Binder performance and testing

Methodology to evaluate oxidative ageing resistance of bitumen binders

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Abstract

A methodology, based on the use of PAV, developed in order to discriminate formulations in respect to their resistance to oxidative ageing will be presented. Statistical analysis of uncertainties will be discussed and different formulation ranked. The multi-criteria methodology developed allows to compare rapidly the impact of formulation on oxidative ageing resistance. For instance, it is demonstrated that standard bitumen base of the same grade can have different resistance to oxidative ageing. Other interesting results will be discussed during the presentation. Finally, this study evaluate the effect of binder oxidative ageing on asphalt mixes performances. It consists in comparing different asphalt mixes, changing only the used binder (standard bitumen, modified ones with polymers or other additives), keeping all other parameters constant. Ageing protocol and tests will be discussed. Clues about the ageing mechanisms and testing method will be discussed.

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1 INTRODUCTION

Roads age with time due to environmental conditions resulting in changes in asphalt properties. Road maintenance is costly, so the less communities have to maintain / replace their roads the better. There are many studies on the ageing of roads, and more precisely the ageing of bitumen even if it only represents 5% of the asphalt mixes, the other 95% being aggregates. Indeed, the binder has a key role in asphalt mixes and the degradation of roads is often caused by the deterioration of binder and the decreased adhesion at the binder/aggregates interface. There are several origins for the deterioration of roads:

- Chemical ageing of the binder: due to bitumen oxidation resulting in modifications of the matrix and hence a hardening and an increased susceptibility to cracking of the binder at macroscopic scale. The exact mechanism of bitumen oxidation is still discussed due to the complexity of the matrix and to the addition of simultaneous phenomenon **[1-5]**. Therefore, it is important to consider several ageing parameters in parallel.
- Asphalt degradation due to weather conditions which results in ageing of the binder. UV lights, presence of water and temperature variations are the most important factors and they are all linked. Thus, it is difficult to simulate ageing resulting from weather conditions **[7]**. Their impact on bitumen properties are similar to those induced by binder oxidation **[4-6]**
- Road traffic has also an important influence which is hard to totally separate from temperature variations and chemical ageing. The two main damages due to road traffic are fatigue cracking and rutting. Hardening of the matrix caused by bitumen oxidation limits rutting and may be responsible for a decrease in fatigue cracking resistance.

Hence, when studying road ageing topic, we need to consider 3 levels: binder, asphalt mix and road.

There are many ways to improve asphalt properties against ageing **[8-20]** by targeting each cause of road deterioration.

The aim of this project is to develop a "durable" binder which will have a longer longevity on roads in order to reduce maintenance and/or replacement costs and emissions. The other aim of this project is to develop a discriminating screening method to characterize the oxidative ageing kinetic of a binder using multiple criteria at both binder and asphalt scales. This method is complementary to methods of the industry to evaluate bitumen and modified binders. The present paper is focused on the results at binder level.

2 MATERIALS AND METHODS

2.1 Bitumen

Three 35/50 neat bitumen (A, B and C) from different refineries, and hence different crude origins, were studied for this research. Two specially designed bitumen of similar hardness were also studied, namely D and E. Formulation D corresponds to binder A modified with specific additives. Needle penetration (NF EN 1426) and ring & ball softening point (NF EN 1427) of each sample are summarized in **Table 1**. For the comparison of the results, base bitumen A was chosen as the reference bitumen.

Table 1. Penetration and softening point of the binders

			35/50 bitumen			Special bitumen	
Test	Unit	Standard	A (reference)	B	C	D	E
Penetration @25°C	dmm	EN1426	38	38	40	38	43
Softening point	°C	EN1427	52.2	53.0	51.4	54.4	57.8

2.2 Experimental work and data treatment

Oxidative ageing of binders is carried out using the PAV (NF EN 14769) for different durations ("Multi PAV") but always at 100°C and 2.1 MPa and directly on the fresh binder without going through a previous RTFOT step. In the PAV standard method, it states that degassing is possible if bubbles appear. In order to obtain the most repeatable method of oxidation possible, it was decided in this study to systematically place the binders removed from the PAV into a vacuum chamber at 15kPa and 170°C for 30 min to carry out the degassing step. In order to study the kinetics of oxidation, analyses are performed on the unaged binder marked t_0 and on the three levels of oxidation: 25 hrs in PAV, 48 hrs in PAV, and 72 hrs in PAV. Pushing further the PAV ageing enables better discrimination between binders as differences appear at longer oxidation time.

