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EFFECT OF F-T WAX ON AGING CHARACTERISTICS OF WARM MIX ASPHALT BINDERS

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ABSTRACT

The use of rheology modifying additives in asphalt mixes for reducing the mix production temperature and/or increasing the reliability of the compaction process in order to obtain durable pavements, is state of the art. F-T wax decreases the viscosity of bitumen and imparts lubricity above its melting temperature range, resulting in improved workability and compactibility of the asphalt mixes. The wax is thoroughly mixed with the bitumen which poses the question of influencing physico-chemical properties of the binder, such as aging properties. In order to evaluate the potential effects on aging, three bitumen samples were prepared in the laboratory: a bitumen 50/70 as control sample and the 50/70 mixed with two F-T waxes of different chemical composition. The binders were evaluated in the fresh state as well as short-term aged (by RTFOT) and long-term aged (by PAV) states respectively. Besides effects on mechanical/rheological properties, the main focus was the detection of ageing effects on the chemical and colloidal composition of the binders. For the rheological characterization, complex shear modulus tests were conducted in a temperature range of 20 °C to 90 °C. The compositions of the binders in terms of major chemical groups were evaluated by IR spectroscopy and by performing SARA-analytics using the TLC/FID technique. The proportions of saturates, aromatics, resins and asphaltenes were measured. The compositions of the asphaltenes were further evaluated by separation into three fractions applying a dissolution/precipitation procedure.

The aging did not change the softening points of F-T wax modified bitumen, which are mainly influenced by the melting temperatures of the waxes, but resulted in the expected increase of the binder stiffness. The latter was observed through an increase of complex modulus and decrease in phase angle. This change in physical behavior caused by aging was a result of changed chemical composition: The percentage of aromatic compounds decreased whereas the fractions of resins and asphaltenes increased. Also the chemical composition of the asphaltenes changed towards the fraction of low solubility. The aging processes of the bitumen were only slightly influenced by the added F-T waxes, whilst one of the two wax types even yielded some minor advantages. These differences between the relative performances of the two wax types can be ascribed to chemical differences between them.

The observed influences of the F-T waxes on the chemical composition are minor compared to the variety found for bitumen from different crude origins. The results show that the chemical composition as well as the ageing properties are predominantly affected by the bitumen characteristics, whereas effects of F-T wax do not compromise the aging properties of the binder.

Keywords: Bitumen Ageing, Chemical Characteristics, FT-Wax, Infrared Spectroscopy, SARA Analysis, TLC/FID

I. INTRODUCTION

By adding Fischer-Tropsch-wax (FT-wax) to bitumen, its thermo-rheological properties can be modified, resulting in reduced viscosities at asphalt mixing- and compaction temperatures. This allows for the reduction of mixing- and compaction temperatures and therefore improves the materials CO_2-footpint and/or prolongs the time available for compaction of the asphalt course in order to improve the reliability of high-quality asphalt road paving.

However, the actual material performance of asphalt pavements changes due to environmental impacts, e.g. weathering and ageing. The latter occurs as short-term ageing during asphalt mix production by distillation and oxidative effects at elevated temperatures and as long-term ageing during service life because of oxidation. Both short-term as well as long-term ageing affect the rheological properties of the bitumen as well as the durability of the asphalt course.

The physical characteristics of a bituminous binder is directly associated with its chemical composition. However, the chemical nature of bitumen is a very complex system of a multitude of different hydrocarbon molecules [3]. A simple way for describing the chemical characteristics of bitumen by colloidal models is the fractionation into chemical families of different polarity. The model of a colloidal system allows the explanation of the thermo-rheological properties of bitumen and is based on the theory that colloids with high polarity (asphaltenes) are peptized to micelles in an oily phase with lower polarity, called maltenes [8].

Based on this bitumen model the thermo-rheological properties can be explained by two different types of materials: Sol and Gel. Sol material can be interpreted as Newton fluent, in which asphaltenes are fully dispersed in the maltene phase which results in non-elastic behavior [7]. Gel material shows non-Newton behavior caused by interaction between asphaltenes micelles. Most bitumen types show properties between these two extremes [6].

Furthermore bitumen ageing will affect the colloidal system and provoke a change from SOL type to GEL type [7].

II. EXPERIMENTAL

2.1 Materials and Aging Procedure

The investigation was performed using 50/70 penetration bitumen and two Fischer-Tropsch (F-T) waxes. Wax 1 is an unhydrotreated F-T wax, i.e. contains besides hydrocarbons also smaller amounts of alcohols and olefins and is characterized by a congealing point of 101.0 °C. Wax 2 is hydro-treated, i.e. consists only of hydrocarbons and has a slightly higher congealing point of 102.5 °C.

The bitumen (further referred to as 50/70) was modified by the addition of 3 wt.% of F-T wax 1 and F-T wax 2 respectively to the heated (160 °C) bitumen and homogenized by stirring for 10 minutes. The resulting wax-modified bitumen samples are labeled as F-T 1 and F-T 2 in this study.

Simulated aging was carried out in two steps applying the standardized procedures for short term aging by RTFOT (Rotating Thin Film Oven Test, EN 12607-1) and long term aging by PAV (Pressure Aging Vessel, EN 14769).

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2.2 Softening Point Ring an Ball

The softening points ring and ball were measured according to the standard EN 1427.

2.3 DSR Complex Modulus Test

The rheological properties of fresh and aged binders were characterized by Dynamic Shear Rheology, using plate-plate tests according to EN 14770. For temperatures between 20°C and 90 °C as well as frequencies between 0.1 to 10 Hz the shear modules and phase angels were measured.

2.4 SARA- Analysis by TLC/FID

Four chemical fractions of different polarity (Saturates, Aromatics, Resins and Asphaltenes - SARA components), were determined by thin layer chromatography with flame ionization detection (TLC/FID) according to IP 469. For the analysis 0.1 g of the bitumen sample was dissolved in 5 ml of dichloromethane, resulting in a 2 wt. % solution. 1 µl of this solution is chromatographically separated on a silica adsorbent (Chromarod) using three different solvents successively, see Table 1.

