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Oxidative Aging of Bitumen: A Structural and Chemical Investigation

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Abstract

The oxidative aging of bitumen was investigated chemically and structurally using SARA analysis (saturates, aromatics, resins, asphaltenes), TOF-SIMS (time of flight - secondary ion mass spectrometry) and AFM (atomic force microscopy). Typical wax-containing and non-waxy bitumen samples were selected. These binders differ considerably in terms of chemical composition and rheology. Short- and long-term aging tests were conducted under standard conditions, and at prolonged aging times. In terms of the SARA analysis, the oxidative aging processes for both the wax-containing and non-waxy bitumen, significantly decrease the aromatic fraction and at the same time increase the content of resins and asphaltenes. AFM shows bee-like structures on the wax-containing bitumen surface, and these structures change when the binder is aged. The bee structures are fewer but larger after the prolonged PAV (pressure aging vessel) of 60 hours. For the non-waxy bitumen, no structures were observed, even not after a severe PAV aging that increased the content of asphaltenes significantly. This implies that asphaltenes are most likely not responsible for the formation of bee structures. By TOF-SIMS analysis, the non-waxy bitumen surface did not show structures, neither in the virgin state nor after the severe oxidative aging, further supporting that asphaltenes do not directly result in structure formation. For the wax-containing bitumen, TOF-SIMS shows aliphatics-enriched structures, which generally become larger after oxidative aging. In addition, with oxidative aging there is a gradual increase in SO_x^- (SO^- , SO_2^- , SO_3^- , HSO_4^-), both for the non-waxy bitumen and the wax-containing bitumen. Whereas the SO_x^- levels are higher in the non-waxy bitumen, the waxy bitumen display higher aging-induced enhancements of O^- and RO_x^- ions, indicating the formation of also other O-containing functionalities on the waxy bitumen surface.

Keywords: Bitumen, Oxidative aging, SARA, TOF-SIMS, AFM

1. Introduction

In asphalt production and during the service life of a road pavement, bitumen ages due to irreversible chemical reactions between bitumen components and atmospheric oxygen. This usually makes the bituminous material harder and more brittle, and consequently, increases the risk of pavement failures, such as surface cracking and raveling (Francken 1997; King et al. 2012; Page et al., 1985). For a durable or long-lasting asphalt pavement, aging of the binders is normally slow so that the asphalt layer remains flexible enough to resist cracking (Lu et al. 2011), and also moisture effects are minimized to retain a high strength for the pavement (Thomas et al. 2006).

Basically, at a given temperature, oxidative aging is controlled by the reactivity of the bitumen and the diffusion rate of oxygen into the bitumen film (Petersen et al., 1993; Tuffour and Ishaï, 1990). Oxidative aging is normally associated with the formation of polar and oxygen-containing functionalities, resulting in more polar molecular interactions in the bitumen (Petersen 2009). The molecular changes may significantly affect bitumen structure and mechanical properties. Stronger molecular interactions may cause stronger associations, possibly leading to larger molecular agglomerates, resulting in less mobility and a more elastic behavior of the material (Halstead, 1985; Goodrich, 1988).

Aging-induced compositional and structural changes have been studied extensively. Very often structural changes are related to a generic fractionation into saturates, aromatics, resins and asphaltenes (SARA), especially asphaltenes, determined according to ASTM 4124 or IP 469. It must be pointed out that IP 469 and ASTM D 4124 may not give identical results, as the SARA fractions are defined as solubility classes rather than chemical component classes; these classes of materials are still very heterogeneous, and slight variations in the separation procedure or in the solvents may cause differences in the fractions (Girdler, 1965; Kharrat et al., 2007). Anyhow, some studies claim that asphaltenes contribute to the bee-like structure observed by atomic force microscopy (AFM) (Loeber & Sutton et al., 1996; Loeber & Muller et al., 1998), while there is also a lot of evidence that bee structures are formed by the crystallizable fractions present in paraffinic bitumen (Blom et al., 2019; Das et al., 2013; Hung & Fini, 2015; Lyne et al., 2013; Pahlavan et al., 2016; Pauli et al., 2001). Various, sometimes contradicting observations with regards to the effect of aging on the AFM microstructure have been reported. For example, in a paper by Wang and Liu (2017), the authors noted that the percentage of bee phase on the surface changed, and that the surface roughness decreased with the degree of aging. In another paper by Zhang et al. (2012), it was reported that the sample roughness increased due to aging. These authors also noted a decrease in contrast between the bees and the surrounding matrix in one case, while in a second sample such contrast was found to increase. Moreover, in a paper by Rebelo et al., the typical bees were not found, instead small spherical particles were recorded on the bitumen surface, which also changed upon aging of the binders (Rebelo et al.,

