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A simple test method in order to assess the effect of mineral fillers on bitumen ageing

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HIGHLIGHTS

- Mineral filler effect on bitumen ageing was reviewed.
- Some controversial results arise from experimental differences.
- A new simple method was therefore proposed.
- This confirmed the age-reducing effect of hydrated lime.
- This allowed comparison with other fillers.

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ABSTRACT

Bitumen has been known to be prone to chemical ageing from the very beginning of its modern use in road construction. It is now well accepted that this results in chemical changes illustrated in particular by an increase in asphaltenes content and in the quantity of functional groups such as sulfoxides and carbonyls. The rheological consequences are a global hardening and embrittlement. However, the role of other potential ingredients of asphalt mixtures on bitumen oxidation kinetics remain poorly documented. If hydrated lime has been observed to reduce ageing for more than 40 years, the role of other mineral fillers is not so clear. Part of the problem comes from the difficulty to use the current standard ageing procedures for bitumen when it comes to mastics (blends of bitumen and filler). The viscosity increase due to the presence of filler decreases the severity of the ageing process in rotating methods such as the celebrated Rolling Thin Film Oven Test (RTFOT). Therefore, we developed a simple procedure based on the existing Pressure Aging Vessel (PAV) and on published equivalence between RTFOT and PAV. This makes it possible to easily quantify the effect of mineral fillers through an increase in ring and ball softening temperature, independent of the viscosity increase due to the filler. Using this method, it is shown that hydrated lime slows down bitumen ageing more than other less active fillers such as hydraulic lime or Portland cement, and that mineral fillers from crushed limestone or granitic aggregate have no effect on bitumen ageing.

1. Introduction

Bitumen has been known to be prone to chemical ageing from the very beginning of its modern use in road construction. As a matter of fact, Joseph Nicéphore Niépce made some of the very first recorded photographs in the early 1820s by exposing a solution of Dead Sea bitumen to light. This procedure created insoluble compounds that could not be washed away and remained as part of the picture [1]. However, the technology did not prevail and industrial use of bitumen ageing capabilities really developed some years later with the advent of modern refining technologies [2]. It was widely known at the turn of the 20th Century that a combination of high temperature and exposure to air flow could harden a soft bitumen base. This evolved into the modern air-blowing process which was already widespread in 1920 [3]. Today, air-blowing remains a key technology especially for the manufacturing of industrial grades of bitumen generally known as air-blown or oxidized bitumen [4,5].

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In parallel, the age-hardening of bitumen upon outdoor exposure was noticed by the road industry at the very beginning of asphalt paving. It had raised sufficient attention for researchers to set-up accelerated ageing methods as early as 1897 [6] and was already presented as a well-known fact in 1913 [7]. It was then recognized that most of the hardening developed due to oxidation rather than mass loss [7]. Standard test methods started to be adopted in the 1940s with the development of the Thin Film Oven Test (TFOT – [8,9]). The test consists in ageing 3.2-mm thick bitumen films in an oven for 5 h at 163 °C. It entered the US paving grade specifications in 1955. Still, the TFOT was later surpassed by the Rolling Thin Film Oven Test (RTFOT - ASTM D2872 - EN 12607), which developed in the early 1960s [10] and "cooks" the binder in 1.25-mm thick rotating films at 163 °C for 75 min. RTFOT is now the preferred standard method in the US and in Europe to simulate the ageing occurring in the asphalt mixing plant [6]. It leads typically to a doubling of the viscosity of the tested material, although the extent of hardening is bitumen-dependent and ranges typically between 1.5 and 4 for the viscosity at 60 °C [11]. In the meantime, the asphaltenes content typically increases by 1–4 wt % [12,13]. Note that the ratio of the viscosity (or any other rheological indicator) after to that before ageing is generally called the "Ageing Index".

Nowadays, two ageing conditions are generally separated for bitumen characterization [5,14]. First, there is the rapid chemical ageing that takes place upon mixing thin films of hot bitumen with the hot aggregate. Second, an in-situ ageing also develops throughout the service life of the pavement.

The first one, also called short-term ageing, occurs for a short time at a high temperature of typically 160 °C, corresponding to the standard conditions in mixing plants [6]. These are the conditions that are mimicked in the RTFOT.