At each step of oxidation, the binders are characterized by empirical methods (commonly used in European specifications), but also by chemical and physical methods. The needle penetration (NP) test at 25°C according to NF EN 1426 and the softening point (SP) following NF EN 1427 were selected, as these methods are widely recognized in the industry as being simple and fast, and yielding easily interpretable information. The binders are also characterized by the following chemical methods: measurement of carbonyl (C=O) and sulfoxide (S=O) levels by infrared according to an internal method and the determination of the level of Total Acid Number (TAN) by the potentiometric method according to NF T66-066. Physical methods make it possible to determine the stiffness modulus by bending beam rheometer (BBR) according to NF EN 14771 as well as the complex shear modulus and the phase-angle (by DSR) according to NF EN 14770. For the DSR test, the measurements were carried out between 30 and 70°C with frequency sweeps of 0.1 rad/s to 100 rad/s, 10 points per decade and level of 10°C, and a temperature equilibrium time of 20 minutes on each level.

For each chemical and physical methods, the linear trend lines of the data evolution as a function of PAV duration were plotted. This enables the quantification of the evolutions of the selected parameters. In addition, the slopes give information about the kinetics of the oxidation and, indirectly, the "resistance to oxidation". By normalizing the values of the slope using equation (1) and taking bitumen A as a reference, it is possible to calculate the resistance to oxidative ageing based on the selected parameter.

$$normalized\ slope = 1 + \frac{slope\ of\ reference\ product - slope\ of\ product\ X}{slope\ of\ reference\ product} \qquad (1)$$

For the softening point, the value of ΔSP after 72 hrs of PAV (i.e., SP_{72hrs} - SP_{t0}) was also normalized following the equation (1) were the slopes are replaced by the value of ΔSP.

This way, we were able to present a spider chart to easily visualize a resistance to oxidative ageing based on multiple parameters.

2.3 Statistical analysis

The internal reliability of the binder oxidation method was established. This step is crucial in order to be aware of uncertainties and therefore determine if there are significant differences between the products under study. All tests were carried out in the same conditions six times on a 35/50 neat bitumen. This validation was carried out on samples after 25 hrs of oxidation in the PAV. The binders were characterized using the previously mentioned tests. Then, the same analysis was done with the same 35/50 neat bitumen after 48hrs and 72hrs of PAV. However, this was very time consuming so all the tests were only repeated three times.

3 RESULTS & DICUSSION

3.1 Statistical review

The internal reproducibility (IR) was established according to NF T90-210. If the difference between two values is superior to the IR, then the two results are significantly different. Furthermore, relative uncertainties for the different tests carried out were calculated by the following formula with a confidence level of 95%: $IR/\sqrt{2}$. We fixed the maximum acceptable uncertainty to 20% (figure coming from a common practice in water treatment field) and all the measurements showed sufficient accuracy level except for the BBR (ΔTc). To improve the accuracy of this measurement, an average of several tests must be carried out.

Table 2 lists the confidence interval according to the type of analysis and the duration of oxidation.

Table 2. Errors to consider according to the type of analysis and the duration of oxidation

Errors to consider								
Duration of oxidation in PAV [hrs]	Needle penetration [dmm]	R&B softening point [°C]	T (S) [°C]	T (m) [°C]	ΔTc [°C]	Carbonyl	TAN[1]	ΔSP[2] [°C]
0	2*	0,2	0,7	0,8	1	0,05	0,1	-
25	2,4	0,25	0,7[3]	0,8[3]	1[3]	0,05	0,1	0,5
48[4]	2	2	1,2	1,5	2,7	0,1	0,1	4
72[4]	1	2	1,4	1,8	3,2	0,15	0,1	4

**Value corresponding to the standard for a 35/50*

[1]Value obtained of 0.085 maximized to 0.1

[2]Value obtained by adding the errors on SP, supposing there could be two errors combined (on the SP at t0 and that after oxidation)

[3]Default value taken as those obtained after 25 hr of PAV (maximized error)

[4] all of the error bars obtained on the long oxidation times are maximized. For the IR, BBR and SP tests in particular we consider that the error will increase with the duration of the PAV according to tests carried out on a binder after 72 hrs PAV. Though the number of tests carried out are not sufficient for a statistical conclusion, the deviations observed between the values were deemed significant.

