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Effects of Natural Antioxidant Agents on the Bitumen Aging Process: An EPR and Rheological Investigation

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Featured Application: Additives obtained from natural waste materials could effectively reduce the hardening effect of bitumen aging in road pavements by exerting an effective antioxidant protection.

Abstract: Bitumen aging is the major factor contributing to the deterioration of the road pavement. Oxidation and volatilization are generally considered as the most important phenomena affecting aging in asphalt paving mixtures. The present study was carried out to investigate whether various antioxidants provided by natural resources such as phospholipids, ascorbic acid as well as lignin from rice husk, could be used to reduce age hardening in asphalt binders. A selected bituminous material was modified by adding 2% *w*/*w* of the anti-aging natural additives and subjected to accelerated oxidative aging regimes according to the Rolling Thin Film Oven Test (RTFOT) method. The effects of aging were evaluated based on changes in sol-gel transition temperature of modified bitumens measured through Dynamic Shear Rheology (DSR). Moreover, changes of Electron Paramagnetic Resonance (EPR) spectra were monitored on the bituminous fractions asphaltene and maltene separated by solvent extraction upon oxidative aging. The phospholipids-treated binder exhibited the highest resistance to oxidation and the lowest age-hardening effect compared to the other tested anti-oxidants. The combination of EPR and DSR techniques represents a promising method for elucidating the changes in associated complex properties of bitumen fractions promoted by addition of free radical scavengers borrowed by green resources.

Keywords: bitumen; antioxidant agent; rheology; electron paramagnetic resonance

1. Introduction

In asphalt industry, the term *aging* identifies the process of deterioration of bitumen due to the occurrence of oxidation mechanisms and progressive loss of volatile components. This alteration occurs over time and causes a change in the chemical, physical, colloidal and rheological properties of the bitumen itself, affecting the useful life of the road pavement as aging tends to make the binder more fragile and therefore the conglomerate more prone to cracking [1]. The aging process is strongly linked to the thermal susceptibility of bitumen and evolves depending on two main factors: the original crude oil and the production process. The bitumen oxidation process is extremely complex. Because of the varied and complex molecular composition, it is unthinkable to isolate and identify the individual species obtained as a result of oxidation. However, understanding the mechanisms by which it takes place is of fundamental importance as it represents the main factor responsible for the hardening of road pavements and therefore of irreversible changes in the physical properties of the binder. Despite the impossibility of isolating the single oxidized components, the main functional groups have been identified. These include predominantly ketones and sulfoxides, accompanied by dicarboxylic anhydrides and dicarboxylic acids in much smaller concentrations [2]. As described by Petersen [3], the oxidation mechanism can be divided into two sequential phases. The primary or short-term aging, which occurs in the phase of production of bituminous mixes and during the paving phase of the bituminous conglomerates, and secondary or long-term aging, which manifests with increasing the pavement service life. Besides, the field aging of asphalt pavements must also be considered, and a number of studies have attempted to characterize the aging viscoelastic properties of asphalt mixtures such as dynamic modulus at different aging times and pavement depths, to account for the effects of long-term aging and non-uniform field aging in the pavement depth [4,5]. Primary aging is a process of short temporal duration, compared to the secondary one and is generated during the mixing phase of the binder with the aggregates and the process of spreading and compacting [6]. Inevitably, the main consequences due to primary aging concern the variation of the chemical composition, caused mainly by oxidation processes. Bitumen storage, even for a long time, does not generate important changes in the consistency of the binder due to the limited access of oxygen. During mixing, transport and spreading of the conglomerate, the thin film bitumen is instead exposed to high temperature and atmospheric oxygen; the resulting chemical changes translate into obvious physical changes. In particular, there is a substantial reduction of the aromatic fraction together with the increase in the content of resins and asphaltenes [7,8]. The saturated content remains substantially unchanged due to the relatively low reactivity of the components in question. The changes in the chemical composition determine an increase in the average size of the molecules present (with increase in molecular weight) accompanied by a hardening of the bitumen [9]. The addition of antioxidant compounds to a bituminous aggregate is therefore a good strategy to increase its durability and prevent deterioration.

Many studies have appeared in the specific literature about the addition of various additives to the bitumen, with the aim to evaluate their antiaging performances. Several organic and inorganic compounds have been tested to improve the aging resistance of bitumen and, hence, its durability in the asphalt mix [10–15]. For example, Banerjee et al. [16] tested Sasobit, Rediset, Cecabase, and Evotherm, of which the first additive is a Fischer–Tropsch paraffin and the other antioxidants are synthetic. Further applications can be found in a recent comprehensive review of aging of asphalt paving materials with focus on antioxidant additives [17]. However, a few studies deal with the application of natural additives or byproducts rich in antioxidants as free radical scavengers to protect bituminous materials from oxidation phenomena [18–20]. The antioxidant properties of many raw materials borrowed from renewable natural resources have yet to be tested such as, e.g., the polyunsaturated fatty components of natural phospholipids. The application of cheap and environmentally friendly anti-aging additives to virgin bitumen would enjoy the double advantage of using sustainable and renewable compounds and at same time reducing the carbon footprint of the products of asphalt industries according to the circular economy's recommendations.

