# QUALITATIVE CORRELATION BETWEEN AGGREGATES DISTRIBUTION AND MECHANICAL BEHAVIOUR OF PURE, AGED AND DOPED BITUMEN

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## ABSTRACT

*Aging of base bitumen has certainly consequences on its structure, morphology and rheology behaviour. By means of some chemical physics techniques such as nuclear magnetic resonance (NMR) and dynamic shear rheology (DSR), we investigated on a 70/100 penetration grade straight bitumen, which was successively processed by rolling thin film oven (RTFO) and also extracted from naturally aged roads (RAP). In the process of recycling, the last was modified by adding commercial doping substances aiming to evaluate their influence on the structure and morphology of the aged bitumen. We combined the data from the used techniques to evaluate their reliability and to obtain new information. The results reflect the changes in the distribution of the aggregates of the original, aged and doped bitumen. The mechanical and thermal behaviour of the investigated materials have been related to the presence of the different types of macro-aggregates.*

**Keywords:** DSR, Bitumen Rheology, NMR relaxation, Bitumen recycling

## 1. INTRODUCTION.

The thermoplastic nature, water resistance and adhesion properties of bitumens, make them fruitfully adopted as binders in road construction and roofing systems. As matter of fact there is a growing customer expectations in terms of environmental impact of the production processes of bitumens while on the other hand a special attention is devoted to the energy cost saving. For example road paving companies, use to remove and recycle deteriorated aged asphalt (RAP) that has been literally scratched out from roadways by huge mechanical tools [1]. In general aged bitumens have higher processing temperature because some of the aromatic components and resins, that give a certain grade of mobility, are oxidized so that their fluidity is reduced [2]. Nevertheless to give a new life to the used bituminous materials, they are currently doped by substances that make their performance suitable for a reuse. In this field the mechanical properties of bitumen are the result of the chemical composition and phases arrangement of the molecular structures. So far, the correlation between the supra-molecular level and the macro-behaviour of the material, is still poorly described. Indeed the characterization of the bituminous materials for its convenient application, is still made by empirical standardized tests. From a simplified point of view, stated the colloidal model [3], the two major constituents of the bituminous materials are asphaltenes and maltenes with the first as the dispersed phase and maltenes as the continuous phase [4]. Asphaltenes are mainly constituted by condensed polyaromatic structures containing alkyl chains, hetero-aromatic compounds with sulphur in benzothiophene rings and nitrogen in pyrrole and pyridine rings. Asphaltenes may also contain polyfunctional molecules with nitrogen, as amines and amides; oxygen, nickel and vanadium metals which are complexed with pyrrole nitrogen atoms in porphyrin rings [4,5]. Considering their chemical structure, asphaltenes are the rigid part of the bitumen [6]. Maltenes are the soft portion of the material and they are constituted by resins, aromatic hydrocarbons, olefins, cyclic saturated hydrocarbons and straight or branched chain saturated hydrocarbons (paraffins) [4]. The rheological behaviour of bitumens is ruled by the chemical-physics interactions of the macro-aggregates and it is strongly dependant on temperature [7]. In the last years researchers focused their attention on the performances of bituminous materials because they play a crucial role in the performance of the corresponding asphalt mix [8-11]. Bitumens should be able to relax the applied stress and, at the same time, their rigidity should not exceed a given value especially at low temperature [12]. Besides the conventional tests, new approaches for the characterization of bituminous materials are developing [13-16]. Different rheological techniques are demonstrated to be a valuable and more sensitive way to asses bitumen properties [17]. Hence a deeper knowledge of the chemical composition as well as the morphology of the bituminous binder is essential to design new additives and the relative obtained materials. In this frame we performed rheological tests and exploited nuclear magnetic resonance by applying for the first time the inverse Laplace transform, trying to find a correlation between molecular organisation and mechanical behaviour.