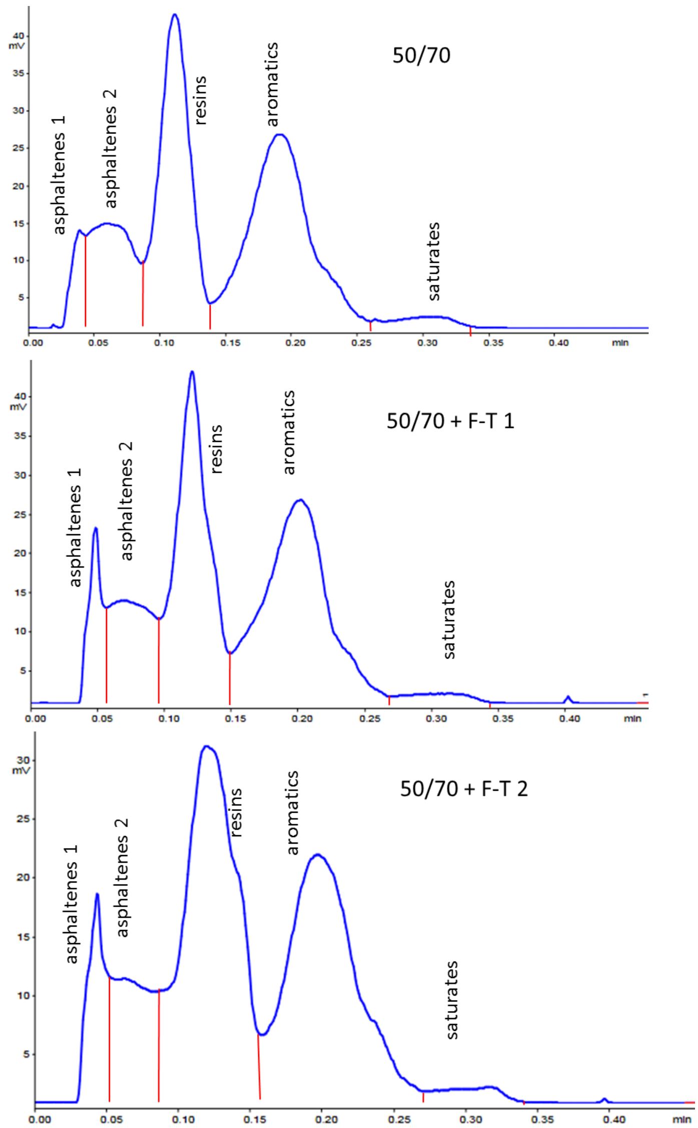

Figure 1: Chromatogram for SARA Components of 50/70 (unmodified and Modified)

Table 1: Fraction Depending on Order of Solvents

Solvents applied for TLC-separation	Fraction
Heptane	Saturates
Toluene/Heptane (80:20)	Aromatics
Dichlormethane/Methanol (95:5)	Resins
Not eluated	Asphaltenes

The chromatogram on the Chromarod was scanned using FID-technique and the proportions of the four bitumen SARA-fractions were determined quantitatively by area determination under the specific peaks. For each sample, five chromatograms were evaluated. The resulting chromatograms for the unaged binder samples are plotted in Fig. 1. The four visible peaks represent the four SARA-fractions. For the F-T-modified bitumen samples, there are two asphaltene peaks detectable. The first peak at the beginning of the Chromarod identifies a portion of non-soluble (considering the solvents applied for chromatographic separation) bitumen compounds in the binder for the temperature, in which the chromatography was conducted (20±3 °C). In order to evaluate this difference to unmodified binder, the asphaltenes are separately described by a 1^{st} and a 2^{nd} asphaltene peak area.

2.5 Compositions of Asphaltenes

The compositions of asphaltenes in term of low, medium and high solubility are measured by a dissolution/ precipitation procedure with three different solvent combinations of iso-octane and cyclohexane as described by Zenke [10], compare Table 2. Each solvent applied can be described with a solubility parameter, compare Fig. 2 [10]. This allows the further distinguishing of the asphaltenes.

Table 2: Fractions depending in order of solvents

Asphaltene solubility	Solvent	Solubility parameter δ $[MJ/m^3]^{1/2}$
High solubility	Iso-octane	14,0
Medium solubility	Iso-octane/cyclohexane (4:1)	14,8
Low solubility	Iso-octane/cyclohexane (1:1)	15,7

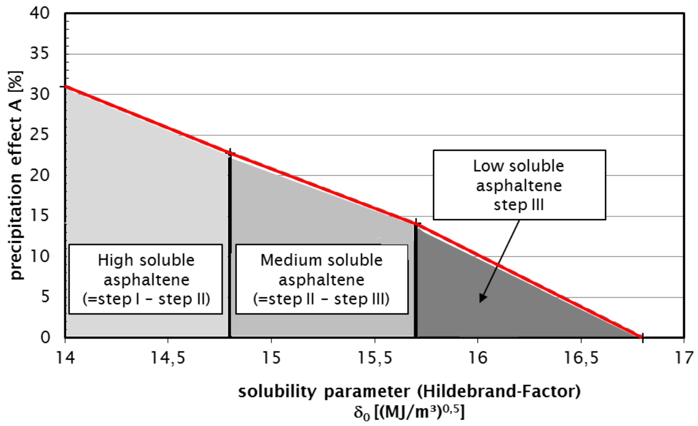

Figure 2: Explanation to Three Asphaltene Fractions in Bitumen

Asphaltenes are distinguished according to the method of identification as well as the applied type of solvent [9]. Whereas for the asphaltene composition experiment, asphaltenes are defined as the insoluble fraction in iso-octane, in SARA-analytics dichloromethane is applied for defining the asphaltene content. Therefore, it is taken into account that the three compositions of asphaltenes are not comparable to the asphaltene content measured by TLC/FID.

2.6 Infrared Spectroscopy

FTIR spectra of the binders were determined by two different procedures. Firstly, the transmission technique was applied by measuring the IR-spectra of the dissolved bitumen samples as 5 wt. % solution in CCl_4 and in 0.5 mm layer thickness.

Secondly the attenuated total reflection (ATR) procedure was applied directly on the pure, unsolved bitumen samples.

For the assessment of the ageing characteristics of the bitumen samples, the peaks in the spectra at a wavenumber of 1700 cm^{-1} and 1030 cm^{-1} were analyzed, representing carbonyl (C=O) groups and sulfoxides in the samples. These groups are formed due to oxidative ageing of the bitumen [1, 3].

III. RESULTS

3.1 Experimental Campaign

The results discussed in the following section were obtained during an experimental campaign conducted in the author's laboratories. The bitumen samples were prepared by SASOL's wax laboratories and shipped to UNI KASSEL laboratories in metal cans. The bitumen samples were re-heated once and separated into the required sub-samples which were used for preparing the needed specimens. By this, additional thermal loads were reduced to a minimum of impact.

