Study of UV rays effects on the evolution of bituminous mix behaviour

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ABSTRACT

During their lifetime, asphalt layers are subjected to aging. Recently, attentions have been paid to the laboratory ageing tests with UV radiation applied to the bituminous binders but there are few studies dealing with the photo-oxidation of binders in a bituminous mix.
So, the aim of this study was to investigate whether the influence of ultraviolet light on bitumen ageing might be assessed in the bituminous mixes using an experimental apparatus dedicated to the ageing of paint. The results show that the influence of UV radiation on the ageing of bituminous mixes containing an elastomer modified bitumen cannot be totally ignored: compared with thermal aging, the UV impact can be found to be dominant for the production of carbonyl functions, the disappearance of C=C double bond of SBS and the increase of binder's hardening. This study has highlighted, on the one hand, that inside the bituminous mix, the UV radiations do increase the rate of oxidation and, on the other hand, that the evolution's kinetics due to a pure thermal oxidation or a photo-oxidation processes are different. Consequently, the UV exposure may affect the bitumen's properties of pavement upper layers more strongly than the laboratory test (without UV action) does.

Keywords: Ageing, Chemical properties, Durability, Modified Binders, Testing

1. INTRODUCTION

During the design phase of bituminous mixtures for road pavements, it is fundamental to be able to predict or at least to estimate the evolution of physical properties of bituminous binders with respect to time, in order to ensure the durability of the whole infrastructure. Indeed, when bituminous materials are exposed to heat, air and ultraviolet (UV) radiation, a gradual degradation of physical and mechanical properties occurs [1]. Consequently, several accelerated ageing methods have been developed in laboratory and standardized at the European level to simulate binder's thermal oxidation in the road [2,3]. However, none of them takes into account the influence of UV radiation [4,5] although, in the real environment, the solar radiation could affect the upper layers of the pavement surfacing and could explain some of the divergences observed between the standardized laboratory simulations of ageing and observations in the field [6]. Therefore, attention have been paid to the laboratory ageing tests with UV radiation applied to the bituminous binders [7,8]. By applying these methods on bituminous binders, several authors have demonstrated that the effect of solar exposure depends on the nature of bitumen [9,6] and that the photochemical reaction had a significant effect on the bitumen films with a thicknress of 3 μm, while thicker films showed a slight effect [10]. Even if this effect of UV radiaton on binder's films have been largely demonstrated and studied [1,6,7,8,11], however there is no studies dealing with the photo-oxidation of binders in a bituminous mixtures in relation with voids, film thickness and permeability.

So, this paper describes a study that investigates whether the influence of ultraviolet light on bitumen ageing might be assessed in the bituminous mixtures. To this purpose, an experimental methodology using a device designed to investigate the ageing of paint [12] was developed based on the previous methods described in the literature [6,11]. An investigation was then carried on the action of UV ray on the ageing of bituminous mixture containing an elastomer modified bitumen : the influence of different oxidation conditions (UV radiation in a weathering oven, standardized ageing methods in laboratory and field exposure) on the binder's properties was assessed.

2. DESCRIPTION OF THE EXPERIMENTAL PART

2.1 Materials

The studied bituminous mixture is a porous mixture 0/10 millimeters (PA 0/10) according to NF EN 13108-7 standard. This drained bituminous concrete has been used in surface course of a French highway, located in the South of France (with both a high level of traffic and a high level of sunlight). The lane without traffic of this road was cored each year from 2003, which is the year of the road construction. Binder was extracted and recovered from each pavement cores using tetrachloroethylene at 70°C [13], analysed by several methods and the results have been compared to laboratory ageing of the same binder that was used for the hot mix production at mixing plant on site. The general characteristics of the mix asphalt are listed in table 1.

Table 1. General characteristics of the drained bituminous concrete

Properties	*Porous mixture 0/10*
European class	BBDR 10
Layer thickness	4 centimeters
Granularity	D = 10 millimeters
Binder content(*)	4,5%
Air voids content	24,3%
Type of binder	Styrene/Butadiene/Styrene modified bitumen

(*) binder content is expressed as a percentage of the total mass of the mix asphalt

This mix asphalt was chosen due to its very high content of interconnected voids which allows passage of water and air in the compacted mixture, so that an intense ageing due to oxygen's action on certain binder's molecules could be

expected. In parallel, a sample specimen was manufactured in laboratory using the same mix formulation and constituent materials in order to perform ageing studies.
The used Styrene/Butadiene/Styrene modified bitumen is a physical elastomer modified bitumen 25/55-55 according to the EN 14023 standard. The grade of this Polymer modified Bitumen (PmB) is detailed in table 2 according to the two tests standards specified at the European level for the conventional characteristics, namely the penetration at 25°C (NF EN 1426) and the softening point (NF EN 1427). The SBS copolymer content was determined according the French testing method ME 71 [14]; it is measured by Fourier Transform InfraRed (FTIR) spectroscopy performed on a solution of bitumen in carbon disulphide (CS_2) with the linear SBS polymer, Kraton D-1184, as reference polymer. The quantification of bituminous binder's oxygenated species is performed according to the experimental procedure described in the French testing method ME 69 [15]; it consists of a semi-quantitative approach in FTIR spectroscopoy based on the definition of two indexes related to carbonyls and sulfoxides functions.