The second one, sometimes called long-term ageing, occurs for a much longer period of time since service life of the pavement can extend to several decades. It depends of course on the position of the bitumen inside the pavement, the top layers being more exposed than the base course. Mix formulation also comes into play, the bitumen thickness and the mix porosity being important parameters [15]. It finally depends on the local climate and all these involved parameters make it quite complicated to accurately describe in-situ ageing [15–17]. Simulation of in-situ ageing is therefore more difficult and a widely used testing procedure, the Pressure Ageing Vessel Test (PAV - ASTM D6521 - EN 14769), consists in conditioning binders in 3.2-mm thick films for 20 h at 100 °C under an air pressure of 2.07 MPa. This procedure was initially shown to reproduce satisfactorily the in-situ ageing of bitumen in surface courses for approximately 4–8 years in locations such as Wyoming and Florida [18]. More recent evidence tends to show that the equivalence between PAV and in-situ field ageing depends on local conditions. For example, a Swedish study showed that 10-years old field specimens aged less than the neat bitumen after RTFOT + PAV [19] but in parallel, a US study proved that specimens after 8 years in Arizona and Virginia were more severely aged than after the usual RTFOT + PAV procedure [16].

Still, and even if bitumen ageing has clearly been studied for decades, the exact chemical mechanisms at play remain debated [15,20,21]. Also, recent works on the impact of additives such as polymers [22], polyphosphoric acids [23], organo-clays [24] or flame-retardants [25] maintain bitumen ageing as a vivid research field.

In this context, it comes as a surprise to see that the effect of minerals on bitumen ageing as received only limited attention. In fact, and as detailed in the background section, some works tend to show that minerals have no effect on bitumen ageing, except for so-called active fillers such as hydrated lime whose beneficial effect has always been recognized, when other works show that limestone or siliceous filler do reduce bitumen ageing. In this paper, we discuss that this controversy probably comes from the way the ageing was studied, in particular when ageing tests sensitive to binder viscosity have been used, such as the RTFOT. Then, we propose to use instead a modified PAV-procedure and show that it gives reasonable data confirming that active fillers do reduce bitumen ageing but minerals filler from crushed rock or gravel have no such effect.

2. Background

As rapidly stated in the introduction, there are some contradictions in the literature regarding the effect of minerals on the ageing of bitumen.

2.1. Effect of hydrated lime on bitumen ageing

The fact that hydrated lime slows down bitumen ageing was first highlighted in Utah at the beginning of the 1970s. Bitumens extracted from recovered field specimens of asphalt mixtures containing hydrated lime, were observed to have a significantly lower viscosity than the reference ones [26]. Now, many studies confirmed this finding and it is now widely documented that hydrated lime slows down bitumen ageing [15,28]. The effect was fully developed with hydrated lime contents as low as 10 wt% based on the mastic [28]. Note that no concentration below this value has ever been tested to our knowledge and it must therefore not be interpreted as the minimum amount necessary to obtain an improved resistance to ageing.

The improved ageing resistance was materialized by a reduced increase in asphaltenes content with hydrated lime-modified than with non-modified bitumens [27–29,19,30]. Reasons for that are linked to acid-base reactions between polar molecules of the bitumen and the lime surface [15,28,31]. In parallel, $Mg(OH)_2$, a weaker base than $Ca(OH)_2$ (hydrated lime), was not seen to reduce bitumen ageing [32], when CaO (quicklime) [29] and dolomitic hydrated lime $Mg(OH)_2 \cdot Ca(OH)_2$ [28] were seen to be active. This suggests that it takes a strong base for this mechanism to develop.

Still, acid-base neutralizations are not sufficient to explain the whole chemical interactions at stakes. Western Research Institute researchers proposed that hydrated lime acts as an inhibitor for the oxidation catalysts naturally present in the bitumen [15,28]. This was in part validated by Johansson et al., who showed that the catalytic effect of vanadium compounds on bitumen ageing was decreased in the presence of hydrated lime, although they could not highlight any specific vanadium – hydrated lime interactions [32]. As a result, the main reason why a strong base such as hydrated lime impacts between ageing, is thought to be linked to the concentration of polar molecules from the bitumen on its surface. This prevents them from further reacting. Since they are especially prone to ageing, their removal generates an overall slower ageing kinetics.

However, some startling results were observed using the Rotating Cylinder Asphalt Test (RCAT - [14,19]). The test was performed either at 163 °C for 235 min (with a rotation speed of 5 rpm and an airflow of 4.0 L/min of air) or at 90 °C for 140 h (with a rotation speed of 1 rpm and an airflow of 4.5 L/hr. Mastics with four bitumens and 30 vol% limestone or mixed filler (limestone containing 25 wt% hydrated lime) were studied before and after ageing [19]. The effect of hydrated lime was seen to be dependent on bitumen paving grade, the harder grades being less affected than the softer ones based on rheological indicators, although Fourier-Transform Infra-Red spectroscopy (FTIR) demonstrated that the lower carbonyl rate was always present even for materials whose age hardening was essentially unchanged. The authors were clearly