3.2 Results of Softening Point Ring and Ball Tests

The measured softening points are given in Table 3. The addition of F-T wax 1 increases the softening point of the bitumen 50/70 by 37.2 °C, F-T wax 2 even by 40.7 °C.

The ageing caused an increase of the softening point of the neat bitumen by 5.8 °C due to RTFOT and additionally by 9.6 °C due to PAV to a final value of 67.2 °C. In contrast, the softening points of the F-T wax modified binders stayed nearly constant at about 90 °C despite the applied aging procedures.

Table 3: Results of Softening Point Ring and Ball Tests

Aging stage	Softening point ring and ball [°C]		
	50/70	F-T 1	F-T 2
Unaged	51.8	89.0	92.5
Short-term	57.6	88.0	90.0
Long-term	67.2	91.0	91.5

3.3 Results of DSR Complex Modulus Tests

In 0and 0the shear modules and phase angles obtained at temperatures of 30 °C, 60 °C and 90 °C at a frequency of 1.59 Hz are summarized.

The complex shear modules measured at the frequencies 0.1 Hz, 1.59 Hz and 10 Hz are plotted versus the temperature in Fig. 3. The corresponding phase angles are plotted in Fig. 4.

The addition of either wax product increases the shear modulus of the bitumen in the unaged stage considerably. This increase is most obvious for the temperature of 60 °C for which the shear modulus is increase by a factor of about 17. The difference at 90 °C (factor of roughly 10) and also at 30 °C (factor of less than 4) is lower than this. Here the viscosity-changing effect of wax addition can be clearly demonstrated. Especially for the temperatures where asphalt mixtures show sensitivity regarding rutting, the shear modulus is increased considerably, whereas the viscosity effect at both lower and higher temperatures are smaller.

For all bitumen samples a stiffening effect due to aging can be observed. For the straight bitumen 50/70, short-term aging by RTFOT results in57 % higher shear modulus at 30°C testing temperature, in 117 % increase at 60°C and 88 % increase at 90°C. After PAV long-term aging, the shear modulus increases further. The increase is highest at the highest test temperature (90 °C) and results in a shear modulus of more than five times higher compared to the unaged samples.

For the wax-modified samples, the aging simulation has less effect on shear modulus results. At a test temperature of 30 °C, the shear modulus is increased only slightly whereas at 60 °C and 90 °C the value is even reduced after RTFOT. Long-term aging results in a shear modulus which is slightly higher compared to the values obtained for the unaged samples.

Table 4: Results of DSR tests: Complex shear modulus |G*| obtained at the temperatures 30 °C, 60°C and 90 °C and a frequency of 1.59 Hz

T [°C]	Aging stage	Shear modulus G* (1.59 Hz) [Pa]		
		50/70	F-T 1	F-T 2
30	Unaged	608 352	2 094 287	2 134 912
	Short-term	953 420	2 547 040	2 377 696
	Long-term	2 035 684	3 357 754	3 192 656
60	Unaged	4 898	87 304	87 802
	Short-term	10 641	86 655	82 871
	Long-term	38 524	122 268	116 134
90	Unaged	176	2 227	1 889
	Short-term	330	1 980	1 709
	Long-term	1 065	2 333	2 097

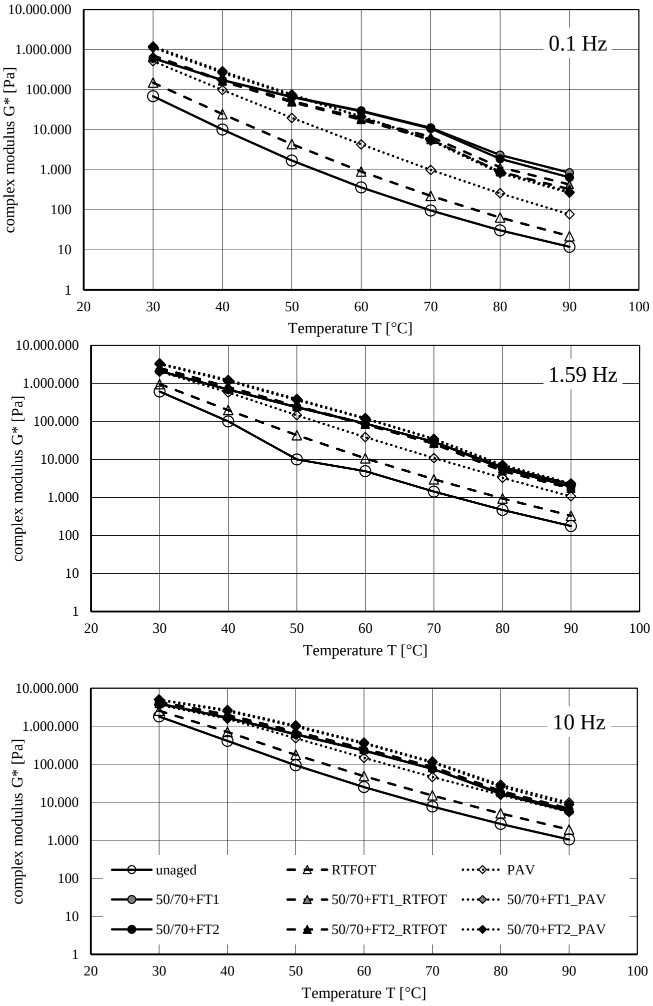

Figure 3: Complex modulus versus temperature measured at 0.1 Hz (top), 1.59 Hz (middle) and 10 Hz (bottom)

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For the phase angle results as indicated in Table 5 and plotted in Fig. 4, the addition of wax modifier to bitumen results in a decrease of the phase angle for all test temperatures which can be interpreted as a shift towards more elastic and less viscous material performance. For the unaged samples, the wax modification effect on the phase angles depends on the loading frequency. At high frequency of 10 Hz the increase in temperature results in an increase of phase angle as also observed for the unmodified bitumen (Fig. 4, bottom).