Table 2. Basic properties of the Styrene/Buutadiene/Styrene (SBS) modified bitumen

Properties	*SBS modified bitumen*	*Test specification*
Penetration at 25°C	41 (0,1 mm)	NF EN 1426
Ring and Ball softening point	56,0°C	NF EN 1427
Polymer content	3,6%	French testing method ME 71 of LPC
Sulfoxide content	5,9%	French testing method ME 69 of LPC
Carbonyl content	0,7%	French testing method ME 69 of LPC

2.2 Ageing methods

At this time, the laboratory simulation techniques of the ageing actions on modified bitumens are still a substantially open problem because they were developed for unmodified binders and need re-evaluation for polymer modified bitumens [13]. However, despite this lack of knolwedge and in the absence of anything better, the two conventional tests normalised at the European level were applied on the study's bitumen to simulate in laboratory the modified binders ageing: the Rolling Thin Film Oven Test (RTFOT, standard EN 12607-1) and the Pressure Ageing Vessel (PAV, standard EN 14769). The penetration at 25°C (NF EN 1426) and the Ring & Ball softening point (NF EN 1427) of the unaged SBS modified bitumen and the aged binder after RTFOT and after RTFOT + 20h PAV as well as their evolution expressed according to the normalized ways (ratio of retained penetration and difference in softening point as in EN 12591 standard) are listed in table 3. As described in the literature [13, 16], the consistency parameters after ageing is generally characterized by a decrease of value penetration and an increase of softening point value. One can note that RTFOT (75 min, 163°C, air flow of 4 l/min) and PAV (20h, 100°C, air pressure of 2.1 MPa) are expected to simulate respectively mixing ageing and field ageing [3,5].

Table 3. Conventional characteristics of the unaged and aged SBS modified bitumen

SBS modified bitumen	*Ageing*	*Penetration at 25°C (0,1 mm)* (1) */ retained penetration (%)*		*R & B softening point (°C)* (2) */ R & B increase (°C)*	
	Origin	*41*	*/*	*56,0*	*/*
	RTFOT 163°C	*30*	*73*	*62,0*	*6,0*
	RTFOT + 20h PAV	*19*	*46*	*71,2*	*15,2*

(1) According to the NF EN 1426 standard
(2) According to the NF EN 1427 standard

RTFOT is claimed to simulate ageing at the jobsite (i.e. mixing and laying). This test uses a temperature of 163°C with controlled air flow and thin films to give rapid loss of the volatile oils and some oxidation of the bitumen. It relies on the bitumen being fluid enough to roll around in the glass bottles as they move on a carousel, thus continously exposing new material to the stream of air [17]. Subsequently, specimens previously subjected to the RTFOT were prepared and tested in accordance with the PAV test. This static test is conducted at 100°C for 20 hours under an air pressure of 2.1 MPa [18]. This ageing siumlation method is claimed to compress several years of exposure in the pavement into a much shorter period of time by using an air pressure and a relative high temperature which is never expected to be experienced by a binder in service. However, the PAV simulated ageing is recognized to be equivalent to several years of service (between 3 and 6 years) in a road for unmodified bitumens, but how long this equivalence is, depends on several parameters, such as voids contents, climate, binder's composition and accessibility to oxygen (depth of the studied layer). Recently, a study of several experimental pavements found this simulated ageing to be equivalent to four years in the case of unmodified bitumens [19]. But, in case of modified bitumens, looking at the only set of pavements investigated [13], it was demonstrated that, according the consistency parameters, RTFOT + 20h PAV ageing approximatively correspond to around 1-2 years of field ageing. However, this observation has to be balanced by the hardening parameters evolution rates and also by the influence of UV ray action on the superficial layer ageing that is not taken into account by the RTFOT + 20h PAV procedure and could explain some of the divergences. It is the reason why photo-ageing test has been developed in an UV weathering oven to investigate the photo-degradation behaviour of bitumen specimens [1, 6, 7, 8, 11]. But no one of these tests was directly performed on bituminous mixtures and so doesn't take into account of the possible aggregate's reactivity during the photo-oxidation.

In order to explain the divergences observed between the evolutions due to laboratory simulation of binder's ageing and field evolution of bituminous mixtures, an experimental procedure was developed to adapt the UV radiation oven accelerated ageing to a bituminous mixture. The sample specimen was manufactured in laboratory according to the European norm EN 12697-33 and its composition was based on the same mix formulation and constituent materials than those used for the porous mixture of the French highway surface layer chosen as a field reference for this study. The optimised experimental conditions of this UV radiation oven accelerated ageing are the followings:

- Q-UV chamber with a spectral irradiance of the fluorescent tubes UVA (without infrared rays) set at a constant value of 0.72 W/m2/nm with the wavelength of 340 nm. Due to the experimental design of the device, the temperature was set at 44°C inside the bituminous mixtures, which is in good agreement with the mean surface temperature of bituminous pavement.
- Dimensions of bituminous mixtures slices: they were optimised in function of the space available in the Q-UV chamber and are about 8 cm width and 24 cm length. It has been chosen a thickness of 1 cm in agreement with the results of Petersen that have demonstrated that in the early stages of pavement life, oxidation had only significantly penetrated the top 1 cm of the pavement [20]. Morover, in order to make the UV to reach all the bitumen film, each longest side of bituminous mixtures slices has been submitted to UV radiation in a horizontal plan.
- UV exposure being composed of several cycles, each cycle being made of 90 minutes of UVA at 340 nm following by 30 minutes of water shower. This UV exposure was carried up to 3200h per sample (meaning 1600h per side). One can note that the Q-UV chamber is equipped with calibrated radiometers dedicated to UV lamps permitting to adjust the lamps power each 400 hours in order to respect the orders and to have a constant irradiance value during the whole test.

