



**HAL**  
open science

## Characterization of aging processes on the asphalt mixture surface

Marcelo da Mota Lopes, Dan Zhao, Emmanuel Chailleux, Malal Kane,  
Thomas Gabet, Cédric Petiteau

► **To cite this version:**

Marcelo da Mota Lopes, Dan Zhao, Emmanuel Chailleux, Malal Kane, Thomas Gabet, et al.. Characterization of aging processes on the asphalt mixture surface. 2nd International Symposium on, Asphalt Pavements et Environnement, Transportation Research Board, of The National Academies, Oct 2012, France. 10p, ill., bibliogr. hal-00849450

**HAL Id: hal-00849450**

**<https://hal.science/hal-00849450v1>**

Submitted on 31 Jul 2013

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## Characterization of Aging Processes on the Asphalt Mixture Surface

Lopes, M. M., Escola Politécnica da Universidade de São Paulo, Brasil  
Zhao, D.; Chailleux, E.; Kane, M.; Gabet, T.; Petiteau, C., French Institute of Science and Technology for Transport, Development and Networks (IFSTTAR), France

**ABSTRACT:** Aging of asphalt binders leads to damage on pavements, due to changes in their rheological behavior and in the binder composition. A hardening of the asphalt can be observed, mainly caused by the oxidation of the asphalt binder itself. Oxidation rate is influenced by temperature, ultraviolet radiation and intrinsic characteristics of materials. In order to be characterized, the binder is extracted from the field-aged asphalt cores that use to have several centimetres in thickness. The aging process, however, depends on the access of oxygen into the field core which varies with the distance from the pavement surface. In order to know the aging conditions of the pavement surface (only) and to evaluate their influence on the adhesion characteristics, it is necessary to recover the surface asphalt binder. Only the surface binder is exposed to ultraviolet rays and weathering. A new test method has been developed in this work. It is based on the asphalt binder recovery from the upper part of the asphalt mixture layer. This method was validated by the infrared spectrometry through comparison with the neat asphalt binder (aged and not aged) and with the conventional extraction. In addition, an accelerated aging protocol was developed with the use of a climate chamber comprised of brightness settings, and moisture and weather conditioning, to relate to the French climate. The aging results obtained in the laboratory and in the field were compared using the same test method. This comparison allowed the establishment of an accelerator factor with respect to the increase of sulfoxide and carboxyl groups. This study provides a better understanding of the influence of aging on the skid resistance and the ability of the material to resist to polishing.

### 1. Introduction

Aging of asphalt binders leads to premature damage on pavements, due to changes in their rheological behavior and in the binder composition (Farcas, 1996). Asphalt undergoes different types of aging, distinguished by their mechanisms, which can be classified as physical and chemical (Ramond et al., 1990; Zhao, 2011). The physical aging is defined by an increase of viscosity without chemical modification of constituents. The chemical aging is the most important and complex, and corresponds to oxidation, cyclization and aromatization reactions. It results to a hardening of the asphalt which becomes harder and brittle (Leseur, 2008). Aging rate is influenced by temperature, ultraviolet radiation and accessibility to oxygen. This last point is driven by characteristics of the material: layer thickness, type of asphalt, percentage of voids and aggregates.

Whatever the type of aging, hardening effects increase the risk of cracking. The binder loses its ability to relax stress during the cooling process (Isacsson, 1997). Hence, the problems of durability are strongly linked to the asphalt capacity to resist to oxidation or physical hardening. Generally, evaluation of thermo-mechanical properties of mixes aged on site are performed on sample cored in different layers. These samples of several centimetres thick are prone to an oxidation gradient due to oxygen accessibility through the thickness. Results, taken from the mix samples or from the recovered binder, represent an average value of the overall aging state of the organic phase.

Investigations done at IFSTTAR to study the evolution of skid resistance of asphalt pavement (Kane et al., 2010) have shown that the friction coefficient for the asphalt specimens extracted at the un-trafficked part of the road (emergency stopping lane on highways) increases strongly in the first moments until reaching a maximum and then remains relatively constant (Figure 1). Therefore, the ageing phenomenon cannot be ignored when designing asphalt pavements and the possible skid resistance evolution.