This table is extremely important, as it will be referred to throughout the entire analysis of the gathered data in the form of error bars.

3.2 Resistance to oxidation of the bitumen base

What kind of variability is due to the bitumen base? This question occurs when the bitumen base varies, no matter its intended application. The present study assesses the impact of this parameter on oxidation resistance. To do so, three bases of the same grade (35/50) coming from different crude origins were studied. Using the entire set of the results obtained from these three bases at different levels of oxidation and the calculating method presented before, it is possible to draw a spider chart of the oxidation resistance of the binders (binder A is used for the reference) shown in **Figure 1**.

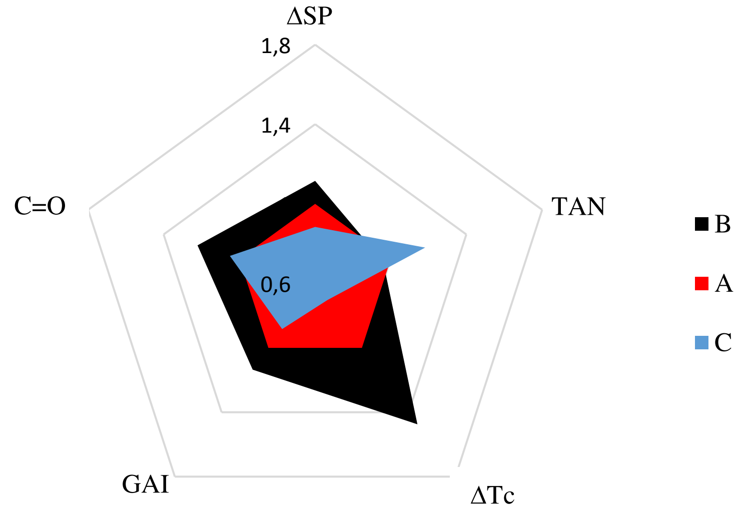

Figure 1: Overall view of the multi factor characterization of resistance to oxidative ageing

C=O represents the oxidation resistance based on carbonyl index which is determined from carbonyl peak integration. TAN represents the oxidation resistance based on the evolution of acidity of the bitumen matrix as it increases with ageing. One of the rheological parameter, GAI ("Complex Modulus (G*) Ageing Index") is calculated following equation (2) to trace the trend lines with duration of PAV and calculate the normalized slopes.

$$GAI = \frac{G^*_{after\ ageing}}{G^*_{t0}} \qquad (2)$$

The **Figure 2** shows the evolution of the GAI according to the angular frequency and for different levels of oxidation (25 and 72 h) for the three neat bitumens.