Table 5: Results of DSR tests: Phase angle δ obtained at the temperatures 30 °C, 60°C and 90 °C and a frequency of 1.59 Hz

T [°C]	Aging stage	Phase angle δ (1.59 Hz) [°]		
		50/70	F-T 1	F-T 2
30	Unaged	65,4	45,8	45,7
	Short-term	58,9	45,8	47,9
	Long-term	45,1	39,9	40,3
60	Unaged	81,9	45,0	44,9
	Short-term	76,9	59,0	54,1
	Long-term	68,0	56,2	55,7
90	Unaged	89,0	44,1	47,2
	Short-term	87,2	58,1	60,7
	Long-term	83,3	71,7	68,8

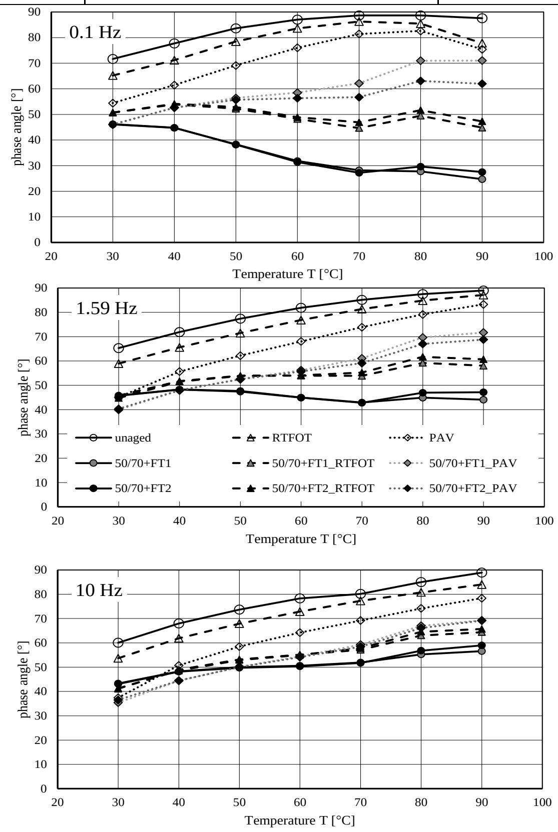

Figure 4: Phase angle versus temperature measured at 0.1 Hz (top), 1.59 Hz (middle) and 10 Hz (bottom)

However, at a low frequency of 0.1 Hz the phase angles of the two unaged wax modified bitumen decreases with increasing temperature. For the medium frequency of 1.59 Hz, the phase angle indicates only small changes with increasing temperature. An explanation for this effect can be found in the structural properties of the wax-modified samples. At high frequency, the bitumen predominates the overall rheological properties in of the wax-modified binder. With lower frequency, more time is available allowing internal flows of the bitumen besides or around the wax structure. Therefore, the wax predominates the type of rheological reaction which results in a phase angle decrease with decreasing bitumen viscosity provoked by increase of temperature. **Error! Reference source not found.**At temperatures between 70 °C and 80 °C, the phase angle plots indicate bends and changing temperature-dependency. This can indicate the beginning melting of the wax, compare [2].

The aging of the straight bitumen sample results in a significant decrease of the phase angle at all test temperatures. For the wax modified samples this short-term aging effect can only be observed for low temperatures and high frequencies. At higher frequencies and especially at all temperatures at the lowest applied frequency of 0.1 Hz, the ageing results in an increase of phase angle. This indicates a shift of the material performance towards viscous properties. Therefore, the difference in the phase angles between unmodified and wax modified samples is reduced with proceeding ageing.

Comparing the phase angles of the bitumen samples modified with different F-T-waxes, it can be observed, that for unaged and RTFOT-aged conditions similar results are obtained. However, for the PAV-aged samples, F-T1 indicates a higher increase in phase angle compared to F-T2.

From the shear modulus G* and phase angle δ obtained at each temperature and frequency (0.1 Hz, 1.0 Hz, 1.59 Hz, 10 Hz), storage and loss modules were calculated. The storage modulus indicates the elastic material properties, whereas the loss modulus can be interpreted as the ability of the material to dissipate energy into viscous motion. For the results obtained on the unmodified bitumen 50/70, the Cole-Cole plots are displayed in Fig. 5. The aging results in a shift of the Cole-Cole plots towards lower loss modules and higher storage modules.

The measured values can be fitted by a potential function as indicated in (1).

$$G'' = a \cdot G'^{b}, \quad (1)$$

where a and b are regression factors.

This rather simplified approach for the interpretation of Cole-Cole plots allows the visual comparison of the aging effect of wax-modified samples in the viscoelastic domain.

Therefore, Fig. 6 shows the aging effect in the Cole-Cole plot. For the samples of 50/70, the aging results as already described in a shift towards reduced viscous and increased elastic stiffness properties.

The diametric other effect can be observed for the wax-modified samples. Here, the aging results in a considerable upward shift of the curves in the Cole-Cole plot. It can be assumed that prolonged long-term aging results in similar visco-elastic properties of the straight and the wax modified bituminous binders. These trends can also be observed for the phase angles results.

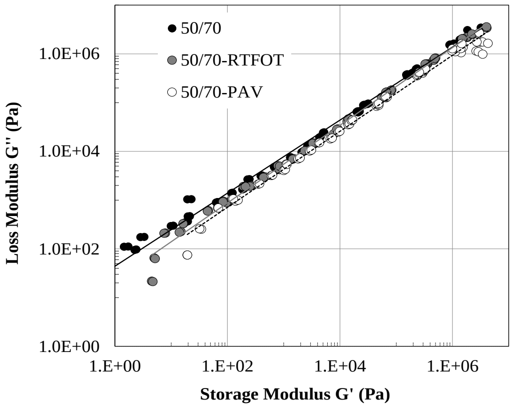

Figure 5: Cole-Cole-plot of the DSR-temperature-frequency sweep tests obtained on the unaged, short- and long-term aged samples of the straight bitumen 50/70 – addition of fitting curves

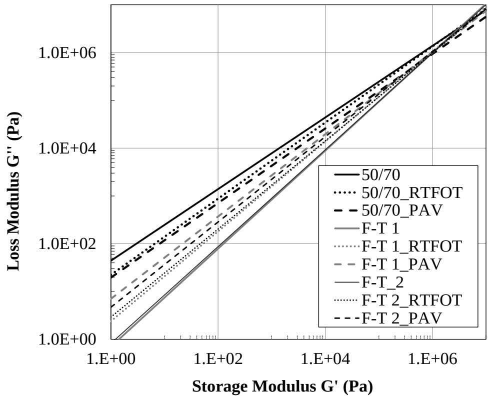

Figure 6: Regressing curves of the straight and wax modified bitumen samples at varied aging stages in the Cole-Cole-plot

3.4 Results of SARA- Analysis

The proportions of the bitumen SARA fractions calculated from the chromatograms obtained from TLC/FID tests are plotted in Fig. 6. When comparing the SARA fractions of the three unaged binders, the F-T wax modified binders indicate increased contents of resins and asphaltenes as well as decreased contents of aromatic and saturates fractions compared to the neat bitumen. Further the asphaltene peak shows significantly different peak shapes, compare Fig. 1. This results in higher area proportions for the 1st asphaltene peak as indicated in Fig. 6 in the increasing magnitude of this first column. Short term ageing results in an increase of asphaltenes and in a decrease of saturates for all bitumen samples. For unmodified binder and F-T 1 an increase of resins and a decrease of aromatics were recognized over the ageing stages. For F-T 2 less ageing effects for resins and aromatics are identified. It is noticeable that the asphaltene content after PAV ageing decreases.