The objective of the present work is to investigate whether the addition to bitumen of antioxidant agents obtained by natural resources improves its resistance towards short artificial aging by Rolling Thin Film Oven Test (RTFOT). The research design is accomplished by investigating the effects of the aging process on both the mechanical response of binders by running Dynamic Shear Rheology (DSR) tests, and the free radical content detected by Electron Paramagnetic Resonance (EPR) spectroscopy on asphaltene and maltene bituminous fractions. The experimental approach is sketched in the flowchart of Figure 1. Bitumen manifests EPR spectra due to organic radicals [21–23] the signal shape of which is susceptible to changes in the oxidative state, and vanadyl ions VO^{2+} [24] associated with porphyrin species, which instead appear to be unaffected by oxidative treatments. Here we will focus our attention on the two most representative components present in the bitumen, namely, asphaltenes and maltenes [25]. The former are macromolecular compounds, comprising polyaromatic nuclei linked by aliphatic chains or rings of various lengths and sometimes by functional groups [26]. A peculiar characteristic of petroleum asphaltenes is the presence of stable free radicals, well detectable by EPR, associated with a non-localized π system of electrons stabilized by resonance. Maltene represents the bitumen fraction soluble in n-pentane, which in turn can be split into saturates, aromatics (also apolar aromatics), and resins (also polar aromatics) [27]. The results of the present work show that it is possible to draw useful anti-aging additives from renewable sources capable to reduce the age-hardening effect and concomitantly protect bitumen against oxidative aging.

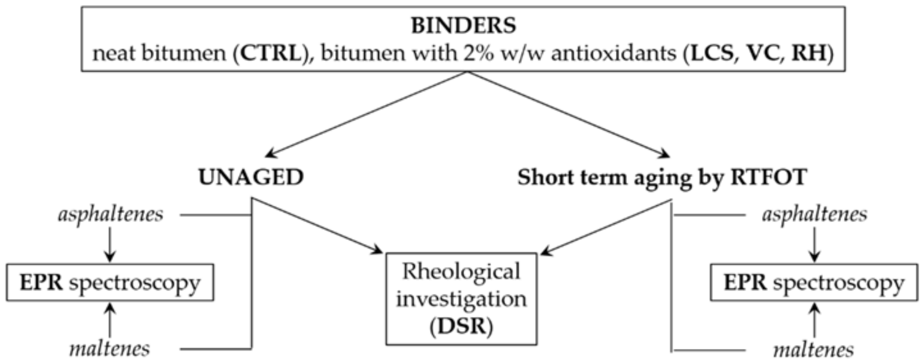

Figure 1. Flowchart of the experimental approach. The tested binders both neat bitumen as control CTRL, and bitumen modified with 2% w/w of natural antioxidants, namely, a mix of phospholipids (LCS), Vitamin C (VC) and rice husk (RH), are subjected to artificial thermal treatment by Rolling Thin Film Oven Test (RTFOT). Then, Dynamic Shear Rheological (DSR) tests carried out on artificially aged binders are compared to those performed on aliquots of unaged samples. A parallel EPR study is performed on both the asphaltene and maltene fractions obtained, respectively, from unaged binders and bitumens subjected to short-term aging by RTFOT.

2. Materials and Methods

2.1. Sample Preparation

A light brown bitumen (penetration grade 50/70), produced in Saudi Arabia and kindly supplied by Loprete Costruzioni Stradali (Terranova Sappo Minulio (RC), Italy), was used as base asphalt binder to test the effectiveness of natural compounds selected as anti-aging additives. The natural antioxidant additives selected for the present research were: (a) commercial mix of phospholipids in form of light yellow powder (hereafter LCS) provided by Kimical srl (Rende (CS), Italy); (b) Vitamin C, also known as ascorbic acid (hereafter VC) provided by Sigma-Aldich (Milano, Italy); (c) rice husk (hereafter RH) obtained from producers located in Mantova, Italy. The raw RH was first washed with distilled water and dried at 60 °C and then ground for 10 min in an electric mixer and sieved with 0.5 mm sieve to get fine powder prior mixing with bitumen. Three aliquots of the starting bitumen were first heated at 140–160 °C and then mixed with 2% by weight (w/w) of LCS, VC and RH, respectively. A fourth aliquot of the same bitumen source was used as reference (hereafter, CTRL). Each compound was separately added to bitumen, under vigorous stirring at the temperature of 150 °C and the stirring was maintained for a period of 30 min. Once the mixing procedure was finished, each of the resulting bitumen mixtures was separately poured into small sealed containers and then stored in a darkened thermostat at 25 °C to preserve morphology.

2.2. Bitumen Separation

Both unaged and artificially aged bituminous samples, either modified with antioxidants or not, were subjected to an experimental procedure based on the bitumen separation by n-pentane extraction according to the American Society for Testing Materials (ASTM) Standard method 4124 [28]. In details, 10 g ca. of bitumen were weighed into a 2 L Erlenmeyer flask and 300 mL ca. of n-pentane were added. A good dispersion of the bitumen was assured through vigorous stirring. The flask was then heated to 90 °C and kept at that temperature for about 1–2 h. Afterwards, the bottle was left overnight for cooling and sedimentation of solid fraction. The next day, the dispersion was filtered through a Büchner-funnel (Whatman 42 ashless) and the insoluble phase, called asphaltene phase, was collected and stored. Then, the n-pentane soluble maltene phase, appearing as a viscous liquid, was obtained after the solvent had been removed by evaporation under reduced pressure. In Table 1 the percentages of asphaltene collected from the unaged and aged samples are reported.