## 2. MATERIAL AND METHODS.

For the present work we used a 70/100 penetration grade bitumen which was produced in Saudi Arabia. To obtain the corresponding oxidized-recycled material a UNI EN 12697/35 procedure has been used. The inert materials were thermostated at 200 °C, fresh straight bitumen (4% w/w of the mixture) is warmed up to 160°C, while the asphalt removed directly from roads (30% w/w of the mixture) is left at room temperature . A Infratest Laboratory mixer 30 $l$ , has been used to prepare the conglomerate and after 120 seconds it was poured into a metallic container. Successively a 5Kg sample was distilled to 1 kg by means of a Tecnotest bitumen extractor with pyrex jar, using perchloroethylene as solvent. To separate the filler from the perchloroethylene/bitumen solution, a Tecnotest steady flow centrifuge was used. The solvent was evaporated by means of a Tecnotest cut-back electric distiller, then a rotavapor procedure was performed to ensure that all of the solvent was removed. To make the conglomerate re-processable two commercial additives were used to obtain two different materials. The ACF20 was added in a 0.9% w/w ratio to the recycled conglomerate. This additive is considered an adhesion promoter of the bitumen to the inert materials, hence it is added by spraying it onto the inert stones [18] . Chemically it is a mixture of aromatic oils and an amidic surfactant. The WML was added in a 0.4% w/w ratio in order to lower to 160/170 °C the temperature of the fresh inert materials in the re-processing procedure [19] . Chemically it is a benzosulfonamide molecule that gives back some of the aromatic parts which were lost in the aged product and contemporary the molecule acts as a surfactant on the surface tension of the bituminous mixture. All the products and their preparation were obtained in collaboration with StarAsphalt S.p.A., S.P. Piana Loc. Garga, 87010 - Saracena (CS) – Italy

### 2.1 Empirical characterization.

The ring and ball test (R&B T) [ASTM Standard D36-D36M, 2009] was used to determine the bitumen softening temperature. The test was performed by ring and ball apparatus B530 (Tecnotest, Italy). According to the standard procedure (ASTM D946), the bitumen consistency was evaluated by measuring the penetration depth (PN) (531/2-T101, Tecnotest, Italy).

### 2.2 Rheological characterization.

Temperature-ramp test experiments were performed on the bitumens. Rheological measurements were conducted using a shear stress controlled rheometer SR5 (Rheometrics, USA) equipped with plate-plate geometry (gap 2.0 mm, diameter 25 mm). The temperature was controlled by a Peltier system (±0.1 ∘C). All the experiments were performed in cooling (1 ˚C/min at). All the experiments have been carried out by using dynamic shear technique (1 Hz). The small amplitude dynamic tests provided information on the linear viscoelastic behavior of materials through the determination of the complex shear modulus [20]

$$G^*(\omega) = G'(\omega) + iG''(\omega) \tag{1}$$

where $G'(\omega)$ is the in phase (or storage) component, and $G''(\omega)$ is the out-of-phase (or loss) component. $G'(\omega)$ is a measure of the reversible, elastic energy, while $G''(\omega)$ represents the irreversible viscous dissipation of the mechanical energy. The applied shear stress of 100 Pa ensures to perform the dynamic rheological tests within the linear visco-elastic region.

## 2.3 NMR measurement and Inverse Laplace Transform.

For the ^{1}H spin-spin measurements we used a homemade NMR instrument. It operates at a proton frequency of 15 MHz. Measurements have been performed at different temperatures ranging from 130 to 25 °C with an error of ± 0.1°C. A classic Carr-Purcell pulse sequence was applied to record the echo decay [21]. The applied width of π/2 pulse was 5.9 μs and that of π pulse was 11.8μs. The τ1 delay time was 0.05 ms.. The $T_2$ is called the spin-spin relaxation time, because the relaxation is concerned with the exchange of energy between spins via a flip-flop type mechanism. It is defined according to:

$$\upsilon_{1/2} \approx \frac{1}{T_2} \tag{2}$$

where $\upsilon_{1/2}$ is the linewidth at half height of a resonance line. In a perfectly homogeneous field the time constant of the decay would be $T_2$ ; but, in fact, the free in signal decays in a time $T_2^*$ that often is determined primarily by field inhomogeneity. A method for overcoming the inhomogeneity problem is to apply the Carr–Purcell technique (CP) [21].
Usually the relaxation time varies all over the sample because of the sample heterogeneity or surface relaxivity differences, then a multi-exponential attenuation of the CP envelope should be observed. Hence if inside the sample, a continuous distribution of relaxation times exists, the amplitude of the nth echo in the echo train is given by:

$$A = A_0 \int_0^\infty P(T_2) e^{-\frac{2\pi\tau}{T_2}} dT_2 \tag{3}$$

where A is the amplitude of the nth echo in the echo train and $A_0$ is a constant depending on the sample magnetization, filling factor and other experimental parameters and $P(T_2)$ is the $T_2$ relaxation time probability density. The last Equation suggests that the analysis of the experimental data using an Inverse Laplace Transform (ILT), might provide the relaxation time probability function [22].
Let f(t) be a function defined for t ≥ 0; the function $L$[f(t)] introduced by means of the expression,

$$L\big[f(t)\big] = \int_0^\infty f(t) e^{-st} dt \tag{4}$$

is the real Laplace Transform of f(t). The inverse process, indicated by the notation f(t)=$L^{-1}$[F(s)], is termed Inverse Laplace Transform (ILT). In the present work the ILT have been performed using an homemade software based on CONTIN [22,23]. This is an iterative fitting software and it has been improved in order to extrapolate the data from the experimental $T_2$ decay. For a given CP decay, there are a certain different number of possible combinations of times which fit well the solution, especially in presence of signal noise. Therefore, the numerical ILT must be used with caution when interpreting the experimental results. As a matter of fact we cross-linked the ILT numbers with the other experimental techniques.

## 3.    RESULTS AND DISCUSSION.

In the present work we investigated four samples based on a 70/100 penetration grade bitumen as it was taken as straight, extracted and finally added with two different doping substances in order to be recycled. We firstly performed an empirical

standard characterization by measuring the penetration grade and the softening point. As expected the bitumen became harder after the reprocessing procedure as its PN is lower and the R&B temperature is higher. This is due to the presence of real aged bitumen and to a partial oxidation of the fresh bitumen after reaching the temperature of production. The RTFO processed sample has intermediate values between the straight and the extracted bitumens. The two additivated samples which, have very close values of PN and R&B to that of the unadditivated extracted bitumen (table 1). However, as matter of fact, the additives make the regenerated conglomerate (bituminous mixture) more workable and, in the case of the WML, processable at a lower temperature.

**Table 1. Penetration depth (PN),Softening point (R&B)and Transition from visco-elastic to liquid (Stress Controlled Rheometer, SCR- ΔT )for all of the investigated samples.**

|  | PN dmm | R&B (°C) | SCR-ΔT (°C) |
|---|---|---|---|
| Straight bitumen | 72 | 48 | 60-64 |
| RTFO (75 mins) | 50 | 53 | 80-84 |
| Extracted bitumen | 31 | 59 | 98-105 |
| Extracted+0.9%ACF20 | 29 | 62 | 95-101 |
| Extracted+0.4%WML | 33 | 59 | 92-98 |