Table 6 presents the average of the SARA components. These values are plotted in Fig. 7, in which also the scatter within the five repetitions is given.

All bitumen types show an increase of resins and a decrease of aromatics and asphaltene content after PAV ageing. The contents of saturates do not show significant changes.

Both wax modifiers have no influence on the SARA composition in unaged bitumen samples. After PAV ageing F-T 2 shows a lower increase of resins and a lower decrease of aromatics compared to 50/70 and F-T 1.

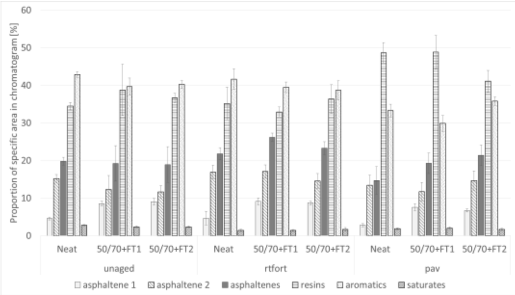

Figure 7: SARA components of unaged and aged binders

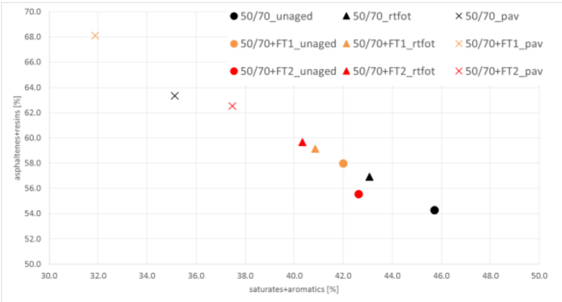

Figure 8: Grouping of SARA fractions

Table 6: Results of SARA analysis: asphaltenes 1, asphaltenes 2, asphaltenes (total), resins, aromatics and saturates

sample	SARA components	unaged	rtfot	pav
50/70	Asphaltenes 1	4.60	4.69	2.80
	Asphaltenes 2	15.23	16.90	13.43
	Asphaltenes (total)	19.82	21.79	14.71
	Resins	34.46	35.12	48.63
	Aromatics	42.89	41.67	33.28
	Saturates	2.83	1.41	1.86
F-T 1	Asphaltenes 1	8.57	9.13	7.58
	Asphaltenes 2	12.29	17.08	11.70
	Asphaltenes (total)	19.23	26.21	19.28
	Resins	38.78	32.94	48.84
	Aromatics	39.64	39.46	29.87
	Saturates	2.36	1.39	2.01
F-T 2	Asphaltenes 1	9.05	8.72	6.73
	Asphaltenes 2	11.68	14.57	14.66
	Asphaltenes (total)	18.93	23.29	21.40
	Resins	36.65	36.38	41.13
	Aromatics	40.27	38.66	35.78
	Saturates	2.35	1.68	1.70

In Fig. 8 the fractions with highest polarity (asphaltenes + resins) are plotted versus the fractions with lowest polarity (aromatics+saturates). This graph visualizes the effect of increasing polarity by increasing resin content and decreasing aromatic content during ageing. Here the effect of lower influence of PAV ageing for F-T 2 becomes more obvious.

3.5 Results of Asphaltene Composition Analysis

The results of the precipitation experiments for separating three types of asphaltenes, total asphaltene and maltene content of all unaged and aged binders are presented in Figure 9.

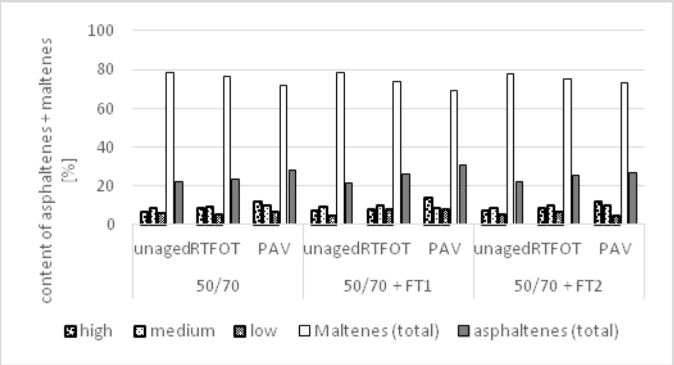

Figure 9: Content of low, medium, high soluble asphaltenes, total asphaltenes and total maltene content

All bitumen samples show in the unaged stage a maximum of medium soluble asphaltenes. As expected the total maltene contents decrease and the total asphaltene contents increase after ageing. However, the increase of asphaltenes for F-T 2 is less severe compared to F-T1 as well as the neat bitumen.

With regards to the proportions of the three types of asphaltenes, a continuous increase of low soluble asphaltenes and a decrease of medium and high soluble asphaltenes can be recognized during ageing for the unmodified binders. The plots of solubility profiles as shown in Fig. 10 allow a further interpretation of the results. The vertical position of the lines indicate that the asphaltene composition is stronger affected by the ageing affects compared to the effects of wax modification. For wax modified binder F-T 1 only a small change in low soluble asphaltenes (solubility parameter of 15.7) content after RTFOT aging is recognized. After PAV ageing a significant increase of these asphaltenes is noticeable. The contents of medium and high soluble asphaltenes are equal. After PAV aging a significant increase of the low soluble asphaltenes and a decrease of medium and high soluble asphaltenes to the same range are noticeable.