2014). Finally, there is clear evidence that bee or bee-like structures are only formed on the bitumen surface, and are not present in the bulk, for example from investigations of fractured surfaces (Blom et al., 2018; Ramm et al., 2019).

This paper aims at studying the effects of oxidative aging on bitumen chemistry and structure, particularly the chemical and structural changes which may take place after severe and prolonged aging tests. For this purpose, typical wax-containing and non-waxy bitumen samples were selected. The bitumen samples were oxidatively aged to different levels of severity in laboratory tests. The chemical and structural characterization was performed using time of flight - secondary ion mass spectrometry (TOF-SIMS) and AFM on air cooled surfaces, as well as by means of SARA analysis.

2. Materials and Methods

2.1. Samples

A non-waxy bitumen and a wax-containing bitumen, coded as B25 and B26, respectively, were studied in this paper. B25 is a straight run bitumen while B26 is a visbroken one; both belong to the same penetration grade of 160/220. Typical properties of the bitumen samples are shown in Table 1. The chemical compositions were determined by thin layer chromatography with flame ionization detection according to IP 469 (Cf. Section 2.2), and the melting enthalpies were measured by differential scanning calorimetry (DSC). For the oxidative aging of the binders, both short-term RTFOT (EN 12607-1) and long-term PAV (EN 14769) tests were performed. The long-term PAV aging tests were carried out at 100°C for 20 hours. To obtain more severe oxidation, PAV was also performed for a prolonged aging time of 40 and 60 hours.

Insert Table 1

2.2. Methods

SARA analysis

As already mentioned, the SARA analysis was carried out using thin layer chromatography with flame ionization detection (TLC-FID, or Iatroscan) according to IP 469. For each binder (virgin and aged), a solution was prepared in toluene at a concentration of approximately 2% (w/v). Then, 1 µl of the solution was spotted on each chromarod using a sample spotter. The fractionation of bitumen into the four generic fractions (SARA) was performed by a three-stage development using n-heptane, toluene : n-heptane (80:20 by volume), and dichloromethane : methanol (95:5 by volume), respectively. The fractions were determined by means of Iatroscan MK 6-S analyzer. It should be noted that the IP 469 method results in a relative ratio between fractions of Saturates, Aromatics, Polar I

and Polar II. Polar I and Polar II fractions are often referred to as Resins and Asphaltenes, respectively (Hung & Fini, 2015; Orea et al., 2002), and this nomenclature is adapted further in the analysis.

AFM

AFM measurements were performed with an Asylum Research MFP-3D AFM. Virgin binders and aged binders by 20h PAV and 60h PAV were measured. All scans were performed in air and at room temperature using a tapping mode, which is a high-amplitude dynamic mode where an amplitude modulation feedback is used to image the sample topography. In preparing specimens, bitumen samples were first heated in an oven at 160°C for about 30 minutes. Afterwards, approximately 20 mg bitumen was placed on an aluminum disk. The disks with bitumen were reheated on a hot plate of 100°C for about 30 seconds to create a thin flat film. Before testing, all specimens were stored in a closed box at room temperature for a maximum of 24 hours.

TOF-SIMS

In TOF-SIMS, molecular information about the sample surface is obtained by irradiating the sample with a focused, high-energy (primary) ion beam and analysing the emitted (secondary) ions with respect to mass. Identification of the secondary ions in the acquired mass spectrum allows for association of individual peaks to specific molecular species on the sample surface. By scanning the primary ion beam over a selected analysis area and acquiring separate mass spectra from each pixel, the spatial distribution of specific molecular species can be mapped over the sample surface (displayed in so called ion images).