To distinguish thermal aging from the UV radiation effect, bituminous mixtures slices with the same formulation and dimensions than those aged in the UV oven were aged at 44°C in a natural ventilated oven during the same durations. So, in comparison with the data obtained from these two types of testing, the contribution of photo-oxidation can be known.

2.3 Characterization methods

First of all, an important step before binder's characterization is the binder's extraction and recovery, carried out according to the following experimental procedure: the pavement cores of bituminous mixtures are broken into small pieces before solvent extracting the binder from the aggregates. The extraction is based on the dissolution in the tetrachloroethylene solvent (heated solvent for modified binders and solvent at room temperature for neat bitumens). This binder solution is then filtered and centrifuged to remove all aggregate particles from the binder solution. After that, the solvent is removed by distillation under air vacuum. It is important to note that after the binder was extracted and recovered, it is analysed by infrared spectroscopy to ensure complete solvent removal (no infrared peaks of chlorine) and the calcination residue during 8 hours at 450°C has to be less than 1% of binder test portion.

After complete solvent removal, differental properties of the binder were determined taking into account of the quantity of bitumen collected after bituminous mixe's UV ageing :

- consistency parameters : measurement of ring and ball softening point (°C) according to the European standard EN 1427.
- structural parameters : determination of the changes affecting the chemical groups using Fourier Transform Infra-Red (FT-IR) spectroscopy analysis. A Perkin Elmer Spectrum 100 FT-IR Spectrometer loaded with Spectrum 6.1 software was used to acquire FTIR spectra recorded in transmission mode with a resolution of 2 cm^{-1} and an accumulation of 32 spectra. Three replicates were prepared and analysed for each recovered aged binder. The monitoring of ageing was performed by studying the changes in different characteristic infrared absorption bands:
    - The quantification of bituminous binder's oxygenated species (carbonyl and sulphoxide indexes) has been performed according to the experimental procedure described in the French testing method ME 69 [15]; it consists of a semi-quantitative approach in FTIR spectroscopoy based on the definition of two indexes related to carbonyls and sulfoxides functions: for the carbonyl index, the carbonyl absorption band from 1720 to 1665 cm^{-1} to the sum of infrared bands at 1376 and 1456 cm^{-1}, and for the sulphoxide index, the sulphoxide absorption band from 1098 to 980 cm^{-1} to the sum of infrared bands at 1376 and 1456 cm^{-1}.
    - The following-up of C=C bands permits the monitoring of the deterioration of the SBS copolymer as a result of the butadiene copolymer modification by diminution of the double bond content. This monitoring has been performed by calculating the following structural indice in order to avoid the effect of the analyzed quantities, that is to say the thickness of the film [11, 21]: SBS butadiene index defined as the ratio of the butadiene absorption band from 980 to 950 cm^{-1} to the sum of infrared bands at 1376 and 1456 cm^{-1}.

3. RESULTS AND DISCUSSION

3.1 Influence of UV radiation on the laboratory ageing of bituminous mixtures

Before studying how laboratory ageing procedures, whatever the nature of the ageing (thermal or UV), correspond to field ageing according to the chosen characterization methods, the contribution of pure photo-oxidation has been determined by comparison of data obtained from thermal aging with and without UV radiation.

Whether it is for 800 hours or 1600 hours of ageing, in comparison of the physico-chemical characteristics of recovered binders, the ones of binders aged after UV exposure at 340 nm (cf. figures 1, 2, 3 and 4) show a higher evolution of characteristics in comparison of the ones after purely thermo-oxidation.