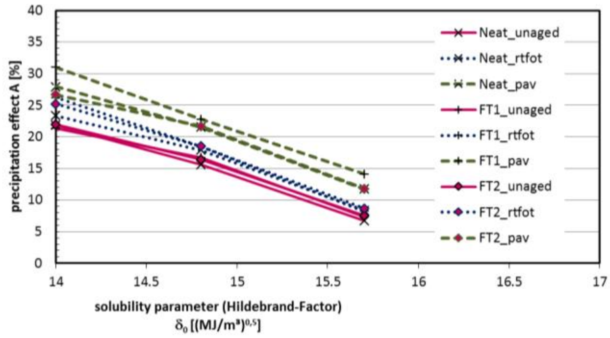

Figure 10: Profile of solubility and precipitation limits

3.6 Results of IR Spectroscopy

Infrared spectroscopy by transmission and ATR techniques (Figure 11 and Figure 12) were carried out to observe the oxidation progress. The IR spectra of the unaged and aged binders differed mainly in the wave number range around 1700 cm^{-1} and 1030 cm^{-1}. Absorptions in the range of 1700 cm^{-1} are caused by carbonyl groups (C=O) whereas the peaks at 1030 cm^{-1} indicate sulfoxides, which result from oxidation [4]. Fig. 11 shows a detail of the IR spectra obtained from the transmission experiments for the C=O peak range. The same range is plotted in Fig. 12 for the ATR experiments. With both techniques similar effects were identified: The unaged binders show high transmission values (Fig. 11) and low extinction results (Fig. 12). After RTFOT, the absorption in the C=O-range was slightly intensified. The long-term ageing by PAV results in significant peaks in the two spectrograms for the C=O.

In order to quantify the extent of oxidation, the area of the C=O peaks were integrated. In Fig. 13 the C=O peak areas as evaluated from the transmission and ATR experiments for the nine binder samples are shown. Whereas the transmission experiment identifies a clear increase of the C=O peak areas due to RTFOR ageing, this increase is in the ATR experiment only in the range of test scatter. However, both types of IR test setup identify significant increases of the C=O peak area for the PAV aged samples. The presence of F-T wax has no significant effect on the oxidation during short term aging but indicates a tendency of reducing the oxidation after long term aging, especially F-T wax 2.

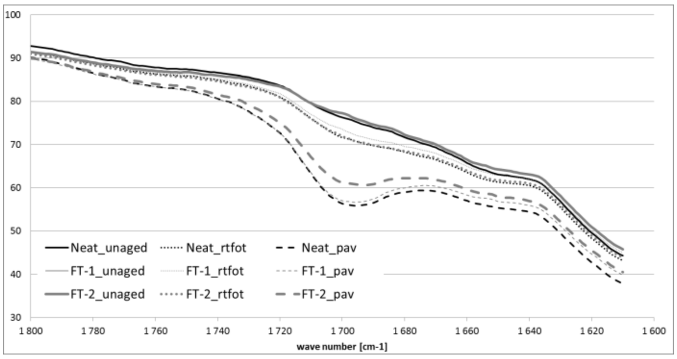

Figure 11: FTIR spectra (detail in 1700cm^{-1} range) of unaged and aged binders in transmission technique

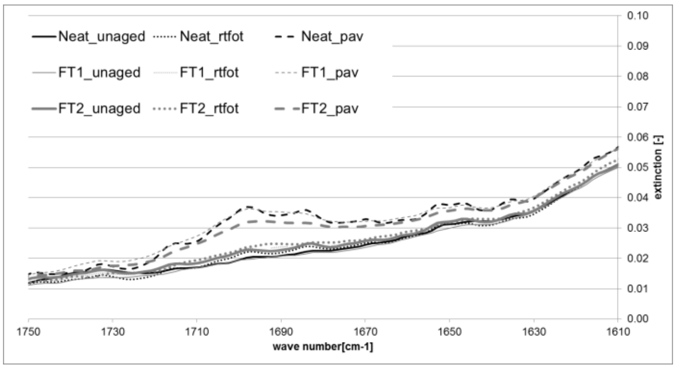

Figure 12: FTIR spectra (detail in 1700cm^{-1} range) of unaged and aged binders in ATR technique

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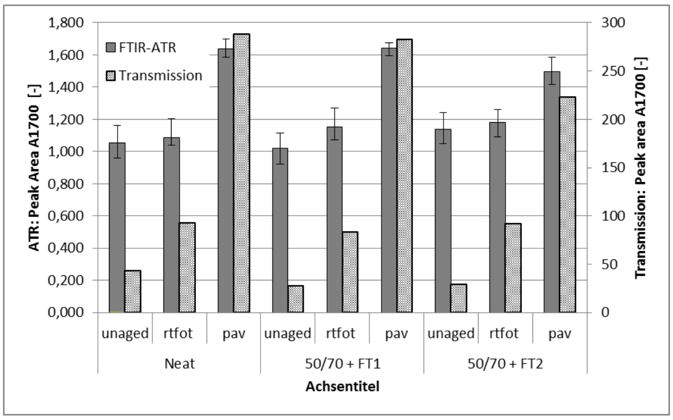

Figure 13: Peak areas of FTIR spectra in the carbonyl range (1720 – 1670 cm^{-1}) at different aging stages

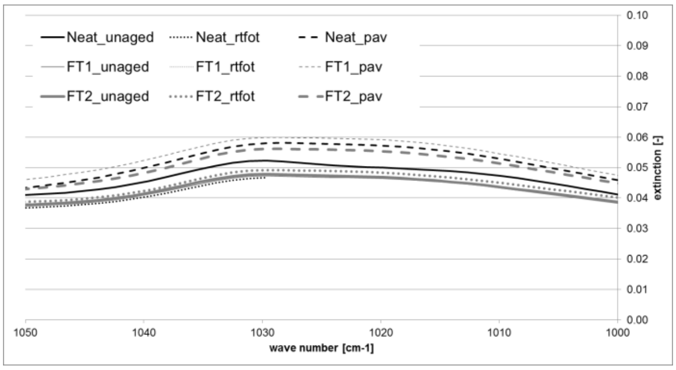

Figure 14: FTIR spectra (detail in 1030 cm^{-1}) of unaged and aged binders in ATR technique

Fig. 14 shows the results from ATR experiments for the wave number 1030 cm^{-1}, identifying the presence of sulfoxides. Similar effects can be observed as for the C=O ageing peak. Whereas RTFOT has a marginal ageing effect, significantly higher peaks can be observed after PAV. Again, the ageing effect in F-T 2 is less intense compared to F-T 1 and neat bitumen 50/70.

Furthermore, the FTIR experiments allow the identification of wax-modification in the bitumen samples. As described in [1] the IR-signal at a wave number of 720 cm^{-1} can be used "as an indication of amorphous and/or crystalline structures in the binder due to wax content" for F-T waxes (Figure 15). It can be observed, that the ageing has no effect on the peak at wave number around 720 cm^{-1} and that the extinction is constant for all bituminous binders so that the difference can be identified as wax components.