SCR- ΔT is the temperature range for the bitumen to pass from visco-elastic to liquid regimen. The discrepancy between the SCR- ΔT and the R&B temperature is due to the fact that the SCR- ΔT is a non-perturbative observation, and then it shows the intrinsic behavior of the material. Nevertheless the penetration index as well as the R&B tests are nonlinear/perturbative measurements. By means of rheology temperature-sweep experiments, the evolution of the storage and loss moduli is continuously monitored during a temperature ramp, at a constant cooling rate (1°C/min) and at a frequency of 1 Hz. Figure 1 shows the time-cure for all of the investigated samples. The temperature at which the elastic modulus G′ begin to have a non-linear behaviour can be considered as the beginning of the transition temperature and the whole process, from viscous to liquid regime, ends when G′ modulus is no longer detectable. In table 1 we see that the addition of the doping substances has a little influence on the transition temperature. However for the straight bitumen the loss modulus (G") is always greater than the storage modulus along the considered temperature range, while for all of the other samples both moduli have similar values at low temperatures. For all samples both moduli decrease as temperature increase. The thermal effects are more evident on the elastic component that, at a critical temperature, goes sharply to zero evidencing the complete transition from a viscoelastic to a viscous liquid regimen. This rheological behaviour is often described by a colloidal model considering bitumen as a multidisperse micellar system with a rather complicated internal structure based on asphaltenes micelles dispersed within a maltene phase [2, 24]. According to this model, the bitumen is described as a weak gel made by asphaltenes aggregates interacting each other and entrapping the liquid maltene phase [2]. Figure 1 shows the time cure test for all the samples.
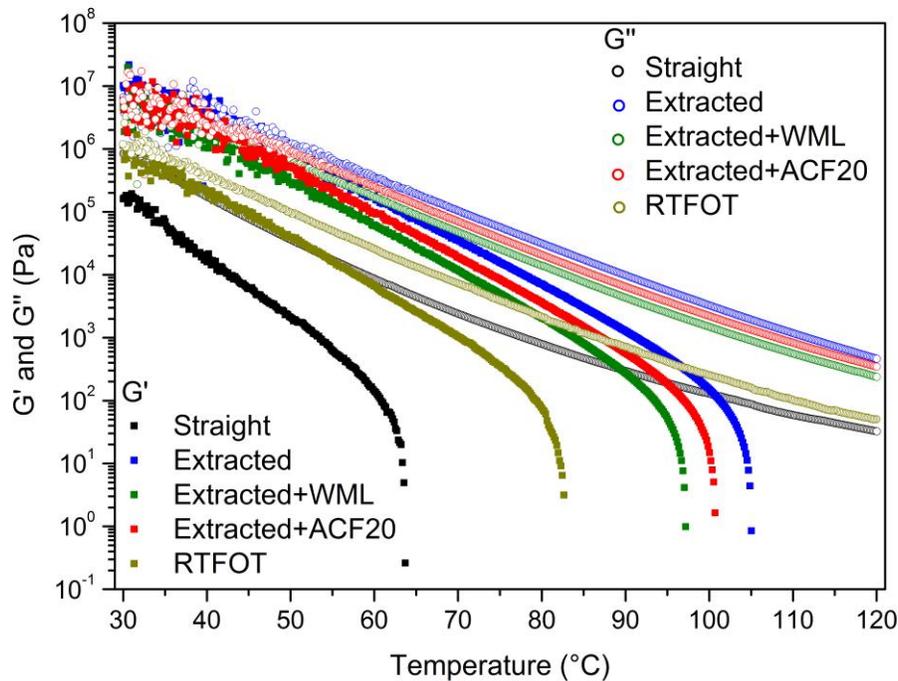
**Figure 1. Time cure test at 1 Hz in the range 30-120°C for all of the bitumen samples.**

Even though the typical trend is similar for the different samples, a discrepancy in transition temperatures and in the numerical values of the moduli can be observed. The extract bitumen (blue lines in figure 1) shows both transition temperature and moduli values higher than the other products. Most likely this effect is the result of an increased fraction of ashaltenes due to the oxidation processes of the resinous materials. This asphaltenes enrichment might cause a stronger interaction between the asphaltene particles, making the material harder or more elastic according to rheology language. Both ACF20 (red lines in Figure 1) and WML (green lines in Figure 1) induced a lowering of the transition temperature from viscoelastic to liquid regimen (SCR-$\Delta$T in table 1). They also reduce the values of the moduli thus making the system less rigid than the simply extracted product. The additive WML seems to have a greater effect in terms of loss of elasticity. As already mentioned, this additive has a bipolar nature. We suppose that the surfactant action of this molecule might reduce the associative interactions between the asphaltene particles by interposing itself between the polar part of asphaltenes and the non polar maltenes. This effect results in a weakening of the colloidal network and consequently a lowering of the transition temperature. The sample that has been RTFO processed (olive-green lines in Figure 1) shows a similar rheo-trend of the extracted bitumen. However it is clear that a longer RTFO treatment is required to obtain a model closer to the real aged bitumen and this is currently the objective of the next work. In order to better clarify what happened at a supra-molecular level to the oxidized-extracted bitumen and the correspondent additivated products, we performed a $^1$H-NMR analysys, by measuring the $T_2$ relaxation time.
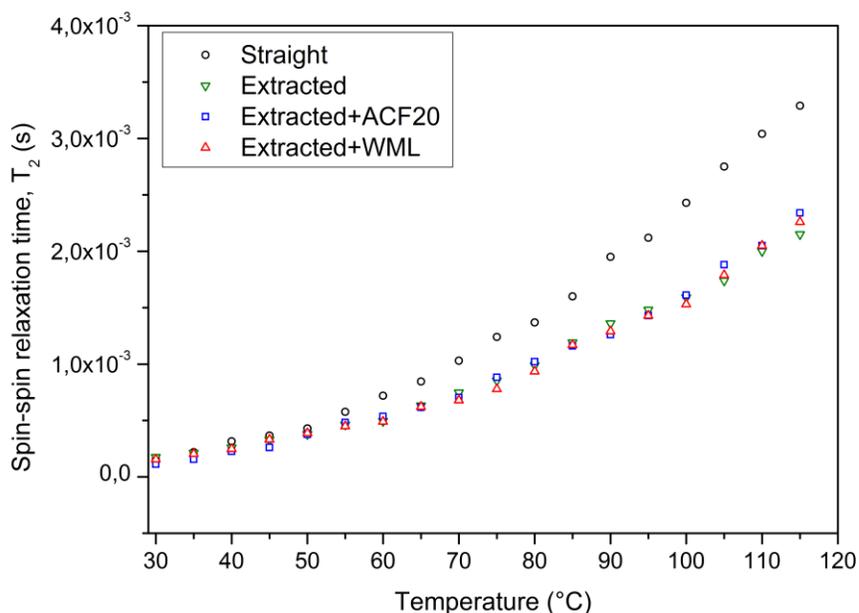
**Figure 2. Plot of the $T_2$ times as a temperature function for all of the samples.**