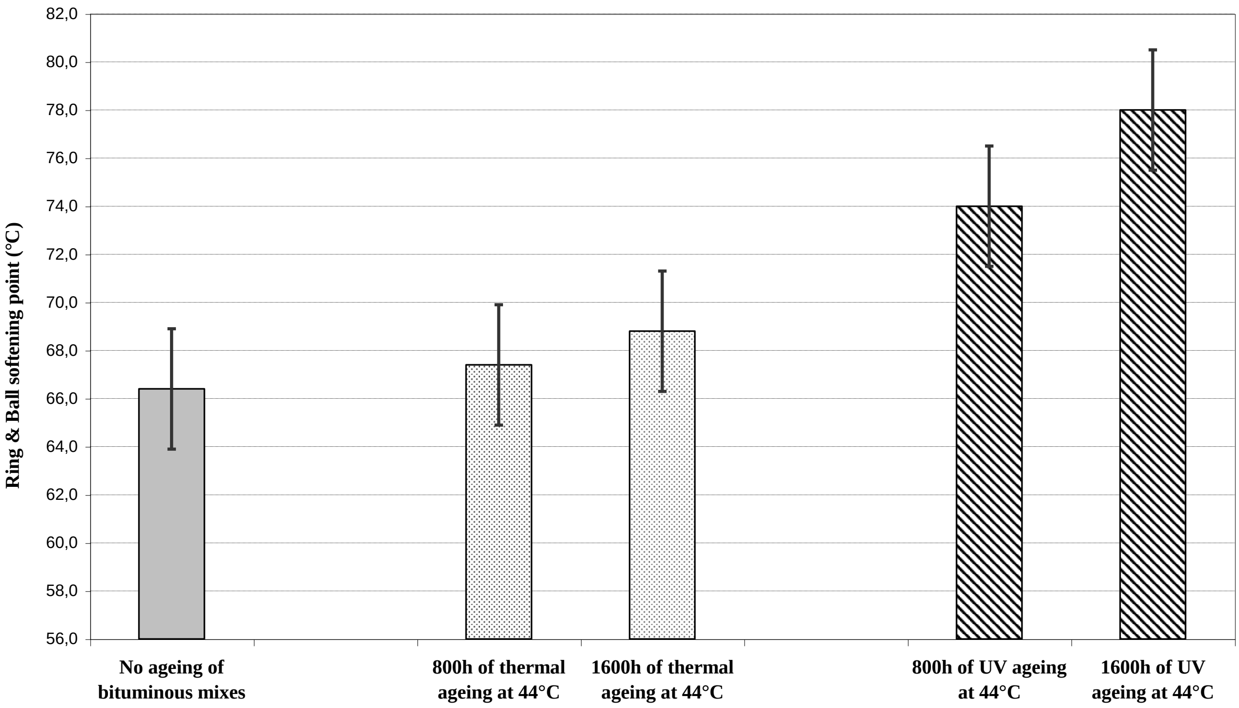

Figure 1. Evolution of Ring & Ball softening point of the binder during UV aging at 44°C and thermal ageing at 44°C.

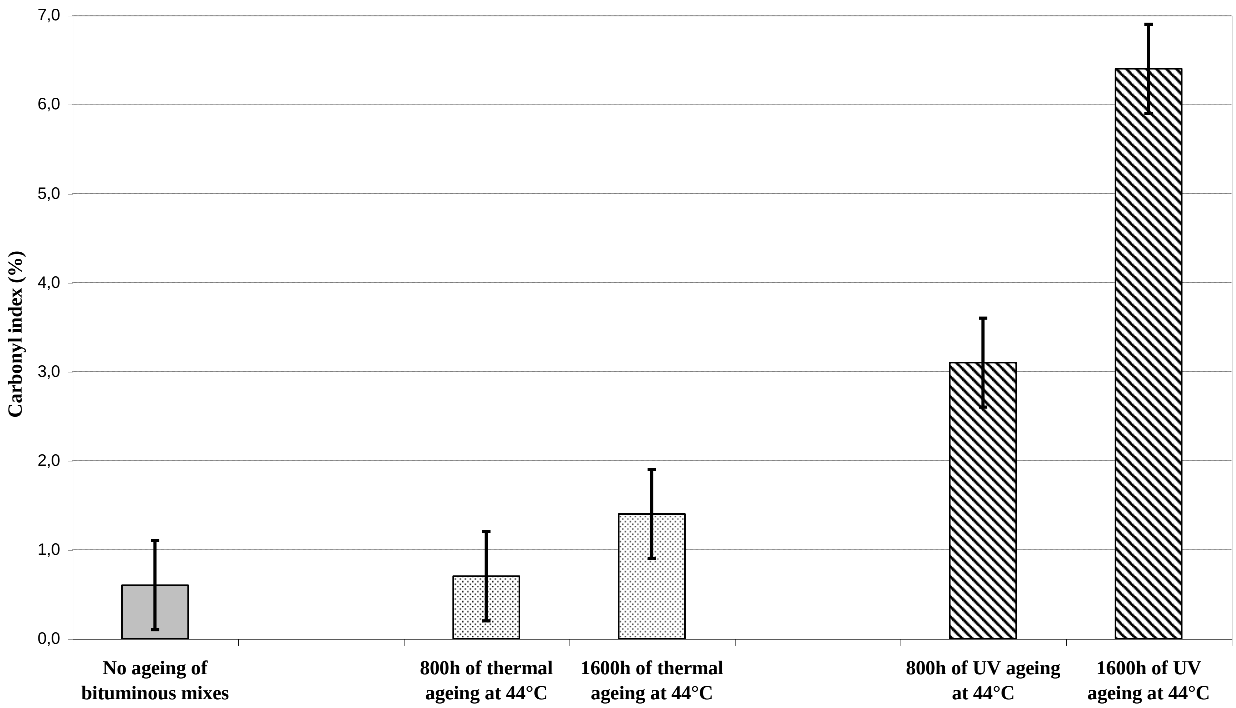

Figure 2. Evolution of carbonyl content of the binder during UV aging at 44°C and thermal ageing at 44°C.

