfoxide functional groups were analyzed, following the methodology outlined by Hofko *et al.* (2017). Elevated intensities detected at wavelengths corresponding to carbonyl- and sulfoxide-related peaks signify higher concentrations of these groups within the bitumen, indicative of increased aging. The wavelengths designated for this analysis, derived from findings reported by Jing *et al.* (2019), are as follows:

Carbonyl-related peaks: 1660 to 1753 cm^{-1}
Sulfoxide-related peaks: 995 to 1047 cm^{-1}
Aliphatic compounds, serving as reference: 1350 to 1525 cm^{-1}

Notably, the region attributed to aliphatic compounds is defined as the cumulative area beneath two distinct peaks spanning wavelengths 1350-1390 and 1395-1525 cm^{-1}. Of particular significance is the former peak's stability, especially when additives like antioxidants are introduced into the bitumen, rendering it an apt reference peak as established by Omairey *et al.* (2019).

2.3 *Rheology tests*

Within the framework of this investigation, the Dynamic Shear Rheometer (DSR) was used to in comprehensively characterize various rheological properties of bitumen. This study encompassed an array of critical tests designed to delve deeper into the analysis of bitumen. These included time sweep assessments, frequency sweep evaluations, the Multiple Stress Creep Recovery (MSCR) test in accordance with ASHTO T350 (AASHTO 2019) guidelines, and the Glover-Rowe parameter (G-R) test. Each of these tests played a unique role in unveiling the intricate rheological characteristics of bituminous materials. It is to be noted that all Dynamic Shear Rheometer (DSR) experiments were executed using the Anton Paar Dynamic Mechanical Analyzer EC-Twist 502, ensuring consistency throughout the rheological analysis process.

3 RESULTS AND DISCUSSIONS

3.1 *FTIR spectroscopy*

In this analysis, the assessment of carbonyl and sulfoxide indices was conducted in achieving a refined and precise comparison of the abundance of carbonyl and sulfoxide functional groups within the samples. The outcomes of these indices are graphically represented in Figure 1.

Evidently, an increase in both carbonyl and sulfoxide groups is observed with the progression of aging across all samples. However, certain unexpected trends manifest, such as the lower carbonyl index observed in KL3 during the TFOT-aged stage in comparison to the unaged stage. This variability can be attributed to inherent fluctuations within the samples. Notably, the carbonyl indices exhibit a greater degree of variability when compared to the sulfoxide indices, a distinction evident in the error bars representing standard deviations.

Initial expectations were that samples containing antioxidants would exhibit higher sulfoxide indices at the unaged stage, primarily due to the extensive one-hour mixing at elevated temperatures for all samples except the control. However, it is noteworthy that these indices display similarities, suggesting either an early effectiveness of the antioxidants in the unaged stage or a relatively minor impact of the high temperature mixing on the aging process.

Divergent trends begin to emerge following short-term (TFOT) aging, with the control sample exhibiting a substantial surge in both carbonyl and sulfoxide indices compared to all four samples containing antioxidants. Both antioxidants, irrespective of concentration, demonstrate a capacity to mitigate short-term aging. Nevertheless, it is worth noting that an increase in kraft lignin concentration appears to diminish the anti-aging effect, as KL3 exhibits superior performance relative to KL5 following short-term aging.

Long-term (PAV) aging presents distinct outcomes for the two antioxidants under study. Kraft lignin, regardless of dosage, falls short in impeding PAV aging. In fact, the carbonyl indices suggest that samples containing kraft lignin experience a more pronounced aging effect compared to the control. The sulfoxide indices, conversely, exhibit values similar to those of the control sample. On the contrary, zinc diethyldithiocarbamate (ZDC) delivers promising results. Both ZDC concentrations demonstrate a similar decline in sulfoxide indices. Regarding carbonyl, ZDC3 outperforms ZDC5, although the difference remains marginal.