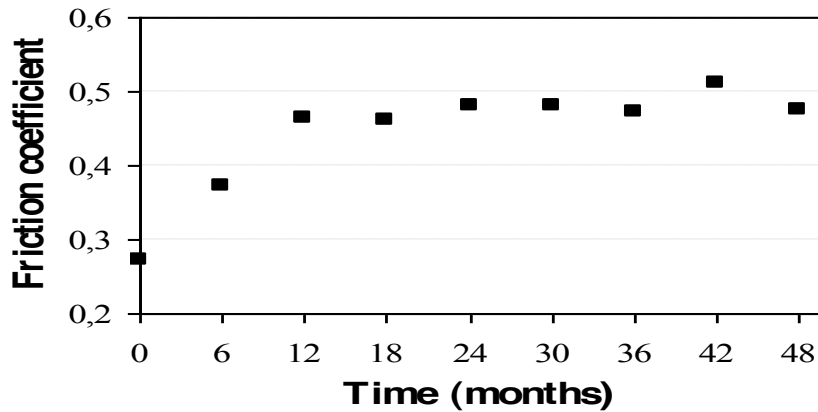


Figure 1. Friction coefficient for the asphalt specimens

To evaluate the effect of aging on a surface property, like the skid resistance, the bulk behaviour is not significant. Indeed, surface appears to be the more stressed zone (environmental condition, sun, rain, air). Hence, it becomes important to focus on the evaluation on the asphalt binder that is exposed to the sun radiation and the weathering. The classical techniques of bitumen recovery by dissolution in a solvent and evaporation cannot select the binder in relation to its depth in the asphalt layer. Indeed, it uses around 1kg of material and moreover these techniques are destructives for the sample.

In this study, a new technique is proposed to characterize the chemical modifications of the binder on the surface of the mixture. The paper describes and evaluates the employed methodology, which use a small quantity of asphalt and an Infrared-spectroscopy measurement without evaporation process. The protocol is firstly validated on model samples. Then, the method is used on binder taken at the surface of mixes, aged on site and in a climatic chamber.

## 2. Materials and Usual Infrared Procedures

### 2.1. Materials

Table 1 presents the characteristics of the aggregates and the binder used in this work. The aggregates were collected at Noubleau quarry and the fines aggregates have a calcareous origin. Three types of asphalt were used: (i) pure binder naphthenic without paraffin; (ii) pure binder with paraffin and (iii) polymer modified binder incorporating SBS polymer (Styrene Butadiene Styrene).

**Table 1: Aggregates and binder**

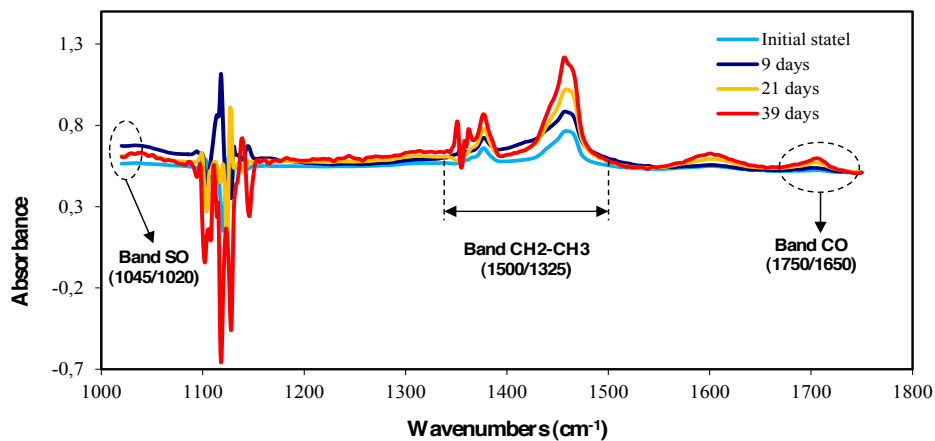
Constituents (BBTM 0/10)	Percentage (%)	
<b>Aggregates</b>	6/10 mm (Noubleau)	55,45
	4/6 mm (Noubleau)	12,32
	Sand 0/2 mm (Noubleau)	24,17
	Filler (Calcareous)	2,84
<b>Asphalt</b>	B1: Pure naphthenic binder	5,21
	B2: Pure paraffinic binder	5,21
	B3: Polymer modified binder	5,21

The hot asphalt mixture studied is a very thin asphaltic overlay, or a *Béton Bitumineux Très Mince* (BBTM 0/10) in French. The mixtures were produced using a mixer BBMAX according to the standard EN 12697-35 [EN 12697-35, 2007]. The loose mix was compacted with dimensions 600 × 400 × 50 mm, using a French roller compactor according to the standard EN 12697-33 [EN 12697-33, 2004]. Three mixes are manufactured (M1, M2 and M3) composed of binders B1, B2 and B3 respectively.