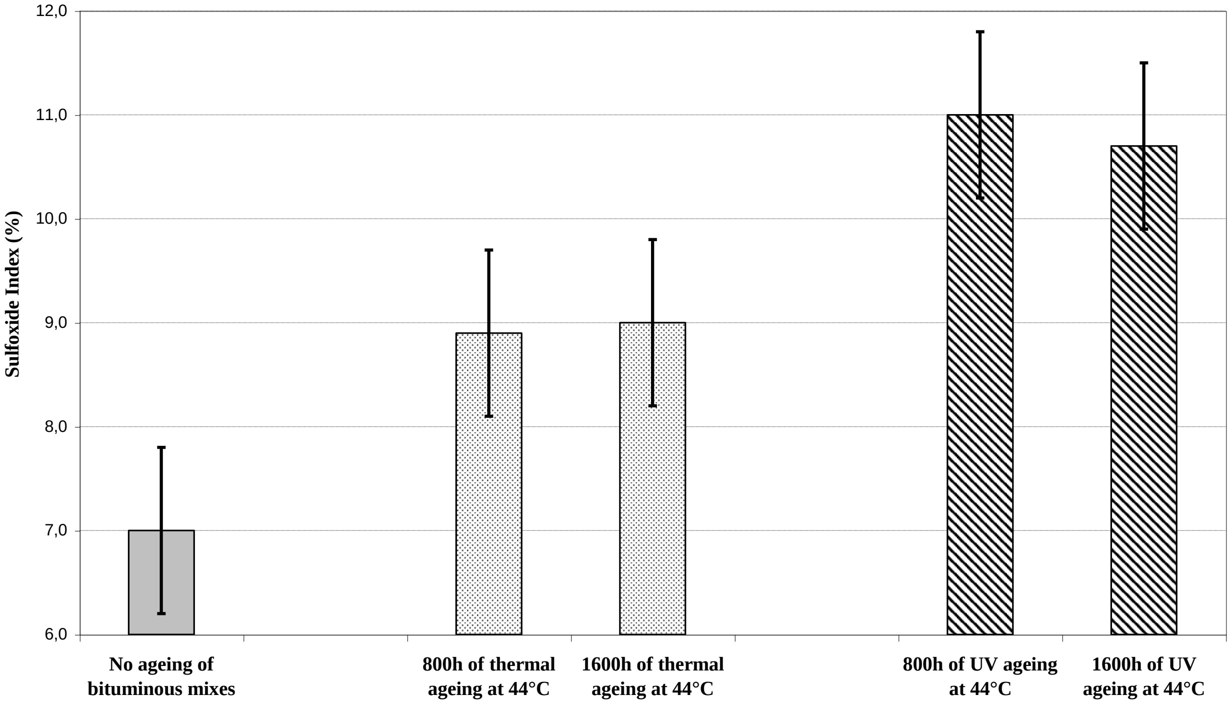

Figure 3. Evolution of sulfoxide content of the binder during UV aging at 44°C and thermal ageing at 44°C.