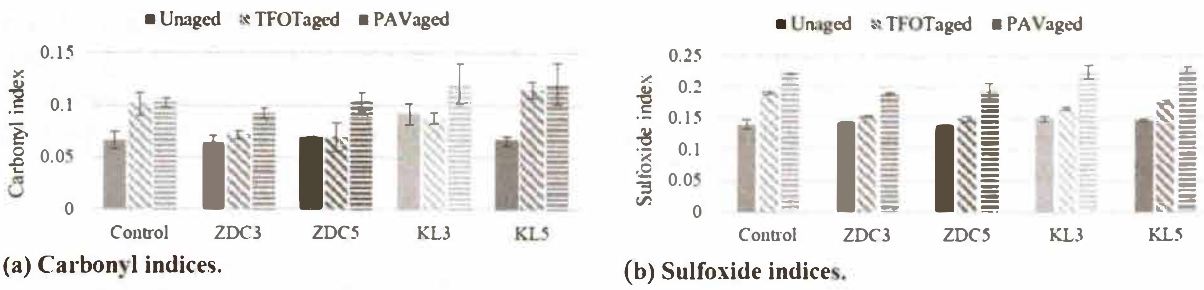

Figure 1. Carbonyl and sulfoxide indices with ageing.

3.2 *Frequency sweep test*

The outcomes of the frequency sweep assessments for all samples shown as master curves, provides details of the complex modulus and phase angle behaviors, as shown in Figures 2 and 3, respectively. Additionally, obtained data concerning the crossover modulus and crossover frequency are presented in Table 1.

A striking observation emerges from the analysis of complex modulus: the most substantial differences among the samples materialize at lower frequencies, corresponding to elevated temperatures. At higher frequencies, reflecting lower temperatures, the influence of aging conditions and antioxidants on the complex modulus appears less pronounced. Conversely, the phase angle exhibits minimal variations both at higher and lower frequencies.

It is important to underscore that a lower complex modulus, indicative of reduced stiffness, implies lesser aging within the sample. Simultaneously, the phase angle diminishes as aging progresses. Generally, bitumen tends to become stiffer and more elastic with aging.

In the context of unaged aging conditions, the antioxidants have not yet demonstrated their potential efficacy in mitigating aging effects. Notably, in the unaged stage, the control sample exhibits the lowest stiffness across all temperatures. This observation can be attributed to the antioxidants acting as fillers, augmenting the overall stiffness of the bitumen. Consequently, the antioxidative properties of these additives have not yet been fully realized. Additionally, it's worth mentioning that the unaged control sample has not undergone the one-hour high-temperature mixing endured by the other unaged samples, which could account for its decreased stiffness.

As for the TFOT-aged samples, the complex modulus at equivalent frequencies becomes more closely aligned compared to the unaged samples. The control sample demonstrates the most notable relative increase in stiffness from the unaged to the TFOT-aged condition, indicative of the antioxidants' effectiveness in mitigating short-term aging.

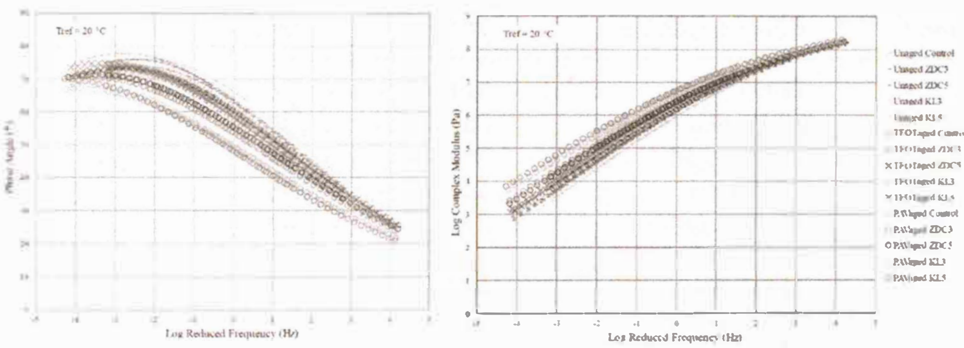

Figure 2. Master curves of bituminous binders with different antioxidants at varying concents.

Table 1. Crossover modulus and crossover frequency derived from master curves.

Sample name	Aging condition	Log Crossover modulus (Pa)	Crossover frequency (Hz)
Control	Unaged	7.38	168.59
	TFOT-aged	7.28	56.29
	PAV-aged	6.91	4.05
ZDC3	Unaged	7.29	76.39
	TFOT-aged	7.26	50.07
	PAV-aged	7.06	13.50
ZDC5	Unaged	7.34	95.65
	TFOT-aged	7.25	54.41
	PAV-aged	7.13	20.10
KL3	Unaged	7.29	72.80
	TFOT-aged	7.24	40.98
	PAV-aged	6.99	4.05
KL5	Unaged	7.32	76.58
	TFOT-aged	7.21	30.38
	PAV-aged	6.97	2.72

3.3 *Time sweep test*

The findings from the time sweep analysis are presented comprehensively in Table 3.6, featuring G*·sin(δ) values calculated using the complex modulus and phase angle measurements. The table also includes aging indices, derived by dividing the PAV-aged aging values by their TFOT-aged counterparts.