Table 1. The weight percentages of asphaltene fraction obtained from crude bitumen (CTRL) and bitumen modified with LCS, VC and RH additives, both unaged and subjected to artificial aging.

Sample	Asphaltene (% *w*/*w*)	
	Unaged	**Aged**
CTRL	26.8	34.2
Bitumen + LCS	29.2	32.8
Bitumen + VC	28.2	35.3
Bitumen + RH	29.5	35.7

2.3. Aging Test

In order to study the effects of aging in the laboratory, the method known as Rolling Thin Film Oven Test (RTFOT) [29,30] was adopted to simulate the short-term aging of asphalt binders that would occur during the hot-mixing process. The apparatus consists essentially of an internal double-wall furnace, in which the hot air circulates conveyed by an internal fan at the test temperature of 163 °C. The test consists in subjecting a thin layer of bitumen, ~1.25 mm, to a hot air jet for 75 min. Each modified bitumen, plus a reference binder free of additives, was divided into two aliquots, of which only one was subjected to the process of artificial aging. Both sets of aliquots were subsequently separated into the respective fractions of asphaltene and maltene by extraction in n-pentane, which were finally characterized through Dynamic Shear Rheology (DSR) and Electron Paramagnetic Resonance (EPR) spectroscopy tests (see the flowchart of the experimental approach in Figure 1).

2.4. Dynamic Shear Rheology (DSR)

Temperature sweep (time cure) rheological tests were performed to analyze the mechanical response of modified bitumens vs. CTRL upon artificial aging process. Experiments were carried out using a controlled shear stress rheometer (SR5, Rheometric Scientific, Piscataway, NJ, USA) equipped with a parallel plate geometry (gap 2.0 ± 0.1 mm, diameter 25 mm) and a Peltier system (±0.1 °C) for temperature control. Bitumen exhibits aspects of both elastic and viscous behaviors and is thus classified as a visco-elastic material [31,32]. DSR is a common technique used to study the rheology of asphalt binders at high and intermediate temperatures [33,34]. Operatively, a bitumen sample was sandwiched between two parallel plates, one standing and one oscillatory. The oscillating plate was rotated accordingly with the sample and the resulting shear stress was measured. The linear viscoelastic regime of both the reference free of additives (CTRL), and modified bitumens was checked by preliminary stress sweep tests. The temperature sweep tests were performed within the range 25–80 °C with ramp 1 °C/min in heating by applying the proper stress values to guarantee linear viscoelastic conditions at all tested temperatures. During the tests a periodic sinusoidal displacement at constant frequency of 1 Hz was applied to the sample and the resulting sinusoidal force was measured in terms of amplitude and phase angle as the loss tangent (tan δ). RSI Orchestrator® software was used to determine the complex modulus (G^*), storage (G') and loss (G'') moduli, phase angle (δ) or tan $\delta = G''/G'$. More details about the mechanical characterization can be found elsewhere [35].

2.5. Electron Paramagnetic Resonance (EPR) Spectroscopy

Nine GHz EPR (X-band) spectra were recorded on a Bruker Elexys E-500 spectrometer (Bruker, Rheinstetten, Germany). Capillaries containing the samples were placed in a standard 4 mm quartz sample tube containing light silicone oil for thermal stability. The temperature of the sample was regulated at 25 °C and maintained constant during the measurement by blowing thermostated nitrogen gas through a quartz Dewar. The protocol of EPR testing is sketched in Figure 2. The instrumental settings were as follows: sweep width, 120 G; resolution, 1024 points; modulation frequency, 100 kHz; modulation amplitude, 1.0 G; time constant, 20.5 ms. From preliminary power saturation tests, r.f. power levels 0.203 and 0.40 mW selected, respectively, for asphaltene and maltene fractions, were found to be sufficiently low to avoid saturation effects. Several scans, typically 4–16, were accumulated to improve the signal-to-noise ratio. Linewidths were measured from first-derivative curves (peak-to-peak). The spin concentration could be estimated by taking the ratio of area of the sample to that of a standard containing a known number of radicals. Therefore, the concentration of paramagnetic centers in both the asphaltene and maltene fractions of bituminous specimens were obtained by double integration of the experimental first-derivative spectrum and compared with EPR spectrum of a known amount of a MgO-MnO solid solution used as standard [36,37] (spin density = 6.83×10^{15} spin/g). The g-value (Landé factor) was determined from the condition $h\nu = g\beta B_r = g_s\beta B_s$, from which $g = g_s B_s/B_r$ where ν is the frequency of the used microwave radiation, β the Bohr magneton for electron, $g_s = 1.9810$ is the g-value for the standard [38,39], B_s and B_r are the magnetic field values of standard and sample, respectively.