Considering the description given in the materials and methods section, the spin-spin relaxation time of a material can be a measure of the molecular mobility, under certain conditions. The relaxation process, in fact, is more efficient when the material is rigid, that corresponds to shorter relaxation times. As matter of fact, higher temperatures correspond to longer $T_2$ times. Hence we measured the proton $T_2$ time along temperature for all of the samples. The results, shown in Figure 2 reveal again that the straight bitumen has a greater mobility (softer) than the extracted. Also in this case we cannot appreciate any difference between the values and trends of the extracted and doped bitumens. As mentioned above the $T_2$ time is obtained from an exponential decay which is the envelope of the recorded echo signals. When the material is not homogeneous, the measured $T_2$ is averaged over all of the contributions of the different macro-structures. These parts have a different intra-molecular arrangement and interactions and they relax-back to the equilibrium in different characteristic $T_2$ times, contributing to the measured echo envelope differently. A sophisticate mathematical process to obtain the $T_2$ distribution times, is to apply an Inverse Laplace transform (ILT) to the measured echo envelope, along temperature. Figure 3 shows the ILT of the straight (A) and extracted (B) bitumens at different temperatures.
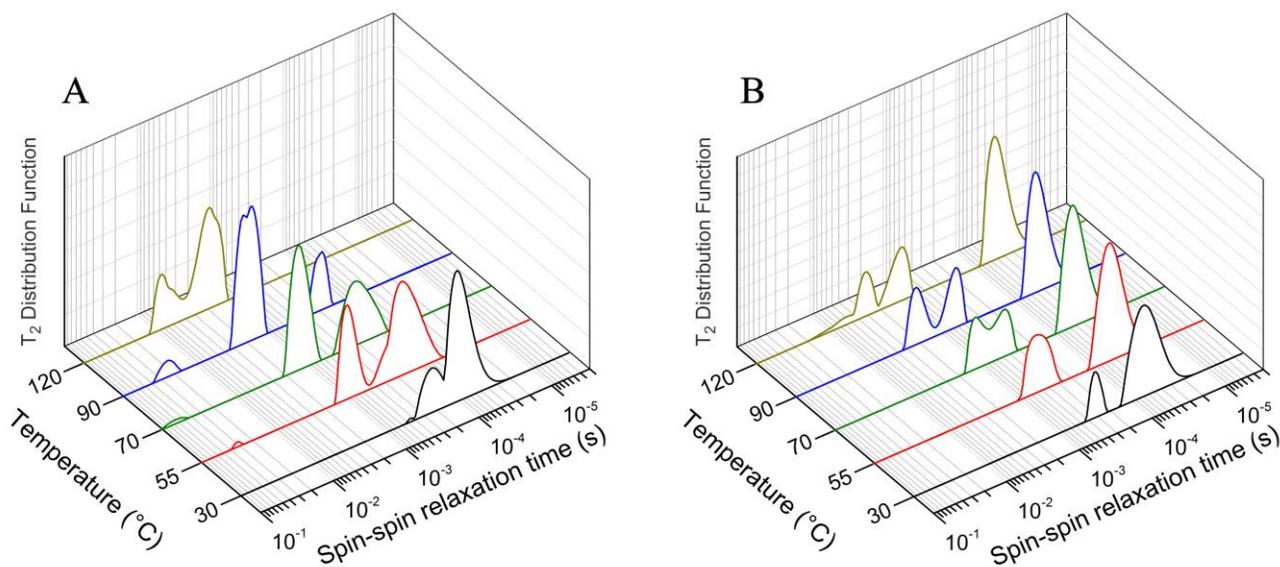