Upon close examination of these values, it becomes evident that kraft lignin exhibits a mild capacity to mitigate aging. Notably, variations in kraft lignin concentration do not seem to significantly impact its effectiveness in reducing aging, as indicated by the relatively consistent aging indices at 30°C.

In contrast, zinc diethyldithiocarbamate (ZDC) demonstrates a considerably more pronounced anti-aging effect. The PAV-aged $G^*\cdot\sin(\delta)$ values for both ZDC3 and ZDC5 show significant similarity, whereas the TFOT-aged values are lower for ZDC5. This observation suggests that the higher concentration of zinc diethyldithiocarbamate (5%) proves more effective in countering short-term aging, whereas the lower concentration (3%) exhibits superior performance in mitigating long-term aging.

Table 2. Time sweep results.

		G*·sin(δ) (kPa)		Aging index	
Sample name	Aging condition	30°C	40°C	30°C	40°C
Control	TFOT-aged	319	51	–	–
	PAV-aged	889	171	2.79	3.35
ZDC3	TFOT-aged	349	59	–	–
	PAV-aged	520	96	1.49	1.63
ZDC5	TFOT-aged	294	49	–	–
	PAV-aged	523	95	1.78	1.96
KL3	TFOT-aged	451	73	–	–
	PAV-aged	1157	224	2.57	3.09
KL5	TFOT-aged	392	70	–	–
	PAV-aged	1040	204	2.65	2.93

3.4 *Glover-Rowe parameter*

Figure 3 presents the G-R parameters for all samples. Notably, none of the samples exceed the G-R threshold of 180 kPa, signifying that block cracking is not anticipated. In fact, all samples exhibit substantial distance from this critical value. The G-R value exhibits an upward trajectory with aging, primarily attributable to age-related hardening.

Remarkably, both ZDC3 and ZDC5 showcase the lowest G-R values, consequently offering the highest resistance to cracking. This highlights the beneficial impact of zinc diethyldithiocarbamate (ZDC) on enhancing cracking resistance.

In contrast, kraft lignin appears to have a minor adverse effect on cracking resistance. Initially, both KL3 and KL5 start with comparable G-R values in the unaged stage. However, as the samples progress through the TFOT-aged stage, KL5 exhibits superior performance. Intriguingly, KL5 performance deteriorates in the PAV-aged condition, though this variation may be attributed to measurement discrepancies.

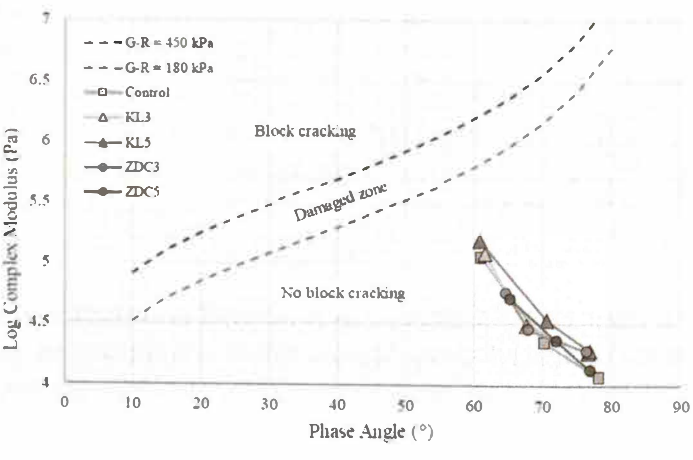

Figure 3. G-R values plotted in a black space diagram.

3.5 *Multiple Stress Creep Recovery*

The Multiple Stress Creep Recovery (MSCR) test provides a robust characterization of rutting behavior. It subjects samples to higher stresses and strains, making it more correlated with performance-related assessments than the traditional high performance grade (PG) test, as demonstrated by Zhang *et al.* (2015). Typically, the MSCR test is conducted at the high PG temperature, initially set at 64°C. However, at this temperature, no sample exhibited any recovery. Subsequently, at 58°C, no recovery was observed at the 3.2 kPa stress level. Ultimately, 52°C was selected as the testing temperature, and the ensuing results are presented in Table 3.