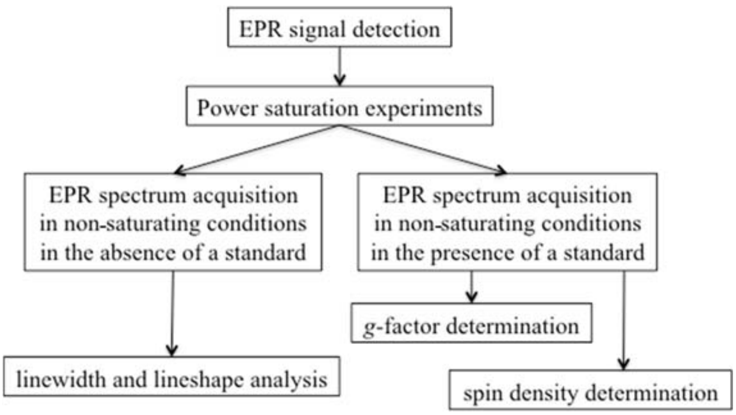

Figure 2. Flowchart of the Electron Paramagnetic Resonance (EPR) test protocol. The preliminary power saturation experiments are necessary to determine the power of the incident microwave beam to be used in the following steps.

3. Results and Discussion

3.1. Mechanical Behavior

Two important parameters are obtained from DSR tests on bitumen: the complex modulus, G^*, and the phase angle, δ. These parameters can be used to characterize both viscous and elastic behavior of the binder [40]. The dependence of these quantities on the temperature gives rise to the so-called time cures. As the temperature increases or frequency decreases, bitumen begins to lose the majority of its elastic behavior (the storage modulus, $G' = G^* \cos \delta$, decreases) and starts to behave as a viscous fluid (the loss modulus, $G'' = G^* \sin\delta$, increases). Thus, the limiting temperature in correspondence of which $\tan\delta \to \infty$ identifies the viscoelastic-sol transition temperature T_{TR} above which viscous behavior is highly predominant over elastic mechanical contribution. Figure 3 shows the time cure curves for virgin bitumen and bitumens modified with antioxidant additives and compared to analogous measurements performed after the aging process (RTFOT). Through data interpolation the asymptotic value of $\tan\delta$ intercepts the temperature axis and identifies T_{TR}. Actually, in Figure 3 the temperature difference $\Delta T = T_{TR}$ (aged) $- T_{TR}$ (unaged) can be read in each graph while the histogram of Figure 4 illustrates a direct comparison of ΔT for all the investigated samples.

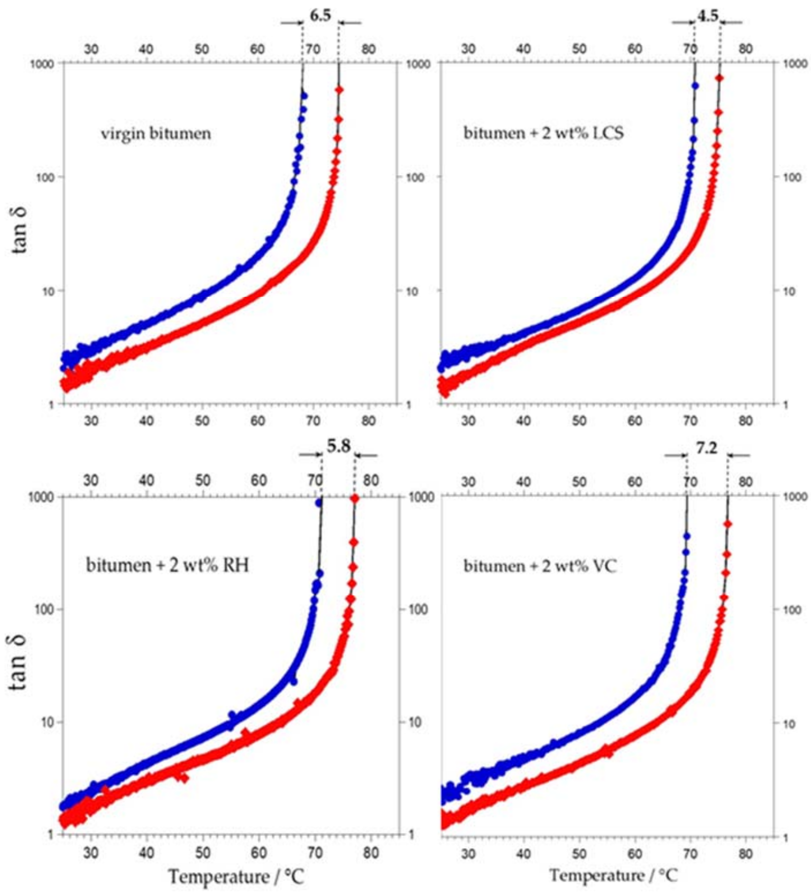

Figure 3. Time cure curves for virgin bitumen and bitumens modified with 2% w/w of LCS, RH and VC antioxidant additives, respectively. The increments of viscoelastic-sol transition temperature between aged (red symbols) and unaged (blue symbols) samples are indicated on the top axis of each graph.