TOF-SIMS analysis was carried out on virgin binders and aged binders by 20h PAV and 60h PAV. For this analysis, a small amount of hot bitumen was deposited on a carefully cleaned silicon substrate using a glass pipette. After reheating to about 130°C, the sample was cooled down to room temperature during approximately one hour, and then placed in a freezer at -20°C for about 1-1.5 hours. After that, the sample was quickly mounted on a sample holder and cooled down inside the load lock, prior to evacuation and subsequent transfer to the analysis chamber for TOF-SIMS analysis.

TOF-SIMS analysis was carried out at a sample temperature of about -80°C in a TOF-SIMS IV instrument (ION-TOF GmbH, Germany) using 25 keV Bi_3^+ primary ions and low energy electron flooding for charge compensation. Positive and negative ion data were acquired separately with the instrument optimized for high mass resolution ($m/\Delta m \approx 5000$, lateral resolution 3-5 μm) or for high lateral resolution ($m/\Delta m \approx 300$, lateral resolution $\approx 0.5 \mu\text{m}$). Mass spectra were acquired from selected analysis areas up to 500 x 500 μm^2 , and ion images of selected characteristic ions were created on different areas of the samples.

The positive ion spectra of the bitumen samples are dominated by peaks corresponding to hydrocarbon ions, $C_xH_y^+$, whereas the negative spectra display considerable peak intensities from heteroatom-containing ions as well as (hydrogen-deficient) hydrocarbon ions. In the positive ion images (see Figures 6 and 12 in Section 3.3), aliphatics are represented by the added signal intensities at m/z 57 ($C_4H_9^+$), 71 ($C_5H_{11}^+$) and 83 ($C_6H_{11}^+$), and the aromatic images show the added intensities at m/z 77 ($C_6H_5^+$), 91 ($C_7H_7^+$), 105 ($C_8H_9^+$), 115 ($C_9H_7^+$), 128 ($C_{10}H_8^+$), 141 ($C_{11}H_9^+$), 152 ($C_{12}H_8^+$) and 165 ($C_{13}H_9^+$). The polycyclic aromatic hydrocarbon (PAH) images show the added ion intensity in the mass range m/z 200-800, which previously has been found to represent mainly PAH-related molecular species (Lu et al., Fuel 2017).

For some of the TOF-SIMS data acquired at high mass resolution, principal components analysis (PCA) was carried out using the Solo software (version 7.9.5, Eigenvector Research Inc., USA) to investigate systematic variations between the spectra of the different samples. The analyses of positive and negative ion spectra included 335 and 313 peaks, respectively, which were automatically selected in the mass range m/z 10-200 of the spectra using the SurfaceLab v6.8 software (IONTOF GmbH, Germany). The PCA uses input data (here, the signal intensities of the selected peaks) to generate principal components (PCs), which are new variables formed by combinations of the old variables (i.e., the selected peaks) that vary in a similar (or opposite) manner between the spectra. For each spectrum, the PCA generates scores for each PC (equivalent to peak intensities of the original variables), and the contributions of the old variables to the PC are given by the so called loadings. Thus, spectra with high/positive scores for a particular PC have relatively high signal intensities of peaks with high/positive loadings for the same PC, but relatively low signal intensities of peaks with low/negative loadings, and vice versa. Since the first PC (PC1) accounts for the maximum amount of systematic variations between the spectra, PC2 accounts for the maximum remaining variation, etc., it is often sufficient to consider the first few PCs when analysing the results. Prior to PCA, the peak intensities (Poisson corrected) were normalized to the sum intensity of all included peaks and pretreatment included mean centering and Poisson scaling.

Other tests

The unaged and aged bitumen samples were also characterized by Fourier transform infrared spectroscopy (FTIR), gel permeation chromatography (GPC), dynamic shear rheometer (DSR), and bending beam rheometer (BBR). Part of these results are discussed in detail in (Soenen et al., 2016).

3. Results and Discussion

3.1 Basic characterization

Empirical measurements (penetration and R&B softening point) are shown in Table 2. Both the binders belong to the same penetration grade (160/220), however, they are very different in terms of aging sensitivity. Table 2 also shows results of the rheological tests (DSR and BBR), as well as chemical measurements with FTIR and GPC before and after aging. A further rheological comparison is shown in Figure 1, where black curves (complex modulus *versus* phase angle) are made for the two binders before and after the standard aging tests (i.e. short-term aging RTFOT, and long-term aging 20h PAV).