The rutting performance is inversely proportional to the non-recoverable creep compliance (J_{nr}) value, with a lower J_{nr} value signifying superior performance, particularly at the 3.2 kPa stress level, which serves as the most indicative indicator of rutting performance (Sun *et al.* 2019). It is evident that the J_{nr} (3.2) value diminishes with aging, while an increase in stress level corresponds to decreased recovery. This trend is further underscored by the recovery data, which indicates heightened stiffness with aging, ultimately enhancing rutting performance at elevated temperatures due to age-related hardening.

Remarkably, samples containing zinc diethyldithiocarbamate exhibit a slight reduction in short-term aging and a substantial decrease in long-term aging when compared to the control. In contrast, kraft lignin fails to mitigate aging, with both KL3 and KL5 exhibiting aging indices similar to the control. Furthermore, the distinctions between the impacts of three and five wt.% antioxidants on bitumen aging appear relatively minor, whether for kraft lignin or zinc diethyldithiocarbamate.

Table 3. Non-recoverable creep compliance and recovery at 0.1 and 3.2 kPa measured at 52°C.

		J_{nr} (1/kPa)		Recovery (%)		
Sample name	Aging condition	0.1 kPa	3.2 kPa	0.1 kPa	3.2 kPa	Aging index
Control	Unaged	0.142	0.171	6.16	0.49	–
	TFOT-aged	0.076	0.091	10.98	3.62	1.88
	PAV-aged	0.015	0.020	34.28	24.08	8.73
ZDC3	Unaged	0.108	0.127	8.05	1.79	–
	TFOT-aged	0.069	0.081	12.52	4.79	1.56
	PAV-aged	0.033	0.040	28.97	15.57	3.19
ZDC5	Unaged	0.120	0.140	6.73	1.28	–
	TFOT-aged	0.075	0.090	12.35	3.97	1.55
	PAV-aged	0.039	0.042	20.56	12.67	3.35
KL3	Unaged	0.106	0.126	7.39	1.41	–
	TFOT-aged	0.059	0.069	13.01	5.61	1.83
	PAV-aged	0.014	0.014	27.50	22.93	9.18
KL5	Unaged	0.099	0.117	7.67	1.60	–
	TFOT-aged	0.053	0.062	13.76	6.30	1.90
	PAV-aged	0.014	0.015	29.95	24.42	7.93

4 CONCLUSIONS AND RECOMMENDATIONS

This study assessed the efficacy of antioxidants in enhancing the durability of bitumen and asphalt mixtures. Four bitumen samples were examined, including two types of antioxidants at varying dosages, alongside a control reference. Comprehensive analyses involving chemical and rheological properties were conducted through Fourier Transform Infrared (FTIR) and Dynamic Shear Rheometer (DSR) measurements. Following are some of the key conclusions:

- Absence of Age Hardening: Notably, the stiffness enhancement associated with antioxidants was not linked to age hardening, a FTIR analyse revealed similar carbonyl and ulfoxide indices in antioxidant-infused bitumen relative to pure, unaged bitumen.
- Zinc Diethyldithiocarbamate Effectiveness: Zinc diethyldithiocarbamate demon trated noteworthy effectiveness in mitigating oxidative aging. Bitumen samples with this antioxidant exhibited ubstantial reductions in aging effects and stiffness when subjected to short and long-term aging. This suggests it potential to counteract aging-induced hardening in bitumen.
- Comparable Performance of ZDC3 and ZDC5: Interestingly both three and five weight percentage concentrations of zinc diethyldithiocarbamate (ZDC3 and ZDC5) di played similar aging reductions, although with variations in rheological properties. This underscores the promise of zinc diethyldithiocarbamate as an anti-aging additive.
- Kraft Lignin's Limited Impact: In contrast, kraft lignin did not exhibit significant potential for aging reduction in bitumen. While it showed improved rutting performance at higher temperatures, as indicated by increased stiffness, intermediate performance grade and G-R values suggested reduced fatigue cracking resistance and block cracking resistance.

In summary, this study highlights zinc diethyldithiocarbamate as a promising anti-aging additive for bitumen, with potential applications in enhancing asphalt durability. On the other hand, kraft lignin, though potentially beneficial for rutting performance, appears less effective in mitigating aging. Further research is warranted to determine the optimal dosage of zinc diethyldithiocarbamate for specific bitumen applications.

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