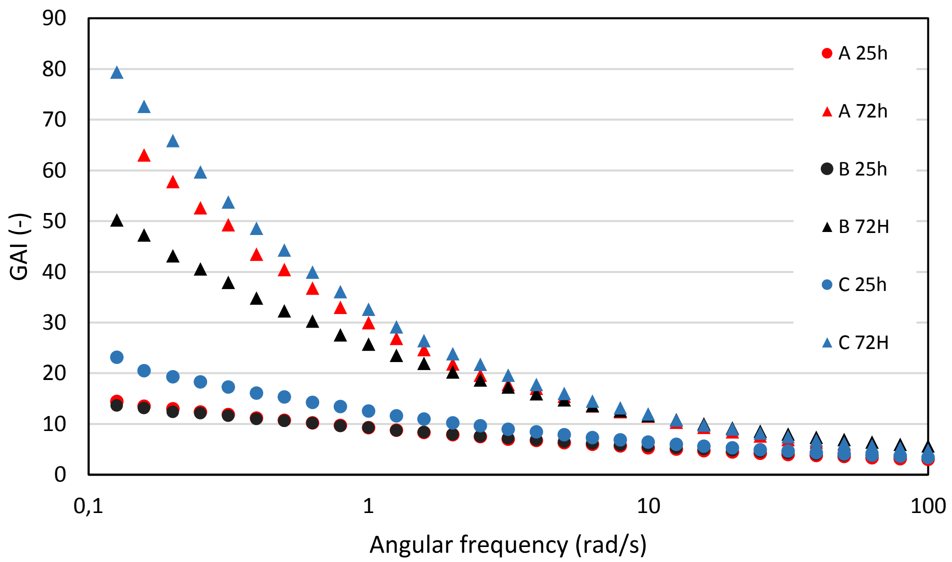

Figure 2: GAI at 30°C as a function of angular frequency

In order to assign an oxidation resistance value based on the GAI, we have chosen to set the GAI at a temperature of 30°C – temperature of service – and an angular frequency of 1rad/s. This temperature and this frequency have been chosen after an analysis of data showing that, in these conditions, the behavior of the GAI is linear to the duration of oxidation in the PAV. In addition, the ageing tendency seen through the frequency sweep at 30°C is well represented at 1rad/s. ΔTc is calculated by subtracting T(m=0.3) from T(S=300MPa). T(S=300MPa) and T(m=0.3) were obtained from BBR test and corresponds respectively to the temperature for which the stiffness is 300 MPa and the temperature for which the slope is equal to 0.3. Regarding the different indexes used, we observe that the ΔTc makes it possible to differentiate the three bitumen bases in a significant way.

More generally, the multi-factor analysis makes it possible to strengthen conclusions as the observed trends for the different indicators are generally coherent and consistent (except for TAN index). Indeed, when considered separately, the criteria could be put into question and may present significant uncertainties while the multi-factor evaluation makes it possible to smooth over these effects.

On this spider chart (**Fig. 1**), the higher the area of the spider score is, the better the performance of the binder is. Then, it is easy to see which binder is the most resistant to oxidation: the best one is binder B followed by A and C. This shows that the oxidation resistance for neat binders of the same grade but from different sources, varies significantly and perceptibly with the different test methods used in this study. The important role of crude origin is highlighted here.

The difference in oxidation resistance for the three neat bitumens of the same grade have strong implications in the comparison of special bitumen. Indeed, an accurate comparison of two different additives requires to use them in the same neat bitumen. If the products are prepared from different bases, then it is not possible to compare the effect of one additivation solution to another, but only the combination of both the effect of the base and the additive.

3.3 Resistance to oxidative ageing of modified binders

In this part of the project, two special binders were studied to assess the influence of additivation on resistance to oxidative ageing. For that, binder A (reference) was modified to obtain binder D. However, binder E was manufactured using a different bitumen base from binder A. Thus, the effect of additivation could not be fully assessed. However, the performance of the whole formulation E compared to the reference binder A was studied. The results are detailed below.

3.3.1 Empirical tests

The evolution of needle penetration with oxidation time was determined and this index was again not very discriminant. We observe that, at t_0, the SP of the binders are quite different (**Fig. 3a**). The presence of additives in the bitumen has an impact on the SP. In an interesting and rather unexpected manner, binder E has a rather high SP (57.8°C) for a weaker penetration value than the reference bitumen (43 vs. 38 for the reference). Modification made to produce binder D has very little impact on the SP (54.4°C vs. 52.2°C for the reference).

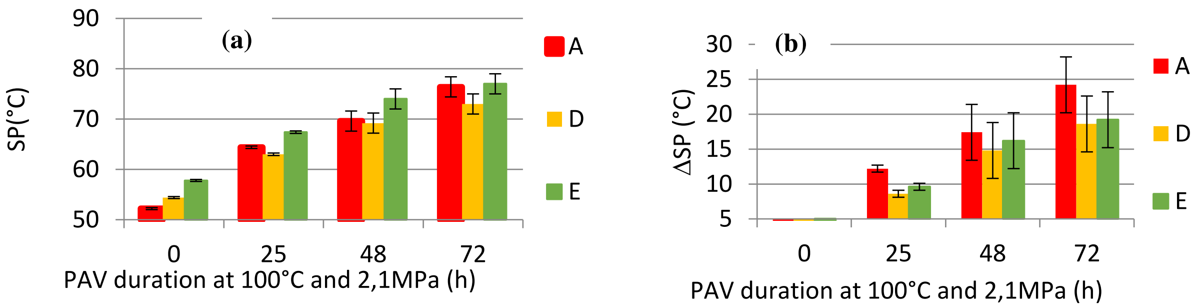

Figure 3: Evolution of SP (a) and ΔSP (b) with oxidation

3.3.2 Chemical methods

Following the evolution of carbonyls (**Fig. 4a**), we can observe that they do not have the same sensitivity to oxidation with rather different evolutions in the carbonyl index. The TAN values are significantly different for the formulations tested (**Fig. 4b**). Formulation E has the lowest TAN, no matter the duration of the oxidation considered.