Upon addition of 2% w/w of anti-oxidants a slight increase of T_{TR} is observed for unaged samples, 69.4 °C (VC), 70.6 °C (LCS) and 71.2 °C (VC) compared to virgin bitumen 68.1 °C. The shift ΔT ($\pm$0.2 °C as estimated error) of T_{TR} recorded upon heating treatment respect to the same unaged sample is an indication of an increase in hardening consistency of bitumen, which in turn can be correlated to the oxidation degree occurred in the material. Aging significantly changes both the chemical and physical properties of asphalts, which results in lower elasticity and higher stiffness. In absence of additive a shift of T_{TR} towards higher temperatures has been observed with ΔT_{CTRL} = 6.5 °C. Then, the following sequence of ΔT values has been detected for bitumen supplemented with inhibitors of free radicals: ΔT_{LCS} = 4.5 °C, ΔT_{RH} = 5.8 °C and ΔT_{VC} = 7.2 °C. Those data clearly indicate a superior performance manifested by LCS in retarding oxidative hardening compared to the other tested antioxidants. Hitherto, the use of raw mixtures of natural phospholipids has been confirmed to be a powerful method to increase both the adhesion properties of bitumen [34] and its mechanical resistance to the action of thermal shocks [41]. Here, the discover of anti-aging properties of LCS adds another advantage of using these green compounds as multi-functional additives to enhance the bitumen performances. The presence of polyunsaturated fatty components in phospholipids providing carbon sites susceptible of oxidation may be responsible for the observed antioxidant activity [42] as it will be also confirmed by the analysis of EPR spectra.

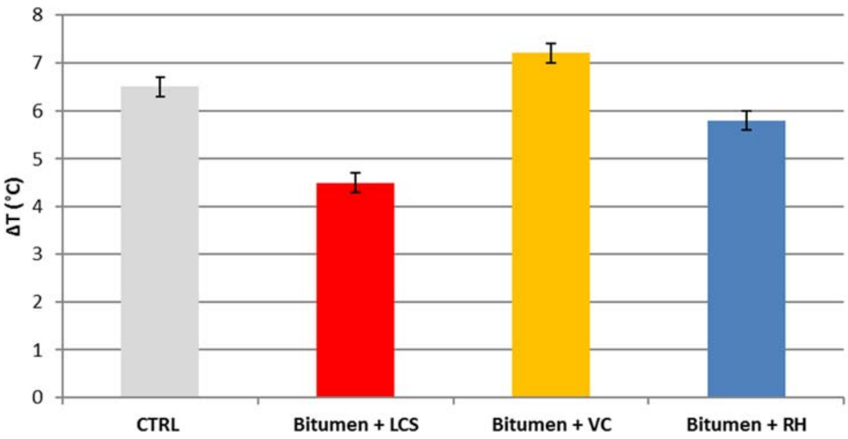

Figure 4. Comparison of $\Delta T = T_{TR}$ (aged) $- T_{TR}$ (unaged) for the series of investigated samples.

3.2. EPR Spectroscopy Investigation

EPR measurements clearly confirm the presence of unpaired electrons in all the investigated systems, according to previous studies [22,43]. The X-band EPR spectra of the bituminous signals consist of two non-overlapping EPR signals, one centered at about 3480 G due to vanadyl ions (spin 7/2), and the second in a range between 3510 and 3530 G associated to organic radicals (see Figure 5 for the asphaltene fractions).

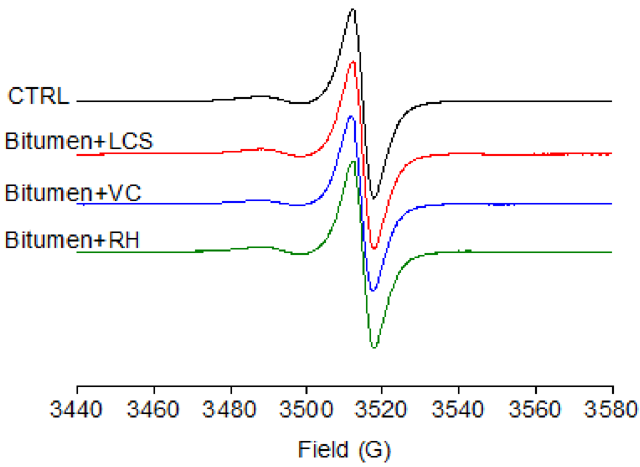

Figure 5. X-band EPR spectra of unaged asphaltene samples mixed with 2% *w*/*w* of antioxidants registered at room temperature. CTRL indicates the control sample with no antioxidant added.

A complete set of spectra acquired for both the asphaltene and maltene fractions is illustrated in Figure S1 of Supplementary Material. Free radicals associated with non-localized π system, stabilized by resonance in polyaromatic centers, can be studied by EPR spectroscopy owing to the influence of the environment on the radical magnetic properties. Therefore, various parameters can be derived from the analysis of spectra, furnishing different pieces of information, sometimes complementary, sometimes partially overlapping.

3.2.1. The *g*-Factor

The *g*-factor (or Landé factor) indicates the magnetic field of resonance (position in the spectrum); it is a parameter sensitive to the chemical environment of the unpaired electron, i.e., to the specific features of the orbital in which it is localized.