Insert Table 2

Insert Figure 1

As can be seen, there are chemical differences between the two binders. The non-waxy bitumen B25 displays a lower aromaticity, as determined by the FTIR absorption at 1600 cm^{-1} ; this corresponds also to the SARA aromatics determined in Table 1. B25 also shows higher apparent molecular weights (M_n - number average molecular weight, M_w - weight average molecular weight) as compared to B26. However, it is not clear at the moment, if these molecular weights are true molecular weights, or related to the formation of associates. In the dilute solutions, which are needed for GPC tests, the formation of associates becomes more likely. More information related to these tests can be found in (Soenen et al., 2016). For both binders, aging increases the apparent molecular weights, the aromaticity, as well as the FTIR carbonyl and sulfoxide indices calculated according to (Donyl et al. 2016). Similar aging-related chemical changes have also been reported in literature (Petersen, 2009).

The binders are also very different in terms of the durability parameter ΔT_c measured by BBR and calculated according to ASTM D 7643. After the RTFOT and 20h PAV aging, a positive value of ΔT_c (3.1°C) is seen for B25, whereas B26 shows a negative value (-6.5°C). From these measurements, one would expect performance differences between the two binders as a more positive value of ΔT_c is related to a higher durability (Anderson et al., 2011). In addition, B26 is more structured as indicated by a lower phase angle at $1\text{ MPa } G^*$ compared to B25, which might be attributed to the presence of wax in B26. This phase angle decreases with further aging. Higher aging sensitivity for B26 is also evident when viscosity results are compared in Table 2.

Further analysis is made on the generic fractions or SARA. The measured SARA fractions, as well as calculated fraction indices (aged / unaged) are shown in Figure 2. As can be seen, the two unaged bitumen samples differ in aromatics and saturates but they are quite similar in terms of asphaltenes and resins. For both bitumen, the aging process, especially the prolonged PAV (40h and 60h),

significantly decreases aromatics and at the same time increases the content of resins and asphaltenes. However, almost no change is seen for the saturates, probably due to their inert nature to oxygen. The compositional changes would suggest a transformation of aromatics to resins and/or asphaltenes, or from resins to asphaltenes. It should be noticed that, with increased aging, the resolution or separation between resins and asphaltenes generally becomes poor, as illustrated in Figure 3. This makes it difficult to quantify the content of asphaltenes for aged samples, particularly after PAV. Nevertheless, the cumulative content of polar fractions (i.e. resins and asphaltenes) in the samples increases with each aging stage.

Insert Figures 2 and 3

3.2. AFM

As already shown, the oxidative aging alters the chemical component analysis of bitumen, showing a decrease in aromatics and an increase in resins and asphaltenes. What is still less understood is how bitumen microstructures are affected by these aging-induced compositional changes. In this study, AFM is used to characterize the structure of bitumen surfaces at micro/nanoscale; height, phase and amplitude images are recorded in a tapping mode. The height images directly reflect height changes of the surface topography, the amplitude images result from the amplitude of the tip oscillation as it changes with the surface topography, while the phase images describe the phase shifts between the AFM probe motion and the driving oscillator. In general, these different types of image are comparable. The AFM images of the air-cooled surfaces of the two selected bitumen samples (before and after aging) are shown in Figures 4 and 5. All AFM images were treated in the same way by using an image processing software called Gwyddion, a modular program for scanning probe microscopy data visualization and analysis. By this treatment, the background noise of the images was somewhat removed; however, some small noise may be still noticed in some cases, especially when the surface is fully levelled and without any topographic feature. All images are presented at $80 \times 80 \mu\text{m}^2$, but the scales of the height and degree levels, as indicated, vary slightly between the samples. For B26, a detailed magnified picture, highlighting the bee structures, is included. The prolonged aging time in PAV was done to further increase the content of asphaltenes and resins (Cf. Figure 2), in order to determine if such chemical changes may contribute to the formation of surface structures.