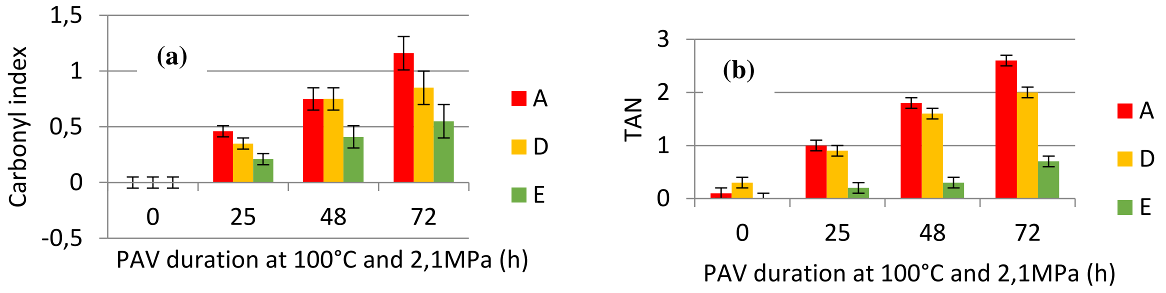

Figure 4: Evolution of carbonyl (a) and TAN (b) with oxidation time

3.3.3 Rheological tests

Rheological analyses bring very interesting results on the studied formulations.

First, regarding the low temperature properties (**Fig. 5**), we observe that the values obtained for binders A and D are very close on both the T(S=300MPa) and the T(m=0.3) at t_0. Thus, in the present study, the initial properties with respect to the BBR are strongly dependent on the bitumen base used. Binder E shows good low temperature properties at t_0 with values inferior to up to 5°C to those obtained for the other binders. However, as binder E is not based on bitumen A, it is not possible to differentiate the effect from bitumen base from the additivation effect.

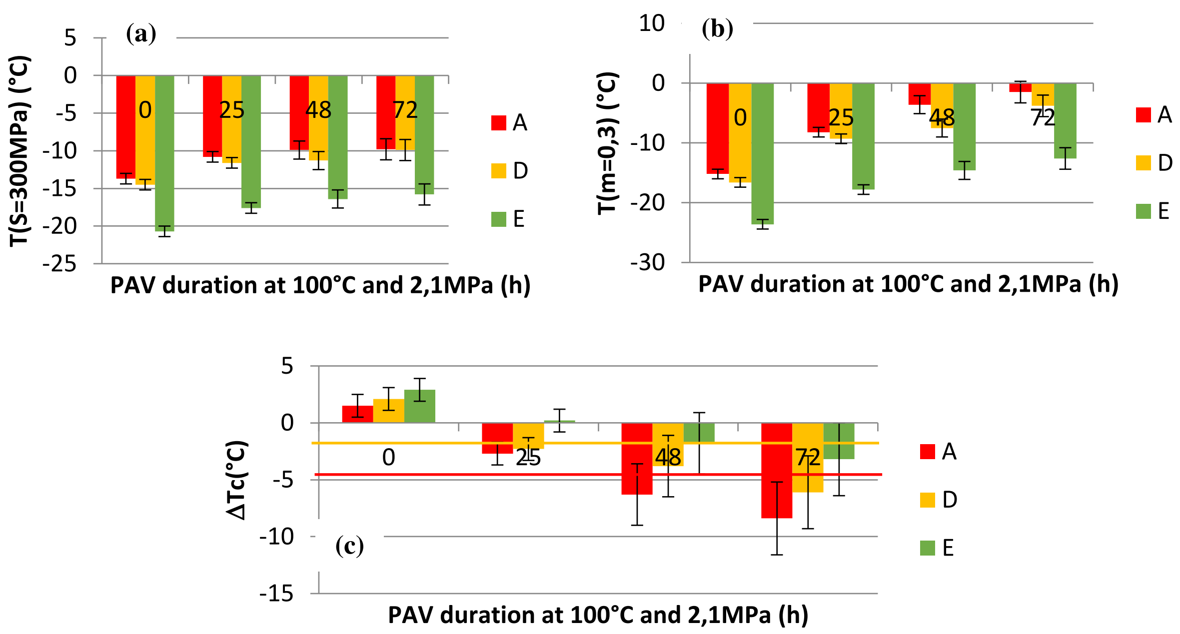

Figure 5: Evolution of T(S) (a), T(m) (b) and ΔTc (c) with oxidation time

Binders A and D show similar value of ΔTc after 25hrs of PAV and are close to the limit of microcracks appearance (-2.5°C), while binder E still has a slight positive ΔTc. After 72hrs of PAV, binder E appears to be near the limit of -2.5°C, while the two other binders have exceeded the limit of -5°C (macrocracks appearance) as reported in the literature **[21-22]**.