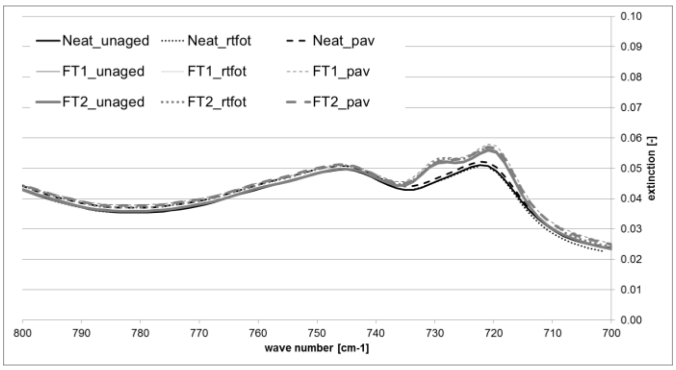

Figure 15: Identifying Wax Modifiers in Bitumen

3.7 Interpretation of Test Results

As expected and described in [1], wax modification in bitumen increases the binder stiffness as observed in increasing softening point ring and ball and in increasing shear modulus in a temperature range from 30 °C to 90 °C for the unaged binders. The decreasing phase angle shows an increase of elasticity caused by wax modifiers especially in a temperature range from 50°C to 70°C. Within this temperature range, the stiffness of the wax network formed within the binder is higher than the stiffness of the neat bitumen and therefore the wax properties predominate the phase angle of the resulting binder. At lower temperatures the high bitumen viscosity as well as at higher temperatures the beginning of wax melting will result in increased phase angles. Loads above the linear viscoelastic range, which more realistically indicate the deformation resistance, were investigated by two research groups applying the MSCR technique [11], [12]. It was found that 2 % F-T wax significantly increased the percentage of recovery and significantly decreased the irrecoverable compliance of unaged bitumen.

Regarding the chemical properties of the unaged binder samples, the modification can be identified in the FTIR-analysis as well as by a significantly changed asphaltene peak shape in the TLC/FID. The high peak at the sample spotting point of the Chromarods indicates highly insoluble compounds in the wax-modified binders as the F-T wax is almost insoluble at the applied temperature. However, besides of these items, no significant differences were identified between the wax-modified and the neat binder. F-T 1 and F-T 2 have the same effect on the SARA fractions in the unaged binder independently of their individual chemical structure.

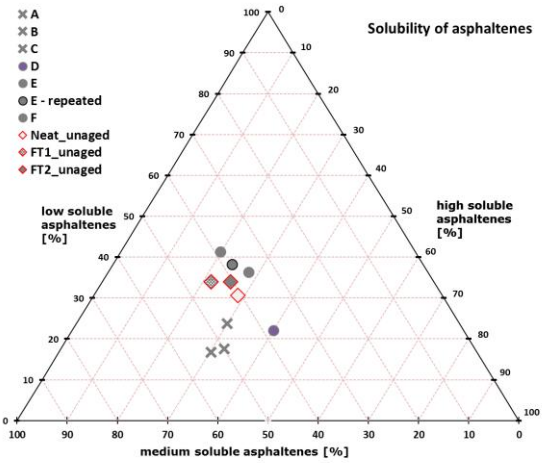

Figure 16: Comparison between asphaltene components by [10] of different 50/70 bitumen types

Figure 16 compares various neat bitumen 50/70 samples from different sources in their components of asphaltenes. A, B, C constitute 50/70 of one supplier, D, E, F represent 50/70 of additional different suppliers. The figures show that all 50/70 do not have the same chemical compositions in spite of them being the same penetration grade. The differences regarding the colloidal composition of neat bitumen shows significantly higher variability compared to the effect of wax modification. It is obvious, that these analytical methods are not feasible for identifying differences in the mechanical properties for wax-modified binders.

Aging usually increases the stiffness of the bitumen (for example its shear modulus) due to a decreasing content of volatile bitumen compounds and the formation of larger molecules due to oxidation. However, ageing also affects the mechanical properties of modifiers in the binder. At the same time, modifiers will influence the chemical stability of the bitumen compounds. These effects can be observed in the results of mechanical and chemical measurements. Firstly, the ageing did not affect the softening point of the wax modified bitumen. The softening point is primarily controlled by the wax modifier and can, therefore, not be applied for identifying the ageing state of the bitumen compounds.

The evaluation of the mechanical properties within a large temperature range applying DSR allows a better identification of ageing effects. At lower test temperatures (30 °C), the wax modified binder samples indicated the expected increase of shear modulus after short-term ageing. Though, at the elevated temperatures of 60 °C and 90 °C the shear modulus of the wax modified samples even indicate a decrease after ageing. Again, at these high temperatures the shear modulus represents the resulting stiffness of the wax network in the sample, whereas the increasing viscosity of the bituminous compounds still result in lower stiffness compared to the wax modification and therefore the ageing effect is not visible. Only with continued (long-term) ageing, the proceeding stiffening of the bitumen will also at elevated testing temperatures result in a stiffening of the wax modified bitumen.

These effects can also be identified by the phase angle measurements. As indicated in Fig. 16 (1), increasing temperature will result in increasing phase angles identifying viscous properties. This temperature-dependent increase can also be observed for aged binders with lower phase angle values. However, for the wax-modified binders (2), three phases of temperature-dependency can be identified. Below the temperature of 40 °C, an increasing temperature results in increasing phase angles as the comparatively high viscosity of the bitumen predominates the overall rheological properties. Though, with further increasing temperatures up to 70 °C the temperature increase results in a phase angle decrease. This can be explained by the increasing importance of the structural wax network within the binder, with higher elasticity. Again, with increasing temperature up to a temperature of 90 °C, the wax network indicates reducing strength at temperatures near its melting point which results again in an increase of phase angle. Whereas the short-and long-term ageing have little effect on the shear modulus of the wax-modified binders, a shift in the temperature-depending phase angle can be observed, see Fig. 17 (3) and (4). Because of the increasing viscosity of the bitumen, the temperature identifying the change of predominating bitumen and wax properties is increasing to approximately 60 °C (after RTFOT) and 70 °C (after PAV).