**Figure 3. Inverse Laplace transform of the measured ^{1}H-NMR echo decay at different temperatures. A) Straight bitumen. B) Extracted bitumen.**

On the x axis the spin-spin relaxation times are reported while on the y axis there is the temperature. The peaks represent the distribution of the spin-spin relaxation times for the bituminous materials and reminding that shorter $T_2$ times correspond to

more rigid material, we can distinguish different macro-aggregate inside the material. Every peak corresponds to the $T_2$ times distributions of a given bitumen fraction, hence in the frame of the colloidal model , shorter $T_2$ times correspond to the asphaltene portion while longer spin-spin relaxation times correspond to the maltene fraction. At 30 °C the the ILT of the straight bitumen (Figure 3A) shows three peaks that are close each other meaning that the material is homogeneous. In figure 3B, at the same temperature, the two peaks are well differentiated, meaning that the material is slightly unhomogeneus. By rising the temperature the maltene component splits, leading to two macro-aggregates.

Furthermore the ILT of the extracted bitumen presents a peak that falls close to $T_2=10^{-5}$s, and it is almost undifferentiated along temperature. This is attributable to a very rigid and compact portion of the material which, very likely, corresponds to the asphaltenes that come from the oxidated RAP material. On the other hand for the straight bitumen (figure 3A), the peak attributable to asphaltenes is centered at $T_2=10^{-4}$s at low temperature, while it shifts towards longer $T_2$ times with progressively increasing temperature. This means that in the fresh bitumen, the asphaltene fraction is well dispersed in the oil phase. Furthermore, the ILT of the straight bitumen (figure 3A), informs that a very soft fraction is present. This is revealed by the small peak present between $10^{-1}$ and $10^{-2}$s which completely disappear in the extracted material. The peak probably corresponds to the volatile part that is removed after the process to make the asphalt mix. This is consistent with the softer character of the straight bitumen as revealed by the other techniques used in the present paper.
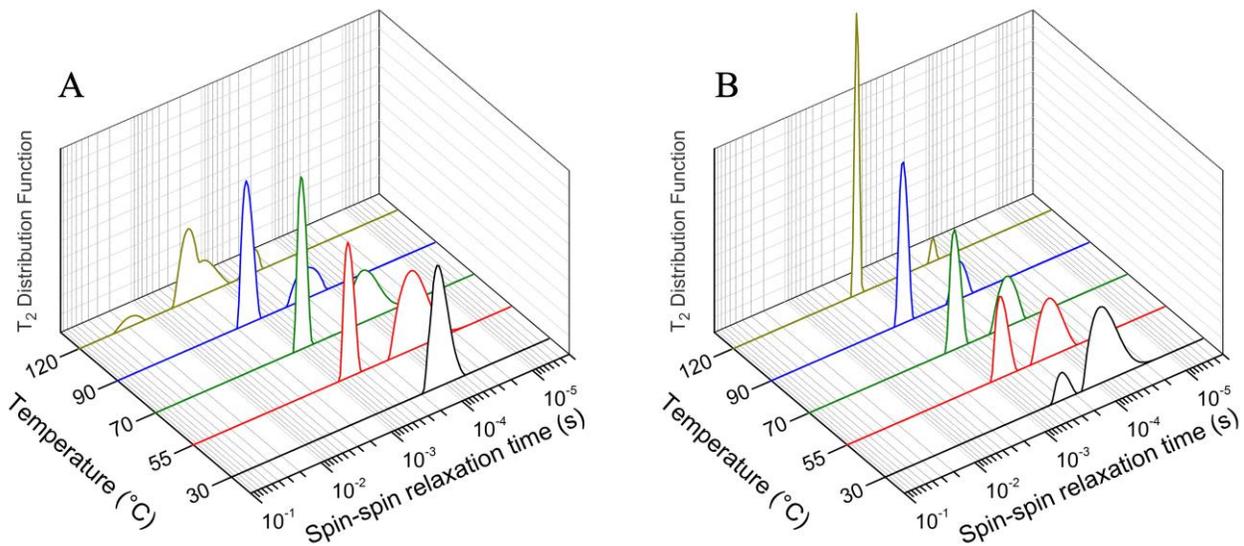