**2.2. Fourier Transform Infrared Spectroscopy (FTIR)**

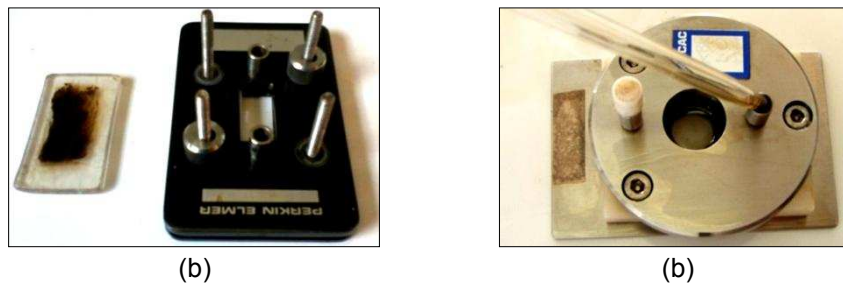
Fourier Transform Infrared Spectroscopy (FTIR) for asphalt binders can be used as an indicator of aging, because it allows the identification of the evolution of two chemical entities resulting from oxidation: the Carbonyl (C=O) and Sulfoxide (S=O) links (Figure 2). In order to eliminate the influence of sample preparation (thickness of the binder film), results are given relatively to another absorption band. In the present study, absorption band of functional group C=O and S=O are calculated relatively to structural group CH2 and CH3. Figure 2 is just given for illustration. Increase of CH2 CH3 absorption band is not linked to ageing but to sample thickness.

The relative increase of C=O and S=O functional groups reflects asphalt aging, accompanied by a hardening (decrease in penetration and increase in the softening point) (Farcas, 1998; Farcas *et al.*, 2010).



**Figure 2: FTIR spectra of a pure asphalt aged (Zhao, 2011)**

Sample preparation can classically performed using two different methods. The first one (method M1) consists in laying the bitumen as a thin film on KBr pellets (Figure 3(a)). The second method (method M2) consists in solubilising the bitumen in a solvent, with subsequent dripping in the KBr cell (Figure 3(b)).



**Figure 3:** (a) Method M1: Thin film of asphalt on KBr pellets (b) Method M2: Asphalt + solvent in a KBR cell

Whatever the method, the functional characteristics are determined by measurement of the infrared absorption bands corresponding to CO and SO functions. They are represented respectively by absorption bands around  $1700\text{ cm}^{-1}$  and  $1030\text{ cm}^{-1}$ . Equations 1 and 2 give the normalized calculus used to determine the oxidation indices.

$$\text{Carboxyl Index (\%)} = 100 \times I_{CO} = 100 \times \left( \frac{\text{Aire from 1650 to 1750}}{\text{Aire from 1325 to 1500}} \right) \quad (1)$$

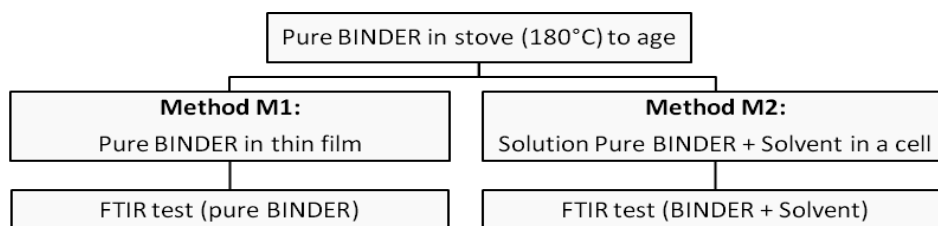
$$\text{Sulfoxide Index (\%)} = 100 \times I_{SO} = \left( \frac{\text{Aire from 1020 to 1045}}{\text{Aire from 1325 to 1500}} \right) \quad (2)$$

### 3. Evaluation of a New IR Procedure

#### 3.1. Comparison of methods M1 and M2

The purpose of this preliminary study was to verify if SO and CO functions measurements of aged asphalt solubilised in tetrachloroethylene solvent are comparable to those measured from the same aged asphalt analysed on a Potassium Bromide (KBr) plates (usual technique). For the validation of the method, some tests were performed and compared on two similar samples aged in the same conditions in stove.

To age the samples, thin films (around 2,0mm) of asphalt B1 (were exposed to air at  $180^{\circ}\text{C}$  during six different periods (0,5h – 1h – 2h – 4h – 8h and 24h). Then, these samples were characterized in IR spectroscopy using both methods M1 (the bitumen in film prepared on KBr pellets) and M2 (the solution bitumen and solvent in a KBr cell) as shown in the Section 2.2. For both methods, preliminary scans are performed on cell filled with tetrachloroethylene alone and on KBr plates in order to get the IR background. The infrared spectroscopy was performed in transmission mode. Spectra of samples were obtained by using 5 scans/sample at  $2\text{ cm}^{-1}$  resolution. The Figure 4 shows the schematic diagram of the experimental set-up.