As illustrated in Figure 5, the wax-containing bitumen B26 shows bee-like structures, and these structures significantly change when the binder is aged. As shown, the bee structures are fewer but larger after aging. By image analysis, bee coverages on the unaged, RTFOT+20h PAV aged and RTFOT+60h PAV aged samples were found to be 2.1, 1.9 and 1.7%, respectively, while average bee length increased from $3 \mu\text{m}$ (unaged), to $5 \mu\text{m}$ (RTFOT+20h PAV) and $8 \mu\text{m}$ (RTFOT+60h PAV). These

changes are probably because of highly increased hardness of the aged binder and/or reduced compatibility between the crystalline fraction and the more polar matrix. On the other hand, for the non-waxy bitumen B25 (Figure 4), no bee structures are observed even not after a severe laboratory aging with RTFOT plus PAV of 60 hours. The small surface structures observed are due to noise. Notice that this non-waxy bitumen initially consists of about 22% asphaltenes, and after the 60h PAV aging, the content of asphaltenes increases to almost 25%, as measured by TLC-FID (Cf. Figure 2). This implies that asphaltenes, unless containing n-heptane insoluble crystallizable materials [Lu et al., 2017], are not the fraction responsible for the structures.

Insert Figures 4 and 5

3.3. TOF- SIMS

The TOF-SIMS analysis was made on air-cooled surfaces of bitumen samples. This section starts with the non-way bitumen B25, then deals with the wax-containing bitumen B26.

In Figure 6, different positive ion images are shown for B25, before and after aging. Evidently, this bitumen does not show any structures, neither on the unaged sample nor after the severe long-term aging. This again suggests that the presence of asphaltenes would not result in a structure formation, supporting the observation already made by AFM.

Insert Figure 6

Figure 7 shows positive ion spectra of B25 (before and after aging). The spectrum of the RTFOT+20h PAV aged sample is very similar to that of the unaged one. However, the 60 h PAV aged sample shows additional peaks in mass region m/z 175-260, which are not yet identified. It is found by PCA that the unaged and the 20h PAV aged samples show more aromatics while the 60h PAV aged sample shows more aliphatics (Figure 8).

Insert Figures 7 and 8

As for the negative ion spectra of bitumen B25 (Figure 9), the 20h PAV aged sample is very similar to the unaged sample, but the 60h PAV aged sample differs significantly at m/z 180-260. The observations are quite similar to those observed in the positive ion spectra. By PCA analysis shown in Figure 10, it is found that the PC1 score increases with aging and that this increase is mainly caused by increasing sulfur oxide (SO_x^-) signals with aging, as also illustrated in Figure 11a. In addition, no significant increase in O^- and RO_x^- was observed after aging (Figure 11b) and only a minor gradual increase in the signal from aliphatic ions (not shown).

Insert Figures 9, 10, and 11

Unlike B25, the wax-containing bitumen B26 displays large (up to 40 μm) structures as shown by the positive ion images in Figure 12. Topographic wrinkles on the larger structures are observed in the total ion images (not shown here). Although the presence of the structures is consistent with the AFM results, some of structures in the TOF-SIMS images are considerably larger than those observed in the AFM images. It is also evident that the crystal-shaped structures become larger after aging. PCA analysis of the positive ions (Figure 13) indicate more aliphatics in the 20h PAV sample compared to the unaged bitumen (PC2 loadings), whereas the PC1 loadings indicate stronger signals in the 60h PAV aged sample from a group of less saturated aliphatic ions and higher signal from the more saturated aliphatic ions in the unaged and 20h PAV samples. This is different from the observations for B25.

Insert Figures 12 and 13

It was unexpectedly found that the 20h PAV aged B26 sample displays similar spectral characteristics as the 60h PAV aged B25 sample at m/z 180-200, probably suggesting a contamination, which may also explain the increased signal from aliphatic ions in these samples. Also, polydimethylsiloxane (PDMS) was present in all the B26 samples, of which the 60h PAV aged sample had the most. The PDMS was mainly localized to the matrix between the wax particles.