Figure 6 shows the Black curves at t_0 for the 2 special bitumen and the reference binder A, enabling the understanding of their global rheological behavior. The Black curve for binder A is typical of a standard bitumen: it is globally viscoelastic except at high temperature and low frequency (upper left part) where the bitumen behaves as a liquid (δ=90°C).

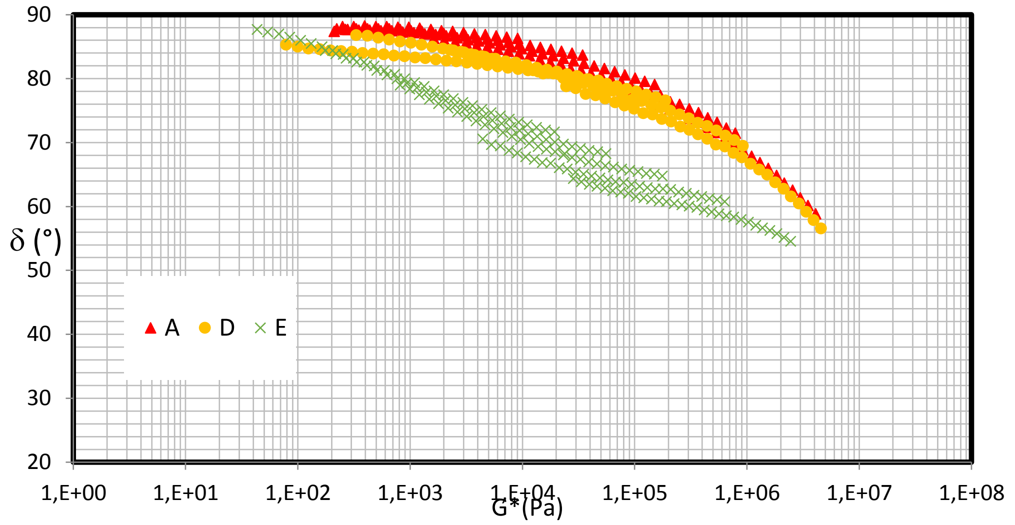

Figure 6: Black curve of the three binders at t_0

The modification made to obtain binder D has relatively little overall effect on the Black curve. We can however observe a shift toward lower phase angles for the same modulus values, which indicates a slightly less "liquid" behavior. Binder E has a very unfamiliar rheological behavior compared to a standard bitumen with appearance of wave effects. Indeed, binder E presents a less viscous-liquid like behavior compared to binder A as its phase angle through temperature and frequency sweeps is lower, especially at medium-lower temperature of the test conditions.

Figure 7 shows the evolution of the Black curves for both special binders and for binder A with oxidation duration.