**Figure 4:** Schematic diagram of the experimental set-up

In Figure 5, the graphics show the FTIR spectra from both methods (M1 and M2) after different levels of aging. Global absorbance appears to be strongly dependent on the conditions of analysis (solvent in a cell, KBr plate). From these spectra, normalized values of CO and SO absorption bands according to Equation (1) and (2) are calculated and reported in Figures 6 and 7.

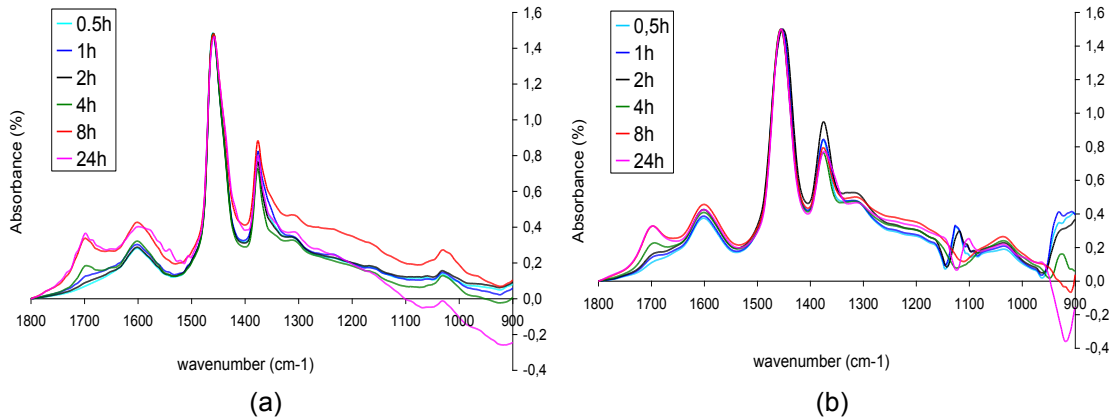


Figure 5: (a) M1 - Pure binder and (b) M2 - Binder + solvent

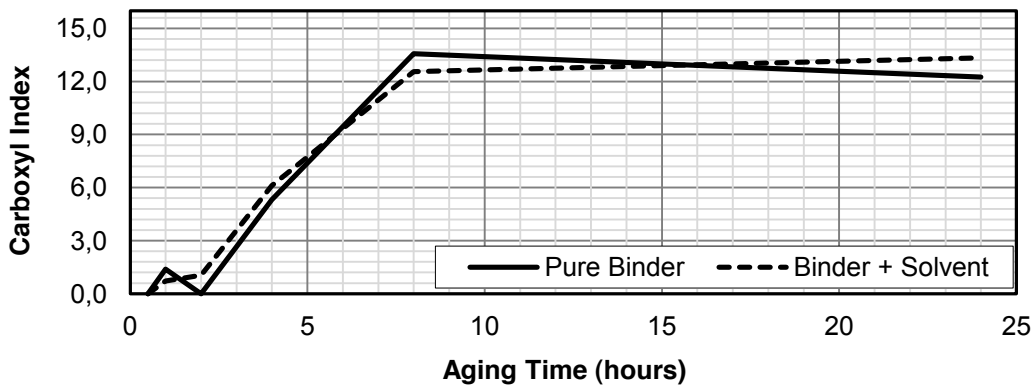


Figure 6: Carboxyl Index

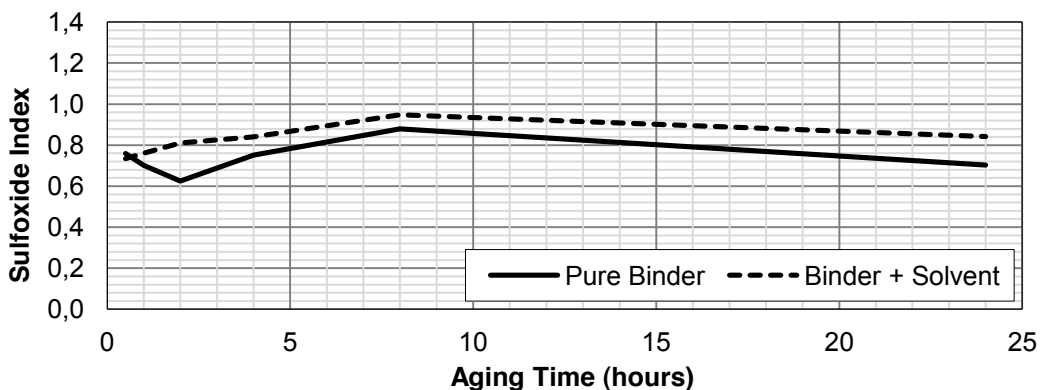


Figure 7: Sulfoxide Index

Aging kinetics of the samples aged during six different periods (0,5h – 1h – 2h – 4h – 8h and 24h) appears to be similar whatever the method. Considering the generally observed repeatability, which is close to 1%, results from both methods can be considered as equivalent. This results means that aging kinetic can be quantified on small amount of