The *g*-factor increases in the presence of heteroatoms, owing to their contribution to the electron molecular orbital. In fact, the heteroatoms shift *g* to values higher than 2.0023 corresponding to free electron [44]. For all the asphaltene samples, whether unaged or aged, the peak assigned to organic radical gives g = 2.0027–2.0028 (see Table S1 in Supplementary Material) very close to the free electron value, thus indicating that if present in these radicals, heteroatoms are not likely to participate in the molecular orbital of the unpaired electron to any significant degree. Even for maltene samples, the Landé factor remains substantially constant in the range 2.0025–2.0029 (see Table S1 in Supplementary Material) comparable with that obtained for asphaltene. A weak reduction has been found only in the case of maltene fraction isolated from CTRL upon RTFOT treatment (2.0028 $\rightarrow$ 2.0025). The effects of the oxidation process are in fact more evident on the reference system free of antioxidants, which inevitably favors the aggregation and condensation of adjacent units, forming more complex structures. The latter are accompanied by an increase in the level of aromaticy responsible for the shift of *g*-factor towards lower values. Finally, the *g*-value for the signal of the vanadyl group does not undergo any variation as a result of the oxidation process for both asphaltene (2.0018–2.0019) and maltene (2.0011–2.0014) fractions analyzed (see Table S1 in Supplementary Material). This condition is in accordance with the fact that in the primary aging process simulated by heat treatment the vanadyl group is not involved in any way.

3.2.2. The Spin Density

Spin concentration is a measure of the number of unpaired electrons in a given amount of sample. Overall, the EPR results show that the spin density of the maltene fraction, in both unaged and aged samples, is around 5% of that determined in the asphaltene phase. This is a further confirmation that the main contribution to the organic radicals detected in bitumen samples comes from unpaired electron in non-localized π system stabilized by resonance in extended polyaromatic macromolecules.

Interestingly, natural antioxidant additives affect the bitumen spin density even in the absence of the aging treatment, just as an effect of mixing. This is specifically true for LCS, the addition of which results in a lower radical content in the asphaltene fraction, ascribable to an effective scavenging action (see Figure 6).

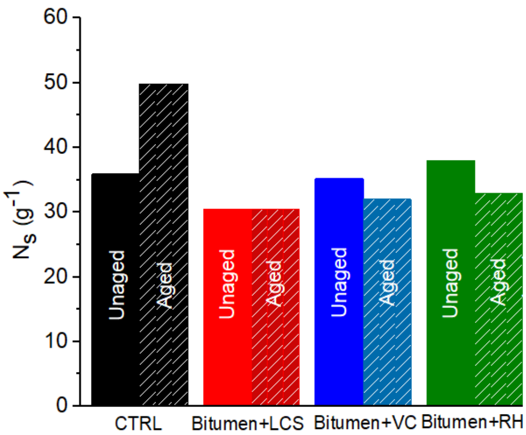

Figure 6. Spin density of asphaltene samples mixed with 2% *w*/*w* of antioxidants, as determined from the X-band EPR spectra registered at room temperature. CTRL indicates the control sample with no antioxidant added. Full bars: unaged samples; striped patterned bars: samples artificially aged through the Rolling Thin Film Oven Test (RTFOT) method.

The RTFOT treatment causes a significant increase of the spin density in the CTRL asphaltene sample, and, to a lower extent, in the corresponding maltene fraction. This indicates aging causes an increase in the average size of the polyaromatic asphaltene molecules, thus resulting in a further stabilization of the unpaired electrons in the extended π systems.

The anti-aging effect of natural antioxidant additives can be evidenced by observing the differences in concentration relative to the aged CTRL. In fact, upon the aging treatment, the addition of LCS, VC and RH leads to a reduction in the density of free radicals in asphaltene fraction of 39%, 36% and 34%, respectively (see Table 2).

Table 2. Concentrations of paramagnetic centers N_s determined in asphaltene and maltene fractions obtained both from unaged bituminous samples and after artificial aging through RTFOT. Relative concentration differences with respect to the aged CTRL have been also indicated in brackets.

Sample	Organic Radical Density N_s in 10^{17} Spins·g^{-1}			
	Asphaltene		Maltene	
	Unaged	Aged	Unaged	Aged
CTRL	35.9	49.8	2.27	2.68
Bitumen + LCS	30.5	30.5 (39%)	1.92	1.27 (53%)
Bitumen + VC	35.2	32.0 (36%)	1.79	1.36 (49%)
Bitumen + RH	38.0	32.9 (34%)	1.96	2.23 (17%)

In particular, among all the additives tested, LCS is the only one able not only to lower the free radical content of the asphaltenic component in response to the heat treatment to which the bitumen is subjected, but also to keep the spin density unchanged before and after aging stress. The relative antioxidant effect recorded on the maltene fraction is much more pronounced compared to the aged CTRL, showing a strong reduction in the concentration of paramagnetic radicals for bitumens modified, respectively, with LCS (53%) and VC (49%) while the effect of RH is somewhat weaker (17%).

3.2.3. Linewidth and Lineshape

The width of an EPR band is inversely proportional to the lifetime of the absorbing species in its excited state. It depends on the interaction between the unpaired electrons and their surroundings; the greater the interaction, the wider the band. Moreover, for complex and chemically heterogeneous samples, spectrum broadening could be the result of unresolved hyperfine structure; in bitumen samples, broadening of EPR signals due to unpaired electrons delocalized in aromatic π systems could arise from the hyperfine coupling with the adjacent aromatic H atoms [45].

The spectral linewidth is generally quantified by measuring, in gauss (G), the peak-to-peak distance (H_{pp}) of the first-derivative curve, which is the experimental output of the instrument. The (H_{pp}) values determined for the examined samples, collected in Table 3, show that, overall, the linewidth of the organic radical signal is only marginally affected by both aging and antioxidant addition. This indicates that both the molecular structure and the supramolecular organization of the sample do not change. Perusal of the table only reveals a slight narrowing for asphaltene in the presence of the LCS additive, thus suggesting reduced local interactions.