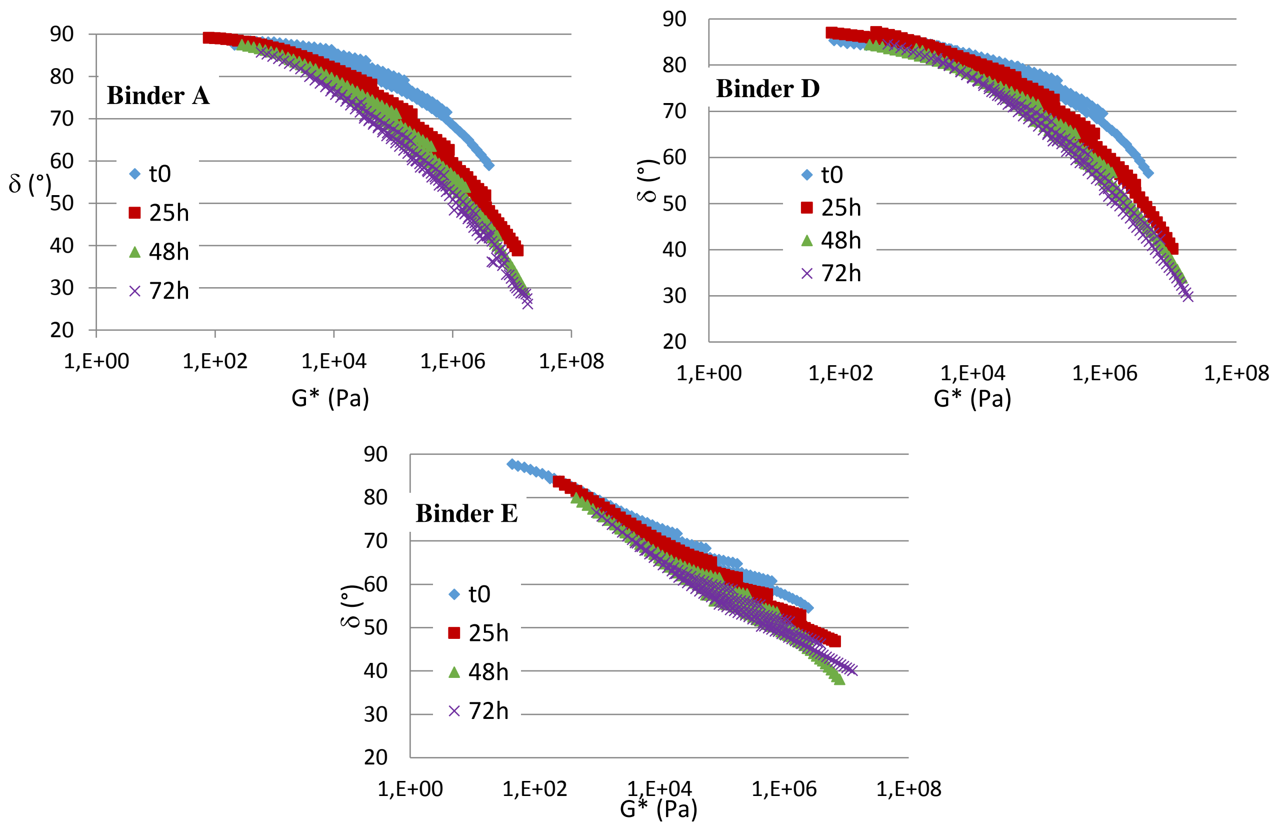

Figure 7: Black curves of the three formulations with respect to oxidation duration

The variation range of the Black curve for binder E with oxidation is noticeably narrow: the curve remains roughly the same with oxidation.

Binder D has a similar behavior to reference binder A, no matter the level of oxidation. Looking closely at the curves, we notice an inversion for binder D. At t_0, Binder D presents lower phase angle for the same modulus, while after oxidation (for example: after 72hrs of PAV), Black curve for binder D is higher than that of binder A (**Figure 8**). This inversion indicates that the modification to obtain binder D influences the reaction of bitumen to oxidation. The mechanism is probably multifactorial and has to be further investigated.

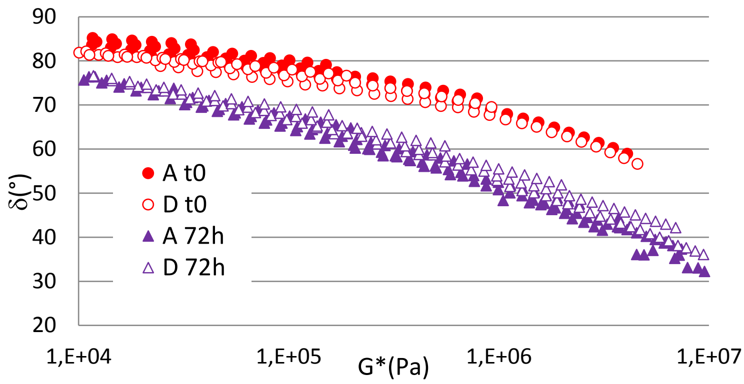

Figure 8: Black curve of binders A and F at t_0 and after 72 hours of PAV

3.3.4 Multi-factor overview of the results

The same methodology as the one used to study the three binders of the same grade was used to differentiate the binders studied in this part. The obtained spider chart representing the resistance to oxidation of the different formulations, like the one presented in Part 3.2 is shown in **Fig. 9**.