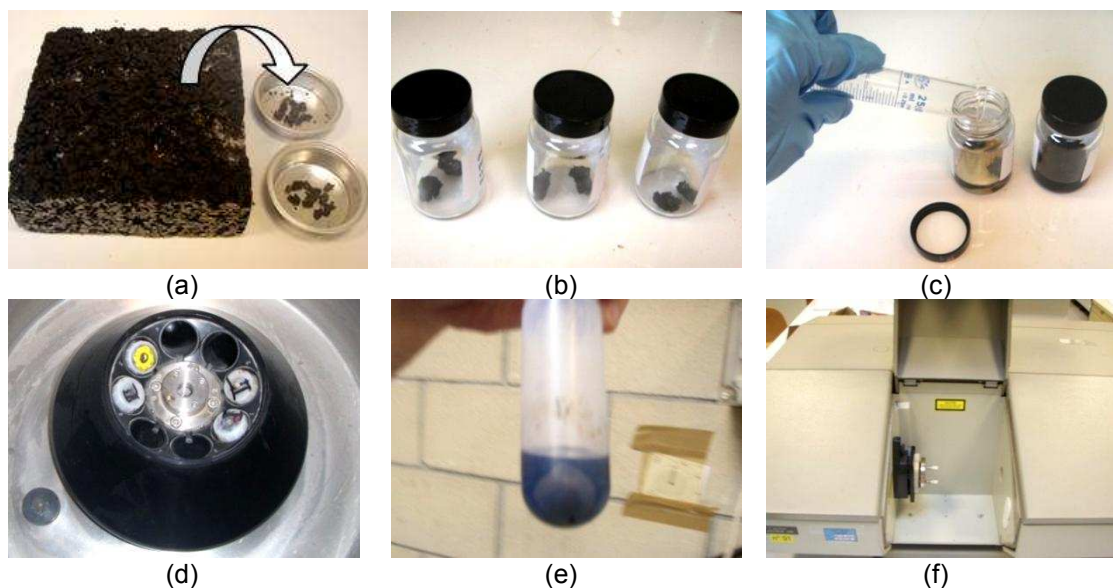
asphalt taken, for example, just on some aggregate particles. This will be studied in the following section.

On the other hand, as it has been already observed that the ISO index appears not to evolve compared to the ICO index, during aging in laboratory (Le Guern, 2011). In the following part, only Carbonyl Index (ICO) will be considered.

### 3.2. Evaluation of aging of asphalt extracted from aggregate particle using method M2 *Aging measurement protocol*

To study the aging of an asphalt mix surface, binder must be extracted from some particles taken directly at the surface exposed to air, sun and rain. In the previous section, it has been shown that only a small amount of binder is necessary using method M2. Quantity of asphalt coated on two particles should be enough. But, key point is to ensure a perfect separation between the binder and the aggregate particles, with attention to the complete elimination of the fines. Indeed, mineral particles disrupt infrared measurement. The following protocol is proposed:

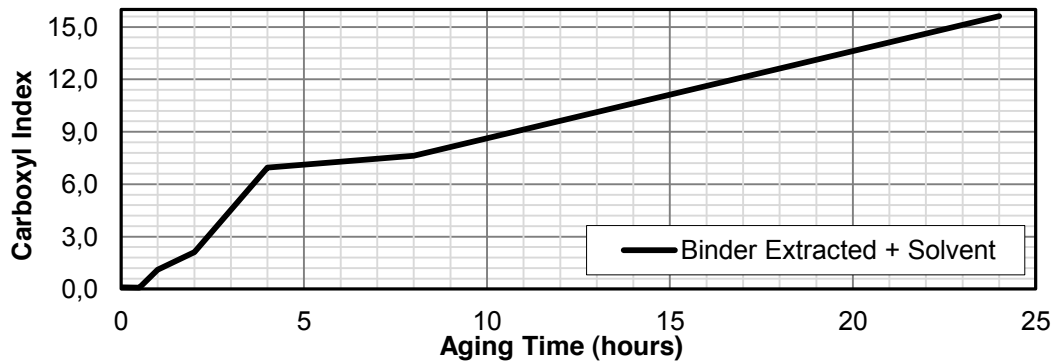
- Extract two grains of the surface of a asphalt mixture after aging (Figure 8 (a) and (b));
- In a glass bottle, put the two grains and 10ml of solvent and let it react during 30 minutes (Figure 8(c));
- Transfer the solution (solvent + asphalt + fines) to another bottle, leaving the coarse aggregate in the glass bottle;
- Use a centrifuge to make the separation between the fines and the solution (solvent + asphalt) for 20 minutes (Figure 8(d) and (e));
- Use infrared spectrometry to analyze the solution (method M2) obtained by centrifugation. Prior to the infrared analysis of the solution (solvent + asphalt), perform an infrared analysis of pure solvent Figure 8(f).