Specific analysis of individual negative ions indicates that there is a gradual increase in SO_x^- (SO^- , SO_2^- , SO_3^- , HSO_4^-) with aging also for the wax-containing bitumen B26 (Figure 14a). However, the normalized TOF-SIMS signals are considerably lower than those for B25 (Figure 11), indicating higher surface concentrations of SO_x functionalities on B25, as compared to B26. Furthermore, a strong increase was observed in the O^- signal after 60h PAV aging of B26, and smaller enhancements also for other RO_x^- ions (Figure 14b). Contrary to the SO_x^- ions, these signal intensities (O^- and RO_x^-) are considerably higher for B26 than for B25, thus indicating that the increased O^- and RO_x^- signals are related to the formation of O-containing structures other than sulfoxides, possibly alcohols, carbonyls or carboxylic acids. A relatively small signal increase was also observed for RNO^- ions upon 60h PAV aging of B26, whereas the aliphatic and aromatic ions showed no significant change (not shown). Finally, high-resolution ion images of the 60h PAV aged sample show that the SO_x^- ions are mainly localized to the matrix between the wax particles (Figure 15), which is consistent with the higher SO_x^- signals observed for wax-free bitumen B25. In general, the TOF-SIMS changes in SO_x^- after aging agree with the results obtained by FTIR. However, it is not possible to identify certain specific TOF-SIMS ions that are linked to the concentration of carbonyls as measured by FTIR.

Insert Figures 14 and 15

4. Conclusions

In this paper, the oxidative aging of bitumen has been investigated both structurally and chemically. Typical wax-containing and non-waxy bitumen samples of an identical pen-grade were selected in the study. From the results presented, the following conclusions can be drawn.

- The investigated bitumen samples differ in terms of chemistry, such as molecular weight, aromatics, and wax content. The SARA analysis shows that the oxidative aging process, especially the prolonged PAV, significantly decreases aromatics and at the same time increases the content of resins and asphaltenes. However, almost no change is seen for the content of saturates probably due to their inert nature to oxygen. With increased aging, the resolution or separation between resins and asphaltenes in TLC-FID generally become poor, making it difficult to quantify the content of asphaltenes for the aged samples, particularly after PAV.
- AFM shows bee-like structures on the wax-containing bitumen, and the structures change significantly when the binder is aged. The bee structures are fewer but larger after the prolonged PAV of 60 hours, probably because of a highly increased stiffness of the aged binder and/or a reduced compatibility between the saturated crystalline fraction and the more polar bitumen matrix. On the other hand, for the non-waxy bitumen, no structures are observed even after a severe aging of 60h PAV that has increased the content of asphaltenes from initially 22% to almost 25%. This implies that asphaltenes are not the fraction responsible for the structures, unless they contain n-heptane insoluble crystallizable materials.
- By TOF-SIMS, the non-waxy bitumen does not show any structures, neither in the virgin state nor after the severe oxidative aging. This again suggests that asphaltenes do not directly result in a structure formation. Furthermore, on the wax-containing bitumen, TOF-SIMS shows large aliphatics-enriched structures with visible wrinkles, and the crystal-shaped structures generally become larger after the oxidative aging. The presence of structures in TOF-SIMS observations is consistent with the results from AFM.
- With oxidative aging, there is a gradual increase in SO_x^- (SO^- , SO_2^- , SO_3^- , HSO_4^-), which is considerably stronger for the non-waxy bitumen, but also evident for the wax-containing bitumen. In contrast, O^- (and to a smaller extent RO_x^-) showed a strong increase upon aging for the waxy bitumen, whereas no change was observed for the non-waxy bitumen, thus suggesting a higher concentration of other oxidation products than sulfates on the waxy bitumen and mostly sulfates on the wax-free bitumen. For the wax-containing bitumen, the SO_x^- ions were primarily located to areas between the wax-rich structures on the surface. No significant changes in aliphatic and aromatic ions were observed upon aging for any of the

two bitumen samples. It should be noticed that these TOF-SIMS observations were conducted on the air-cooled bitumen surfaces and may differ from the bulk composition, especially for the wax-containing bitumen.

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Table 1. Properties of the virgin bitumen samples.

	B25	B26
Penetration, 1/10 mm	187	190
Softening point, °C	36.9	39.2
Chemical compositions		
Saturates, %	7.6	5.6
Aromatics, %	44.4	50.3
Polars I (Resins), %	23.2	22.9
Polars II (Asphaltenes), %	21.8	21.2
Melting enthalpy, J/g	0	9.6

Table 2. Empirical, rheological and chemical measurements.