Further information can be obtained from the analysis of the EPR signal lineshape. In general, it is affected by the unresolved hyperfine structure and the anisotropic effects and is classified as either Lorentzian or Gaussian. EPR lines have a trend toward a more Lorentzian character with increasing aromaticity [46]. However, radical species with different relaxation behaviors give rise to independent narrow absorptions, which yield a Gaussian-shaped envelope [46]. The accordance with one lineshape rather than another can be estimated by evaluating the ratio R_n of H_n to H_{pp} where H_n is the width at the position $1/n$ of the peak-to-peak height of the first-derivative curve. For $n = 5$, the expected R_5 values for a Lorentzian and Gaussian lineshape are 1.72 and 1.17, respectively [46].

The peak-to-peak separations of the asphaltene and maltene EPR derivative signals (H_{pp}) and the lineshape ratio $R_5 = H_5/H_{pp}$ are reported in Table 3. It is observed that for both the series of unaged and aged asphaltenic samples, the reference parameter R_5 remains almost constant and intermediate between Lorentzian and Gaussian lineshape, implying that the core size of the polyaromatic clusters remains essentially unchanged upon thermal treatment.

Table 3. Peak-to-peak separation of the derivative peak (H_{pp}) and lineshape parameter (R_5) of EPR spectra of asphaltene and maltene fractions obtained both from unaged bituminous samples and after artificial aging through RTFOT.

Sample	Asphaltene				Maltene			
	H_{pp} (G)		R_5		H_{pp} (G)		R_5	
	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged
CTRL	6.2	5.8	1.4	1.5	5.4	4.9	1.5	1.5
Bitumen + LCS	5.9	5.6	1.4	1.5	5.2	5.3	1.5	1.3
Bitumen + VC	5.9	5.8	1.4	1.4	5.6	5.4	1.4	1.4
Bitumen + RH	5.7	5.7	1.5	1.4	5.7	5.6	1.4	1.4

An exception of this feature regards the unaged sample modified with RH additive, in correspondence of which a significant increment of R_5 is recorded compared to the asphaltene samples of the same series. Considering the maltene fraction, calculated R_5 data are slightly scattered compared to asphaltene, though manifesting the same intermediate character of the signal lineshape. Only for the sample supplemented with LCS a marked Gaussian tendency is observed in response to the aging treatment. In this case, this tendency is probably due to the presence of radical species characterized by quite different (less homogeneous) relaxation times, leading to independent absorptions.

3.2.4. Saturation Curves

Analysis of saturation curves of asphaltene samples shows a typical homogeneous saturation trend, as shown in Figure 7, characterized by the presence of a maximum followed by a decrease of the signal, which indicates the onset of spin saturation process. The homogeneous saturation trend is generally observed when a given set of spins is exposed to the same net magnetic field and has a uniform distribution in space. In fact, decrease of amplitude with increasing microwave power is characteristic for free radicals homogeneously located in the sample. Homogeneous saturation occurs when all free radical spins behave as a single spin system with the same relaxation behavior. In other words, the energy absorbed from the microwave field is distributed to all the spins and thermal equilibrium of the spin is maintained through resonance.

The observed homogeneous saturation is in agreements with the molecular structure of asphaltenes, which can be visualized as polycondensates of a multicomponent system made up of individual molecules of aromatics, paraffins, naphthenics, macrocyclics, and heterocyclics characterized by extensive conjugation and wide electronic delocalization. As illustrated in Figure 7, all the saturation curves are affected neither by the presence of additives nor by the aging process.

Analogous tests have been carried out on maltene samples isolated from both CTRL and bitumen modified with LCS, VC and RH additives, respectively. The correspondent power saturation curves, shown in Figure 8, manifest a definitely more complex trend.

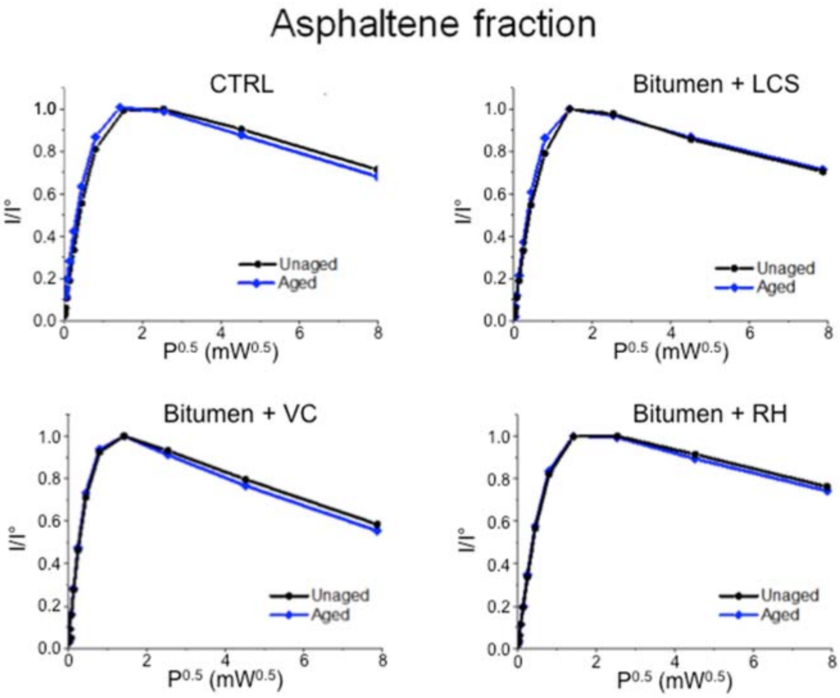

Figure 7. Power saturation profiles for asphaltene samples mixed with 2% *w/w* of antioxidants, as determined from the X-band EPR spectra registered at room temperature. CTRL indicates the control sample with no antioxidant added. Black lines, full circles: unaged samples; blue lines, full diamonds: samples artificially aged through the RTFOT method.