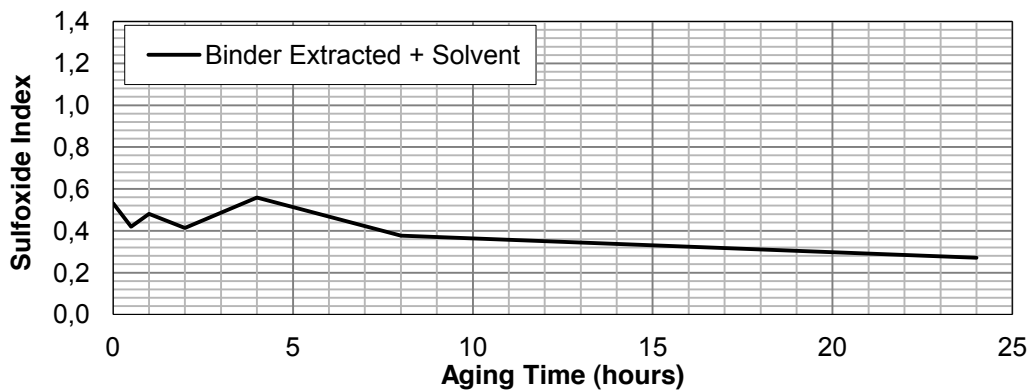
**Figure 8.** Steps of the analysis of aging (a) extraction of grains on the surface (b) samples with two grains of mixture, (c) grains in the solvent, (d) centrifuge, (e) solution after centrifugation and (f) infrared analysis

*Validation of the protocol*

Samples of the loose asphalt mixture (using the pure naphthenic binder: B1) were aged in stove during six different periods: 0.5h – 1h – 2h – 4h – 8h and 24h at a temperature of 180°C. Then, the samples were submitted to the asphalt extraction procedure presented above. In Figure 9, it is possible to observe that there is an increase of the CO index which characterizes the aging of the binder on the samples evaluated. Figure 10 shows that there is not an increase of the SO index. Thus, the new method from the extraction on two particles without any distillation of the asphalt binder, followed by the IR test, is able to characterize the aging kinetic of the asphalt mixture.



**Figure 9:** Carbonyl Index for the solution (binder extracted + solvent)



**Figure 10:** Sulfoxide Index for the solution (binder extracted + solvent)

**4. Applying the Method to the Evaluation of Natural and Laboratory Surface Aging**

Some compacted samples were aged in open air, which corresponds to a natural aging, while other samples were aged in an oven called Weatherometer (SUNTEST XXL+), allowing accelerated aging (Figure 11). This machine has an internal water tank for spray and humidity functions, so it is ideal for simulating weather effects. The Weatherometer machine is also equipped with filtered Xenon lights to reproduce solar radiation. Temperature is controlled using an air blowing system. Artificial aging parameters were chosen in order to apply during 40 days, one year of solar irradiance and rain in Nantes (France), where the natural aging is performed (820 mm of rain per year from 1961 to 1990 and average annual solar radiation of 215 MJ/m<sup>2</sup>). Hence, 500 cycles of 2 hours in the machine will be applied. Each cycle is composed of 2 minutes of watering and 118 minutes of drying. Relative humidity during the drying period is maintained at 70%. Irradiance (controlled in the UV range, 300-400 nm) is fixed at 60 W/m<sup>2</sup>. Temperature of the sample is maintained at 60°C.



Every month (for natural aging samples) or every three days (for accelerated aging samples), two grains of the mixture were recovered from the samples surface, in order to perform infrared tests. The three mixtures M1, M2 and M3 are tested in order to evaluate the binder effect on aging kinetics.