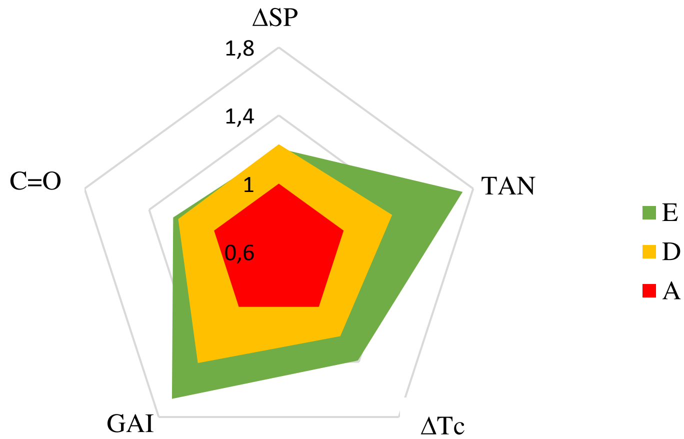

Figure 9: Resistance to oxidative ageing of the four formulations

Binder E shows the biggest area, making it the formulation with the greatest resistance to oxidation based on the criteria studied here. However, the bitumen base used to obtain this binder was different from the reference binder (A) which may have a significant impact as we have seen previously. Thus, it is not possible to conclude on the additivation influence but only the performance of the whole formulation. In addition, additivation on binder A to obtain binder D has also a positive effect on oxidation resistance as it shows significantly larger range than binder A. These may be indirect effects.

Figure 10 shows the comparison of all the binders studied here (three neat and two modified binders) still taking binder A as the reference.

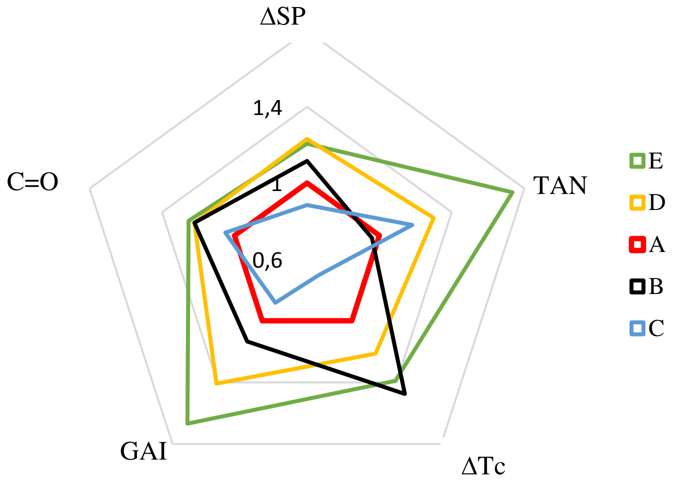

Figure 10: Multi-factor characterization of the resistance to oxidative ageing of all the binders

In the final ranking of the different formulations in this study with respect to resistance to oxidation, specially developed binders showed better performances than neat binders. Binder E was the most resistant and the least was binder C.

On top of this study, additional framework methods dedicated to ageing evaluation were carried out under the cooperation with the Western Research Institute **[23]** in the United States in order to obtain complementary information about oxidation kinetic aspect regarding additivation to reduce binder ageing.

4 CONCLUSION AND PROSPECTS

A methodology for studying the oxidation resistance of bituminous formulations was presented and assessed. This methodology made it possible to represent the oxidation resistance of the different formulations under study in the form of a spider chart. We can therefore quickly and visually assess the impact of the formulation on oxidation resistance.

This methodology proves that standard bitumen base of the same grade may have very different levels of oxidation resistance. Thus, crude oil origin plays a significant role in bitumen properties.

We can state that the properties of special binder E of grade 35/50 studied in this paper, change less with oxidation than the other products at binder level.

Moreover additivation used to obtain special binder D from binder A has a significant positive impact on its resistance to oxidation.

It is important to notice the limitations of this method. The present approach features criteria that may be strongly impacted in the case of certain formulations, especially those modified with polymers. The addition of another criteria to assess the elasticity of the binder will probably complete the methodology and help to give a better assessment of formulations modified with polymers.

Further experience with the method, increased data, and the link with asphalt properties scale and field scale will make it possible to refine the assessment criteria. In this study, only the factor of oxidation was assessed, although, as mentioned earlier, oxidation is only one of the components of durable road pavement. Therefore, it is key to connect the results obtained here and the properties of asphalts produced from the same binders. On the other hand, the study of the influence of RAP on the oxidation resistance properties of promising formulations is crucial. Likewise, the recyclability of the formulations in question must be assessed.

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