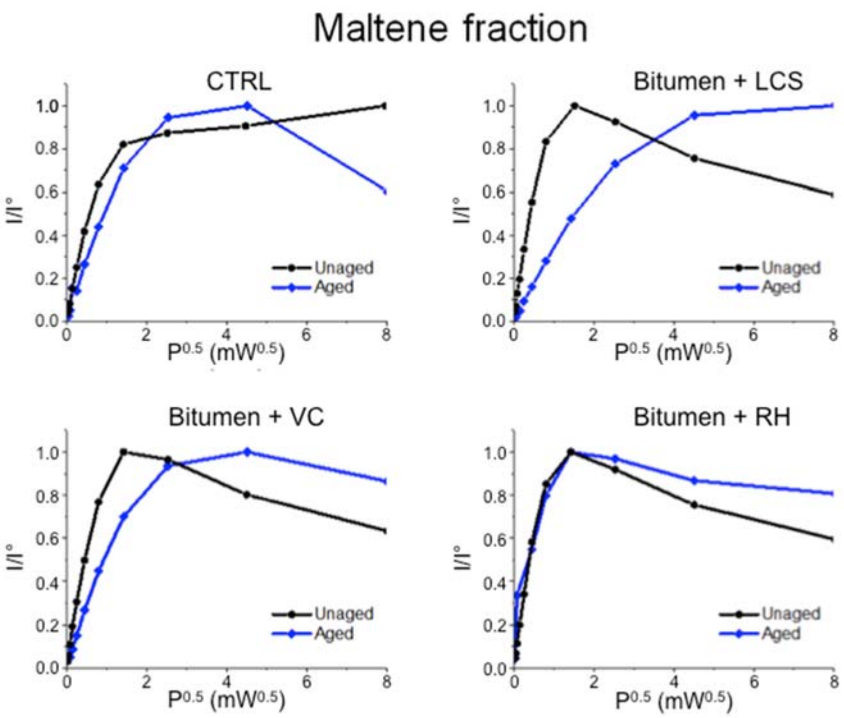

Figure 8. Power saturation profiles for maltene samples mixed with 2% *w/w* of antioxidants, as determined from the X-band EPR spectra registered at room temperature. CTRL indicates the control sample with no antioxidant added. Black lines, full circles: unaged samples; blue lines, full diamonds: samples artificially aged through the RTFOT method.

Maltene phase free of antioxidants shows a heterogeneous trend characterized by the absence of a maximum, which becomes homogeneous by following the simulated aging process in the laboratory, (see Figure 8). This circumstance may occur because aging of bitumen promotes a progressive increase of aromaticy accompanied by a consequent decrease in mass of saturated oils and resins [1]. The presence of antioxidant agents imparts an inversion of trend shown by the reference, i.e., from homogeneous to heterogeneous saturation upon RTFOT treatment. This aspect might be a consequence of a reduced oxidability of the organic matrix due to the antioxidant activity, the efficiency of which qualitatively increases along the series RH < VC < LCS.

4. Conclusions

The effectiveness of natural compounds as anti-aging additives in the reduction of age-hardening effect and concomitant bitumen protection against oxidative aging was evaluated by measuring the rheological properties and EPR spectra of asphalt binders in unaged samples and after artificial thermal treatment. Addition of phospholipids turned out to be beneficial in minimizing the shift of viscoelastic-sol transition temperature towards higher values in temperature sweep rheological tests, which is a typical fingerprint of bitumen hardening in response to oxidative phenomena. The apparent scavenging action manifested by phospholipids was confirmed by a lower radical content detected in the asphaltene fraction compared to the reference system as observed by EPR results. An increase of heterogeneity of distribution of radicals in maltene fractions was inferred by the power saturation profiles determined from the X-band of EPR spectra upon addition of natural anti-aging compounds. However, that effect was more pronounced in presence of phospholipids, in a minor degree for vitamin C and even less for rice husk, thus indicating a greater aging inhibitory effect promoted by the former additive. The present study confirmed the usefulness of considering green compounds from renewable resources of reduced carbon footprint as anti-aging additives for bituminous materials.

Supplementary Materials: The following are available online at http://www.mdpi.com/2076-3417/8/8/1405/s1, Figure S1: X-band EPR spectra of asphaltene and maltene fractions obtained from bitumen samples mixed with 2% *w*/*w* of antioxidants, Table S1: Landé factor (*g*) of EPR signals of asphaltene and maltene fractions obtained both from unaged bituminous samples and after artificial aging through RTFOT.

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