Figure 11: (a) natural aging and (b) test of accelerated aging (Zhao, 2011)

The ICO and ISO indices were measured for each sample. However, only the ICO index is presented here, because it has a more significant increase with the aging time. The results of the ICO evolution of the samples after the natural and accelerated aging are given in Figures 10 and 11. The curves respectively show the evolution of the ICO as a function of the two time scales (days in Figure 12 and months in Figure 13). In both cases, the ICO index increases with the aging time. However, the samples submitted to accelerated aging show higher final values of ICO, indicating a higher degree of aging at the end of the process. ICO indices don't stabilize during the time of the study showing that oxidation could continue until a higher value. Contrary to what we expected, 40 days of accelerated aging appears more severe than one year of natural aging. Indeed, ICO measured after 40 days of artificial aging is 2% superior to ICO measured after one year of natural aging, whatever the binder used.

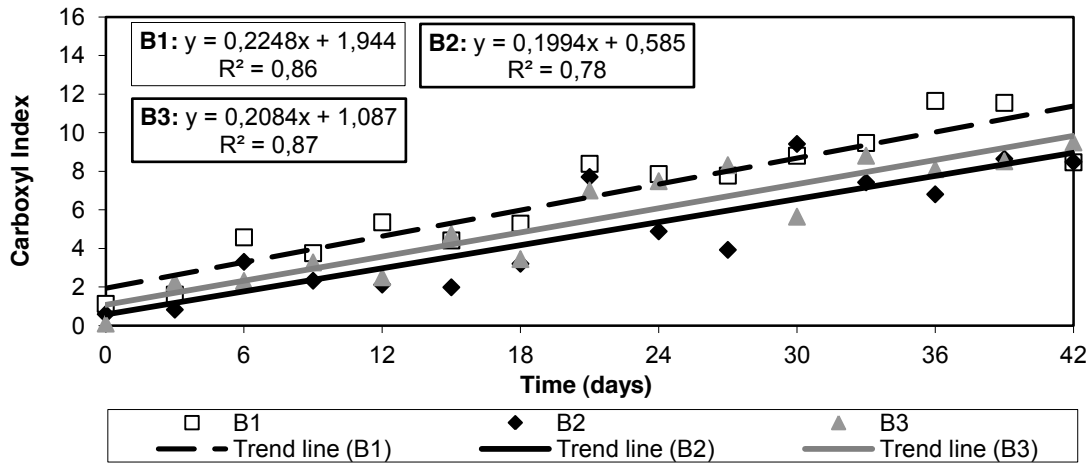


Figure 12: ICO as a function of the Accelerated Aging (adapted from Zhao, 2011)

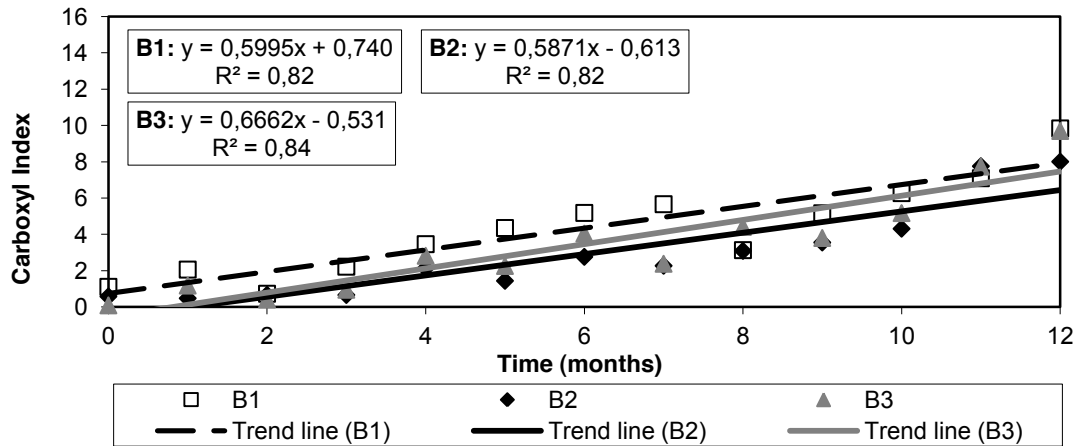


Figure 13: ICO as a function of the Natural Aging (adapted from Zhao, 2011)

Table 2: Synthesis of the slope and the R<sup>2</sup> values on ICO measures

Asphalt Type	Accelerated			Natural		
	Intercept (%)	Slope (%/day)	R <sup>2</sup>	Intercept (%)	Slope (%/month)	R <sup>2</sup>
Pure Binder (B1)	1,94	0,22	0,86	0,74	0,6	0,81
Binder + paraffin (B2)	0,58	0,2	0,78	-0,61	0,59	0,82
Binder + SBS (B3)	1,1	0,21	0,87	-0,53	0,67	0,84