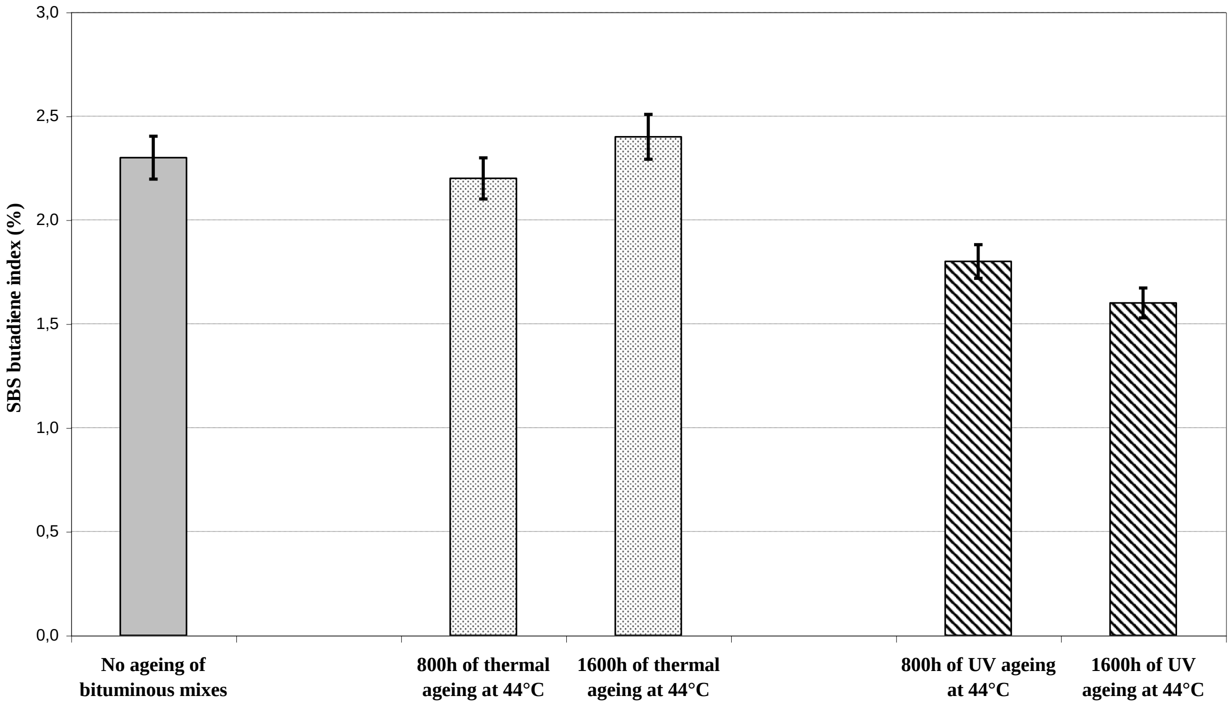

Figure 4. Evolution of SBS butadiene index of the binder during UV aging at 44°C and thermal ageing at 44°C.

By calculating the percent of UV contribution in the oxidation process (cf. table 4), the effect of UV rays can be assessed: it is very pronounced for the carbonyl production (around 78% for 800h or 1600h of exposure time), which reflects more oxidation reaction happened in bitumen samples when adding UV exposure to thermal oxidation. This means that the rate of carbonyl production is accelerated under UV radiation, as already observed on UV ageing of bitumen's films [6]. For the disappearance of SBS copolymers trans-butadiene double bond, the loss is due to a radical cleavage of polybutadiene chain as demonstrated previously in the literature [22, 23]. However, this evolution seems to be directly dependent on the UV exposure time: when the duration is multiplied by two, the contribution of UV radiation to SBS butadiene double bond content disappearance is increased by a factor of two. Consequently, the C=C double bond seems sensible to the quantity of ultraviolet irradiation used during the ageing process.

Table 4. Contribution of UV exposure to the evolution of physico-chemical characteristics

Measured characteristics	Duration of ageing	$\lvert \Delta_{((Thermal+UV)\text{ - }Thermal)} \rvert$	Percent of UV contribution in oxidation process
Ring & Ball softening point	800h 1600h	6,6°C 9,2°C	8,9% 11,8%
Carbonyl content	800h 1600h	2,4% 5,0%	77,4% 78,1%
Sulfoxide content	800h 1600h	2,1% 1,7°%	19,1% 15,9%
SBS butadiene index	800h 1600h	0,4% 0,8%	22,2% 50,0%

However, it is important to note that the evolution kinetics from the "zero point" (namely the recovered binder from a bituminous mixture without ageing) are different according to whether it is a pure thermal oxidation or a photo-oxidation combined to a thermal process:

- ✓ *Evolution's kinetic due to a pure thermal oxidation*: whether it is for 800 hours or 1600 hours of ageing, thermal oxidation at 44°C doesn't lead to a significant increase of physico-chemical characteristics of the binder compared to the zero point, except for the sulfoxide content (see figure 3). This is mainly due to the fact that during thermal ageing of binders at low temperatures (<100°C), the first oxidation compounds that are produced are predominantly sulfoxides [24]. When there is no more oxidizable sulphur site available inside the binder, the sufoxide content remains stable despite the increase of ageing duration.
- ✓ *Evolution's kinetic due to photo-oxidation*: on the contrary of thermal process, whatever ageing duration is, the evolutions of binder's characteristics are signicantly higher than the zero point after photo-oxidation at 44°C. Moreover, the UV exposure duration has a significant influence upon the production of carbonyl functions (see figure 2) and the disappearance of C=C double bond of SBS (see figure 4). It could be related to an important polymer exposure to UV radiation because the studied mix asphalt displays a very high content of interconnected voids which allows passage of oxygen in the compacted mixture and the film of binder around aggregates and filler is very thin, typically comprised between 5 microns and 15 microns thick [25, 26].

3.2 Comparison of the bituminous mixtures ageing level after UV exposure in laboraory with field exposure

Now that the experimental methodology described previously has permitted to determine the contribution of UV ageing during the UV radiation oven test, an investigation has been undertaken to assess the kinetic curves of binder's ageing inside the bituminous mixture under different oxidation conditions (UV radiation in a weathering oven, standardized ageing methods in laboratory and field exposure). The follow-up of binder's properties evolution allows to study how laboratory ageing procedures, whatever the nature of the ageing (thermal or UV), correspond to field ageing according to the chosen characterization methods (see figures 5, 6 and 7). It clearly shows the scale of the effect of exposure to UV radiation in relation to the PAV test and service in a road: based on the oxidation indexes, the level of oxidisation achieved by RTFOT + PAV simulation is reached around 1600 hours of thermal ageing at 44°C and is exceeded from 800 hours of photo-oxidation at 44°C (see figures 5 and 6). Besides, the oxidation level measured after 44 months of field ageing is not reached after 3200 hours of thermal or photo-oxidation ageing.