**Figure 4. Inverse Laplace transform of the measured $^1$H-NMR echo decay at different temperatures. A) Extracted + ACF20 bitumen. B) Extracted + WML bitumen.**

Trying to understand the role of the ACF20 and WML in the regenerating process of the aged bitumen, figure 4 reports the ILT for the two additivated extracted bitumen. It is clear that the addition of the ACF20 and WML to the extracted bitumen makes the asphaltene distribution peaks to shift to longer $T_2$ times in both cases. These peaks are centred around $2\times10^{-4}$ s which in turn means that the additivated extracted bitumens have a more mobile asphaltene fraction. However we can appreciate substantial difference in the two graphs. At 30 °C the ILT for the bitumen containing ACF20 (Figure 4A) presents only one peak, meaning that the structures composing the material are very close and interacting each other. On the other hand the WML additivated bitumen at the same temperature, shows two peaks meaning that the rigid and soft fraction are less compact. At 55 °C the peak in figure 4A splits and two macro aggregates can be distinguished. If we analyze the ILT evolution along temperature, we observe that the WML additivated extracted bitumen seems to be more regular. It always presents only two peaks that, as expected for thermal reasons, progressively fall at longer $T_2$ times. The ACF20 bitumen instead tends to disaggregate at higher temperatures. This is probably due to a better dispersion of the particles promoted by the aromatic oils and to the lowering of the surface tension, introduced by the amidic component of the ACF20. However the blend nature of the additive (oil and surfactant) tends to separate at high temperature.

In the case of the sample containing WML, the material seems to be structured in a better defined network with asphaltene micellar phase well dispersed into the maltene oily medium. This can be deducted by the net compartmentalization of the two components, i.e. the peaks are quite sharp and differentiated along the investigated temperature range. The last seems consistent with the fact that this sample has the greatest effect in lowering the transition temperature of the extracted bitumen (table 1, Figure 1).

## 4. CONCLUSIONS

We reported a new analytical approach to improve the usual bitumen classification and to evaluate the chemical changes caused by the given additives. On a 70/100 penetration grade bitumen, we performed standard empirical tests, rheology analysis, spin-spin proton relaxation time measurements. The same experiments were conducted on the bitumen extracted from a real aged road asphalt, in the industrial recycling procedure. The resulting extracted bitumen was then added by two commercial additives that claim to make the recycled bitumen more processable at a lower working temperature . When the extracted bitumen has been doped, the rheological data showed a lowering of the temperature transition from visco-elastic to liquid behaviour. The amphiphilic nature of the ACF20 and WML additives shields the asphaltene-asphaltene interaction leading to a weaker colloidal network so that producing a lowering of the processing temperature in the recycling procedure. Due to its blending nature (aromatic oils and surfactants), the ACF20 resulted less efficient of the WML which is a single molecule that contains the aromatics and the surfactant parts. We found a good agreement with the expectations and related the rheological behaviour of the different materials to the distribution of the different aggregates within the materials. In addition by means of the ILT we identified the macro-aggregates inside bitumen at different temperatures.

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