In first approximation, ICO values are linearly interpolated. Slopes, intercept and R<sup>2</sup> values of the trend lines are shown in Table 2. Intercepts, which represent initial ICO indices, are negative in some cases. This non-physical effect has to be attributed to experimental scattering observed during ICO index evolutions in comparison to the assumed linear evolution. Nevertheless, regarding intercepts, ranking of the binders are the same for natural and accelerated aging. Moreover, for each aging condition, interpolated lines show similar aging kinetic whatever binders tested: 0.21 % per day for accelerated aging and 0.62 % /month for natural aging (mean value of slopes). Finally, using the aforementioned aging methods, it can be concluded that surface aging can be accelerated by 10 by means of the accelerated method, or in other words, 3 days of accelerated aging corresponds to one month of natural aging.

### 5. Conclusions

In this paper, the possibility to measure oxidation indices by infrared spectroscopy on a small amount of asphalt taken from some aggregate particles has been studied. This study has firstly verified that aging could be quantified by means of a FTIR analysis. Two conditions of analyses have been compared: the first one, the more used, consisting in laying the bitumen as a thin film on KBr pellets, and the second one consisting in dissolving the bitumen in a solvent. They have shown the same results for the same materials. Then, a new test method developed to characterize the aging of the surface of a surface layer has been presented. This method allows to recover the bitumen of some particles of the upper part of the asphalt mixture layer only. This method is quite more convenient for analysing surface aging because it needs fewer amounts of materials compared to standard methods. Finally, an accelerated method for aging surface bitumen has been proposed. A comparison between bitumen aged both on site and according to this accelerated method has highlighted that this method was relevant and could accelerate the aging of bitumen by a factor of ten. It will now possible to link aging of the surface to skid resistance. Further papers will focus on this subject.

### Acknowledgments

The first author would like to thank the financial support during the Master course from the Program of Human Resources Training in Petroleum and Natural Gas Science and Engineering (PRH/ANP-31). The research leading to these results has been partly performed by means of an apparatus funded by the Europeans Community's Seventh Framework Program (FP7/2007-2013) under grant agreement n° SCP-GA-2008-218747.

### References

1. AFNOR, NF EN 12697-33, Mélange Bitumineux – Méthode d'Essai pour Mélange Hydrocarboné à Chaud – Partie 33 : confection d'éprouvettes au compacteur de plaque, Juillet 2004.
2. AFNOR, NF EN 12697-35, Mélange bitumineux – Méthode d'Essai pour Mélange Hydrocarboné à Chaud – Partie 35 : Malaxage en Laboratoire, septembre 2007.
3. Farcas F. Étude d'une Méthode de Simulation du Vieillissement des Bitumes sur Route, Études et Recherches des LPC, Série Chaussées, CR21, Ed. LCPC, 1998.
4. Farcas F. Etude d'une Méthode de Simulation du Vieillissement sur Route des Bitumes. Thèse de Doctorat de l'Université Paris VI, 1996.
5. Farcas F., Mouillet V., S. Besson, V. Battaglia, C. Petiteau and F. Le Cunff. Identification et dosage des fonctions oxygénées présentes dans les liants bitumineux, 2010.
6. Isacson U. and Zeng, H. Relationships Between Bitumen Chemistry and Low Temperature Behavior of Asphalt. *Construction and Building Materials*, 11(2):83--91, 1997.
7. Kane Malal; Zhao Dan; Do Minh-Tan, Chailleux Emmanuel., Exploring the Ageing Effect of Binder on Skid Resistance Evolution of Asphalt , *ROAD MATERIALS AND PAVEMENT DESIGN*, Volume: 11, Special Issues: SI, Pages: 543- 557 DOI: 10.3166/RMPD.11HS.543-557, Published 2010
8. Le Guern, M. Structure Physico-Chimique et Résistance à la Fissuration des Bitumes. Thèse CIFRE TOTAL de l'Ecole Doctorale Génie des Procédés et Haute Technologie de l'Université de Pierre et Marie Curie, 2011.
9. Lesueur, D. The colloidal structure of bitumen: Consequences on the rheology and on the mechanisms of bitumen modification. *Advances in Colloid and Interface Science*, In Press, Corrected Proof, 2008.
10. Ramond G. and Such, C. Bitumes et Bitumes Modifiés - Relations Structures, Propriétés, Composition. *Bulletin de liaison des laboratoires des Ponts et Chaussées*, 168:65-87, 1990.
11. Zhao, D. Evolution de l'Adhérence des Chaussées : Influence des Matériaux, du Vieillissement et du Trafic – Variations Saisonnières, Thèse de l'École Doctorale Science pour l'Ingénieur, Géosciences, Architecture, 2011