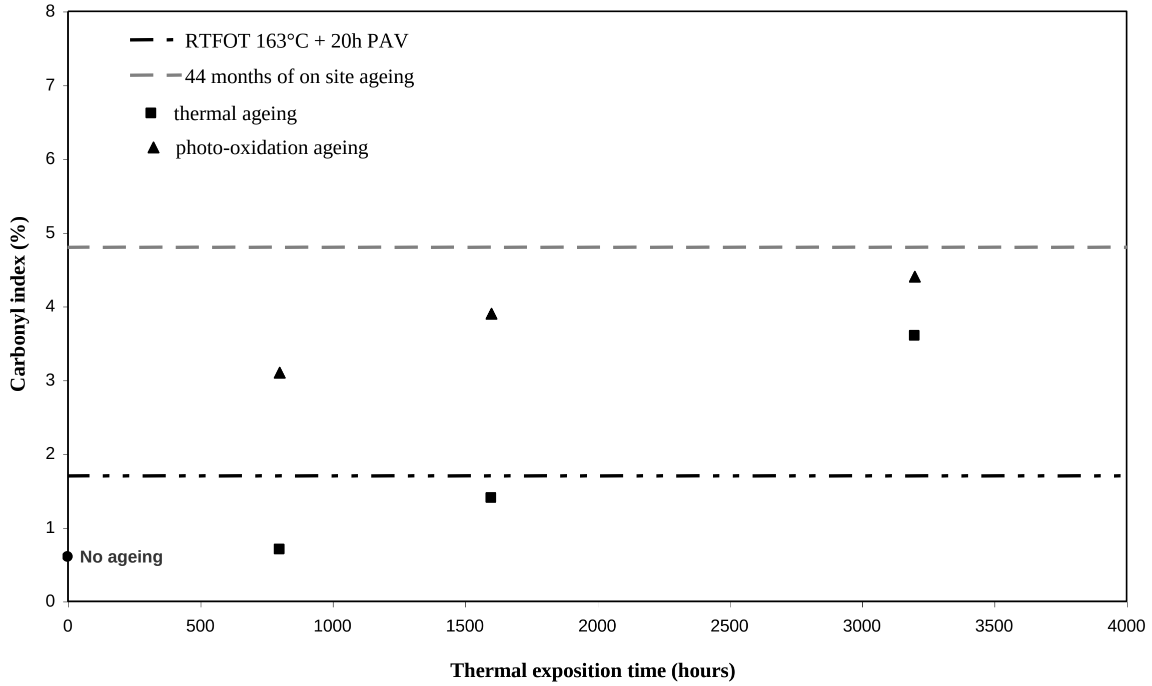

Figure 5. Kinetic's curve of carbonyl content versus thermal exposure time.

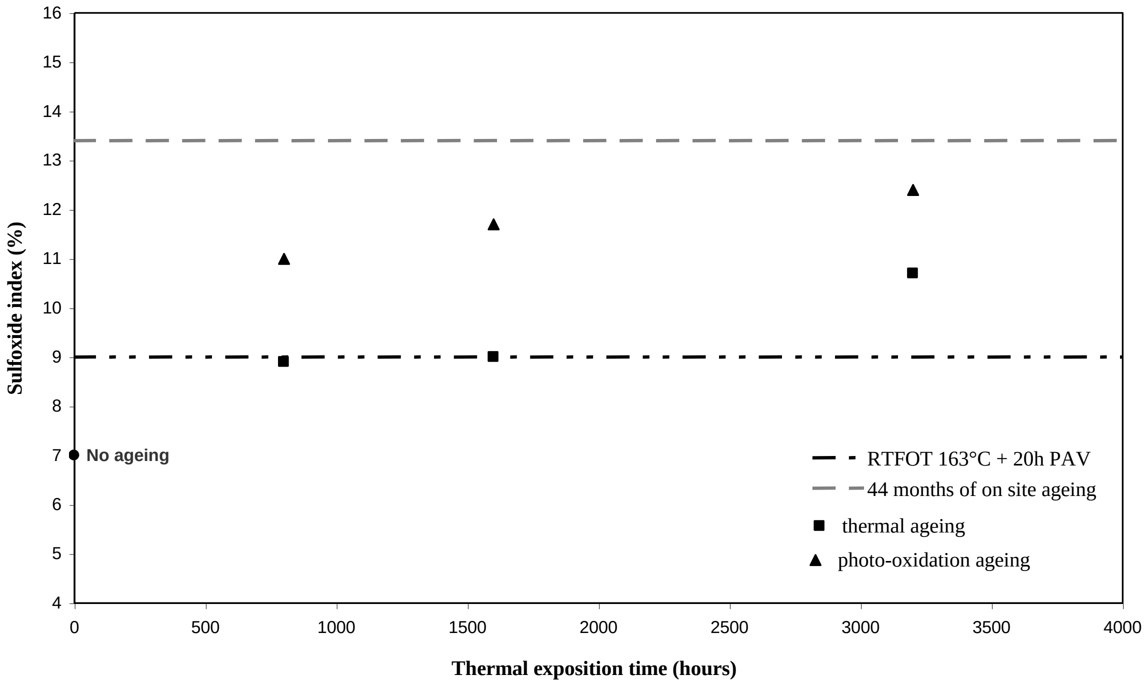

Figure 6. Kinetic's curve of sulfoxide content versus thermal exposure time.