Parameters	B25			B26		
	Unaged	RTFOT + 20h PAV	RTFOT + 60h PAV	Unaged	RTFOT + 20h PAV	RTFOT + 60h PAV
Penetration, 1/10 mm	187	63	35	190	26	10
Softening point, °C	39.6	50.0	59.9	39.2	69.0	87.7
DSR phase angle at 1 MPa G*, deg	72	52	54	63	47	39
DSR viscosity at 90°C and 0.01 Hz, Pa.s	3.3	13.0	37.4	3.0	81.1	1740
BBR LST, °C	-23.5	-21.6	--	-27.2	-20.5	--
BBR LmT, °C	-27.6	-24.7	--	-28.3	-14.0	--
BBR ΔTc, °C	4.1	3.1	--	1.2	-6.5	--
FTIR aromaticity	0.140	0.150	0.160	0.170	0.200	0.250
FTIR carbonyls	0.015	0.069	0.119	0.000	0.032	0.102
FTIR sulfoxides	0.007	0.082	0.110	0.050	0.121	0.148
GPC M _n	955	1204	1225	851	1143	1205
GPC M _w	2252	3653	3813	1359	2566	2799
GPC M peak	894	945	943	1123	1253	1267

Figure 1. Black curves of B25 and B26 before and after the standard aging tests.

Figure 2. Effect of oxidative aging on bitumen SARA fractions (upper) and fraction indices (lower).

Figure 3. TLC-FID chromatograms of B25 and B26 and effect of aging.

Figure 4. AFM images of the non-waxy bitumen B25 before and after aging.

Figure 5. AFM images of the wax-containing bitumen B26 before and after aging.

Figure 6. TOF-SIMS positive ion images of bitumen B25 before and after aging. The ion signals representing aliphatics, aromatics and PAH are specified in Section 2.2. Field of view 100x100 μm^2 . MC: maximum counts per pixel, TC: total counts in entire image. Note that differences in signal intensities (counts) between samples do not reflect analyte concentration differences. The horizontal features in the lower right image are data acquisition artifacts not related to compositional variations in the sample.

Figure 7. TOF-SIMS positive ion spectra of bitumen B25 before and after aging.

Figure 8. Scores (left) and PC 1 loadings (right) from PCA analysis of positive ion spectra of bitumen B25. The high PC1 scores for the spectra of the 60h PAV aged sample (B25 60h) indicate higher signal intensities of aliphatic ions (positive PC1 loadings), whereas the lower PC1 scores of the untreated and 20h samples indicate higher signal intensities from aromatic ions (negative PC1 loadings).

Figure 9. TOF-SIMS negative ion spectra of bitumen B25 before and after aging.

Figure 10. Scores (left) and PC1 loadings (right) from PCA analysis of negative ion spectra of bitumen B25.

Figure 11. Effect of aging on the signal intensities of (a) sulfur oxide-related ions, SO_x^- , and (b) oxygen-related ions, RO_x^- , in negative TOF-SIMS spectra of bitumen B25.

Figure 12. TOF-SIMS images of positive ions representing aliphatics, aromatics and PAH of bitumen B26 before and after aging. Brighter pixels correspond to higher signal intensities, as indicated by the adjacent color scales. Field of view 200x200 μm^2 . Note the high contrast in the PAH images, indicating stronger lateral variations in the signal intensity of ions in the higher mass range (m/z 200-800), as compared to the, possibly less specific, aromatic ions in the lower mass range.

Figure 13. Scores (top) and loadings (left: PC1, right: PC2) from PCA of positive ion spectra of bitumen B26. Characteristic ions for PDMS at m/z 73, 75 and 147 were excluded from the analysis.

Figure 14. Effect of aging on the signal intensities of (a) sulfur oxide ions, SO_x^- , and (b) oxygen-related ions, RO_x^- , in negative TOF-SIMS spectra of bitumen B26.

Figure 15. Negative ion images of $\text{C}_3\text{H}_2^- + \text{C}_3\text{H}_3^- + \text{C}_4\text{H}_3^-$, representing aliphatics, $\text{SO}^- + \text{SO}_2^- + \text{SO}_3^- + \text{HSO}_4^-$, representing sulfates, and an overlay image of these two from bitumen B26 after 60h PAV aging (same sample and analysis area as in Figure 10).