When applying the Sol/Gel-model, the decreasing phase angle as a result of wax modification can be interpreted as increased Gel characteristics in this bitumen.Regarding the effects of ageing on the chemical composition of bitumen, the expected results are obtained for the unmodified bitumen (50/70). In the SARA analysis, decreasing contents of saturates and aromatics are observed, whereas resins and asphaltene contents increase. Only the decrease of asphaltenes for the PAV-aged samples is unreasonable. Here, the procedure for SARA detection may explain this value. Bitumen is dissolved in dichloromethane at the beginning of the TLC/FID and afterwards separated on chromarods using three different solvents successively. Non-soluble compounds in dichloromethane will not be analyzed in the test as they do not show up in the applied samples. Reference [5] supports this assumption with the same experience describing "further oxidation of the asphaltenes to insoluble carboids. The carboids […] do not dissolve in the solvent employed in spotting the sample on the Chromarod. Because the carboids are not transferred to the rods, the sum of the areas […] is reduced." Therefore, SARA analyses by TLC/FID demands for the separation of the asphaltenes prior to the experiment for detection of resins, aromatics and saturates.The increasing asphaltene content by ageing can be observed better by the results of asphaltene compounds analysis. Here a clear increase of asphaltene contents can be observed for the neat bitumen. The modification of the binder with F-T wax is influencing the ageing properties of the bitumen. Especially F-T wax 2 beneficially results in higher maltene contents (identified by asphaltene precipitation) as well as high contents of non-polar compounds of aromatics and saturates indicating less aged bitumen properties. This confirms the reduced ageing susceptibility observed in the DSR experiments.

Nonetheless, the following statements can be made about influence of F-T wax 2 on ageing with regard to the chemical characteristics:

- Lower increase of sulfoxides and carbonyl groups measured by infrared spectroscopy
- Lower content of resins and higher content of aromatic components within SARA analysis
- Higher content of maltene phase and lower content of asphaltenes (iC_8- asphaltenes) measured by the Zenke test.

On the basis of lower iC_8-asphaltenes and higher maltenes after ageing the colloidal structure is more comparable to a Sol-type. As result of the chemical analyses it may be stated that F-T wax 2 has favorable properties compared to F-T wax 1.

With regards to rheological properties the following statements may be summed up from this study:

- Whereas the presence of wax considerably increases the shear modulus of the bitumen in unaged stage, it reduces its further increase due to ageing.
- For unaged wax-modified bitumen the wax will improve the binder´s elasticity especially in the range of elevated service temperature. Due to ageing this beneficial effect is reduced but simultaneously counteracted by increasing binder viscosity.
- Similarly, the phase angle decrease due to ageing is superimposed by higher elasticity of the wax modifier.

The results of the phase angle measurements can be interpreted as follows: The wax modifiers change the bitumen characteristics in an unaged binder first into Gel bitumen and after ageing to Sol bitumen while the resulting stiffness is nearly constant.

With regard to rutting resistance assessed in the dynamic shear rheometer, the F-T modification shows the lowest phase angles at low frequencies. This will result in higher resistance against permanent deformation especially for slow moving or even static loads.

Caused by the lower content of iC_8- asphaltenes (degree of ageing) and higher elasticity F-T 2 has more positive ageing properties and better rheological properties compared to F-T 1 and the neat bitumen 50/70.

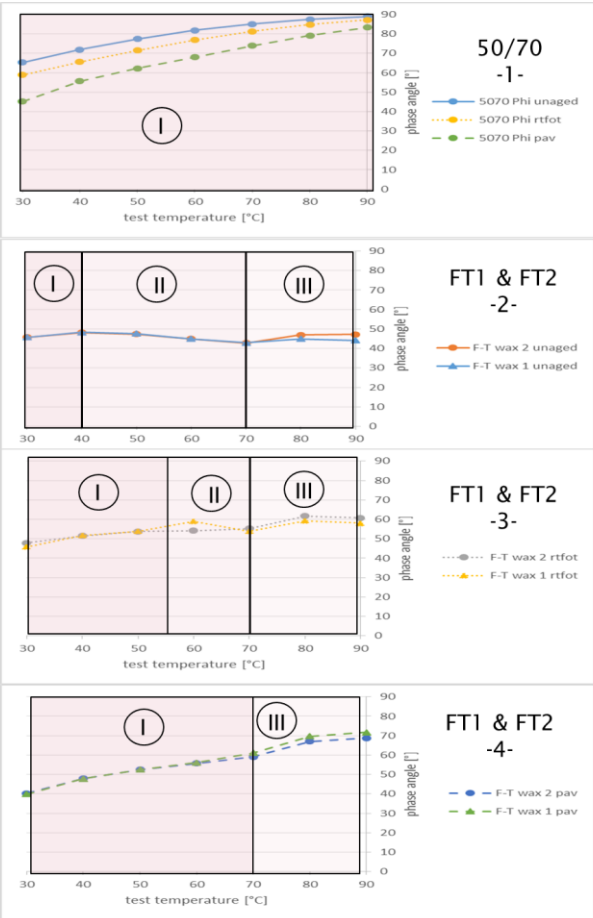

Figure 17: Effect of F-T wax based on phase angle

IV. CONCLUSIONS

The following conclusions can be drawn from the results of the presented test campaign:

The evaluation of asphaltene contents shall be done by solution/precipitation procedures in order to include also non-soluble compounds especially of aged binders into the SARA evaluation. For conducting SARA evaluations, the asphaltene contents shall be evaluated by precipitation experiments. Afterwards the contents of saturates, aromatics and resins can be measured by TLC/FID of the residual maltene fractions.

Wax modification does not significantly affect the colloidal proportions of unaged bitumen. Differences between various neat bituminous binders of similar penetration grade are higher compared to differences originating from wax modification.

Wax modifiers change the chemical structures in bitumen and their physical properties. This results in reduced ageing susceptibility. There are no significant differences in the chemical and rheological behavior of F-T 1 and F-T 2, but in some aspects F-T 2 shows favorable ageing properties.

The stiffening effects of wax in bitumen are most pronounced in fresh bitumen. Aging results in a reduction of the elasticity-increasing effect of wax-modified bitumen. Especially at early age of the asphalt pavement, wax will reduce the rutting susceptibility of the asphalt mixture.

From DSR temperature-frequency sweeps the effects of ageing and of binder modification can be clearly evaluated. Especially the temperature-dependent phase angle provides valuable information regarding the rheological properties of modified binders.

The softening point ring and ball of wax-modified bitumen is predominated by the wax properties which hides any ageing effects of the bitumen. Therefore, this parameter is not feasible for estimating the properties of modified bitumen even after long-term ageing.

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