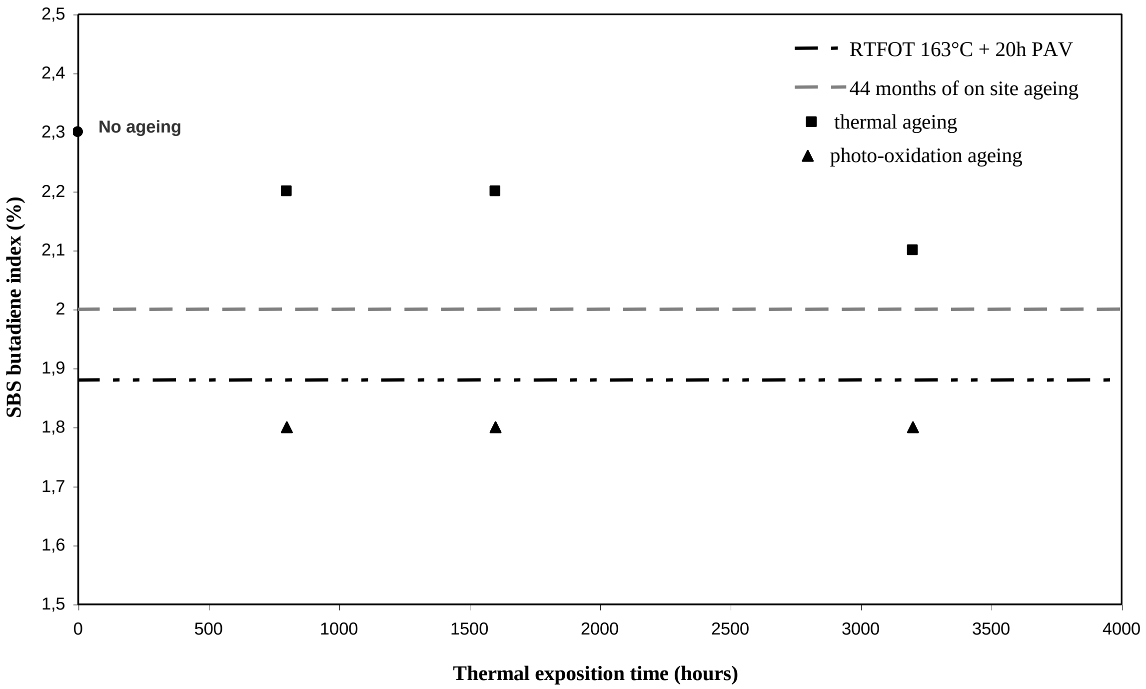

Figure 7. Kinetic's curve of SBS butadiene index versus thermal exposure time.

Taking into account the SBS butadiene index, one can assess that 22% of the polymer is degraded after 800 hours of exposure to UV light (see figure 7) and this level remains stable when increasing the exposure time to photo-oxidation. However, when the ageing mechanism is purely a thermal process, the polymer degradation level is around only 4% after 800 or 1600 hours of exposure and goes up to 9% after 3200 hours of exposure time. This demonstrates that the loss of SBS double bond is senstive to UV action combined to thermal process but this disappearance of SBS trans-butadiene double bond remains weak (22%). These results, that are in agreement with previous studies [6, 11], can be explained either by the anti-oxidizing effect of certain bitumen's components, like phenols [27], or by the fact that UV radiation go into only few micrometers of the bitumen film inside the bituminous mixtures [1] and consequantly only the polymer being at the bituminous mixture surface is affected. It is also important to note that the thermal ageing kinetic doesn't reach the SBS degradation's level measured after PAV or after 44 months of field ageing unlike the photo-oxidation kinetic that, from the beginning, displays a higher SBS degradation level than PAV and 44 months of on site ageing.

4. CONCLUSIONS

The influence of UV radiation on the ageing of bituminous mixtures containing an elastomer modified bitumen can not be totally ignored : compared with thermal aging, the UV impact can be distinguished and found to be dominant for the production of carbonyl functions, the disappearance of C=C double bond of SBS and the increase of binder's hardening. The kinetic curves of binder's ageing inside the bituminous mixture under different oxidation conditions (UV radiation in a weathering oven, standardized ageing methods in laboratory and field exposure) allow to conclude that:

- the level of ageing achieved by RTFOT + PAV simulation is reached around 1600 hours of thermal ageing at 44°C and before 800 hours of photo-oxidation at 44°C according to the the production of oxidation products. Moreover, from 800 hours of exposure to UV light, the level of SBS polymer degradation is exceeded while it is not yet reached after 3200 hours of thermal exposure.

- the field ageing after 44 months of natural is not reached after 3200 hours of thermal or UV exposure at 44°C according to the production of oxidation products. However, from 800 hours of exposure to UV light, the level of SBS polymer degradation is exceeded while it is not yet reached after 3200 hours of thermal exposure.

This study has permit to highlight, on the one hand, that inside the bituminous mixture, the UV radiation do increase the rate of oxidation and, on the other hand, that the evolution kinetics due to a pure thermal oxidation or a photo-oxidation processes are different: the evolution due to 44 months of on site ageing is better assessed by photo-oxidation process than by pure thermal oxidation. Consequently, the UV exposure may affect the bitumen's properties of pavement upper layers more strongly than the PAV simulation in laboratory (without UV action) does. This standardized ageing method in laboratory probably underestimates the real evolution of the binder in a bituminous mixture used in surface course.

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