

# Wax morphology in bitumen

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Wax crystallisation and melting in bitumen is usually considered detrimental to bitumen quality and asphalt performance. The objectives of this paper are to study wax morphology in bitumen and to investigate effects of time, temperature, and thermal cycling on wax crystallisation. Various samples were selected, including eight waxy bitumens of different sources and three laboratory blends prepared by adding a slack wax and two isolated bitumen waxes to the non-waxy bitumen. Test methods used were differential scanning calorimetry (DSC), polarised light microscopy (PLM), confocal laser scanning microscopy (CLSM), and freeze etching (fracture) in combination with transmission electron microscopy (FF-TEM). The DSC results indicated that the selected bitumen samples differ widely in wax content and wax crystallisation starting and melting out temperatures. It was found that non-waxy bitumen displayed no structure or crystals neither in PLM, CLSM or FF-TEM, while waxy bitumens from different crude origins showed a large variation of structures. The morphology of wax crystals was highly dependent on crystallisation temperature as well as temperature history. The wax which has been isolated from waxy bitumen and mixed into non-waxy bitumen displayed similar morphology as the wax in the original bitumen. It was also found that bitumen wax usually melted at temperatures lower than 60°C although in one case a temperature of 80°C was needed until complete melting of the wax. © 2005 Springer Science + Business Media, Inc.

## 1. Introduction

Bitumen is a semi-solid material, which can be produced from certain crude oils or found in nature as natural asphalt. It is a mixture of hydrocarbons of different size and polarity containing heteroatoms such as sulphur, nitrogen and oxygen, as well as traces of metals (e.g. vanadium and nickel). The true nature of bitumen is not completely known. However, analytical techniques have identified some functional groups, such as normal- and iso- aliphatic chains, cycloalkanes, aromatics, carboxylic acid, and ketone [1]. Crude oils for bitumen production could be classified as waxy crude oils or non waxy crudes (naphthenic crudes). The waxy crudes are characterised by their ability to precipitate wax at lower temperature. In general, these waxes consist of two fundamental types of petroleum wax, paraffin wax and microcrystalline wax [2, 3]. After production of bitumen through distillation, parts of the waxes may be retained in the bitumen. Paraffin wax refers to the group of n-alkanes with few or no branches. These substances crystallise in large and flat plates or needles, and the crystals formed of paraffin

wax are known as macrocrystalline wax. In contrast, the microcrystalline wax primarily consists of aliphatic hydrocarbons with considerable amount of iso- and cycloparaffins. Normally this type of wax crystallises in tiny microscopic needles [4]. In bitumen, certain aromatics and molecules with polar functional groups may also crystallise upon cooling [5, 6].

Due to the varying molecular characteristics of waxes and the complex nature of bitumen components, wax crystallisation and morphology in bitumen and its effect on bitumen quality can differ greatly. Examples of such observations can be found in references [7–11]. These imply that, at a given wax content, wax type and crystallisation characteristics may have an impact on bitumen performance.

The main objectives of this work are to study wax morphology in bitumen, to determine effects of time, temperature, and thermal cycling on wax crystallisation, and to demonstrate bitumen source dependence of wax crystallisation and melting. For these purposes, different test methods are used, including differential scanning calorimetry (DSC), polarised light microscopy

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(PLM), confocal laser scanning microscopy (CLSM), and freeze etching (fracture) in combination with transmission electron microscopy (FF-TEM).

Use of DSC [12] and PLM in characterising wax crystallisation was reported earlier by other researchers [7]. PLM uses transmitted light, which means that the sample has to be thin enough to let light pass through. Another requirement is that crystals have to be large enough to be detectable. In [7], the crystallised (well-organised) domains were found to be 10–15  $\mu\text{m}$ . Recently, a study of bitumen structure using CLSM (fluorescence mode) has also been published [13]. The authors demonstrate a pattern in micro photographs of light spots of a size 2–7  $\mu\text{m}$  from two bitumen samples, which they interpret as asphaltenes. They did however not conclusively identify the spots as asphaltenes and might have mistaken waxes for asphaltenes.

In this paper, different microscopy techniques at different length scales are used to study wax morphology in bitumen. To confirm wax crystallisation, various bitumen samples are selected for cross-checking. Those samples include one non-waxy bitumen, eight waxy bitumens of different sources, and three laboratory blends prepared by mixing the non-waxy bitumen with a known commercial wax, and with two waxes isolated from waxy bitumens.

## 2. Materials

Nine bitumens of different sources and three laboratory blends were studied. Typical parameters of the samples are listed in Table I. One of the bitumens, B1, is considered to be wax free and the other eight contain various amounts of natural wax. To confirm that the pattern observed in the micro photos originate from wax it was decided to prepare three laboratory blends containing known amounts and known types of waxes. The laboratory blends B2, B5 and B6 were prepared by mixing bitumen B1 with 6% slack wax, 6% wax isolated from B7, and with 6% wax isolated from B9, respectively. The slack wax was a commercially available product with a congealing point (DIN-ISO 2207) of 42.5°C.

The GC-MS analysis indicated that the slack wax was composed of about 50% n-alkanes with C<sub>19</sub> to C<sub>36</sub>, and 50% other larger molecules [15].

The isolation of wax from bitumen followed a procedure proposed by Petersen *et al.* [9] and McKay *et al.* [10]. This procedure was considered to separate a wax fraction which best represent the wax in the bitumen. In the first step, larger or associating molecules were removed from the bitumen using preparative size exclusion chromatography (PSEC) performed in toluene. The fraction containing small size and non-associating molecules was collected, and the solvent was evaporated, and followed by dilution in toluene by a ratio of 5 g to 14 cm<sup>3</sup>, and further by 2-butanone with 11.25 cm<sup>3</sup> for each gram of dry small size fraction. The solution was cooled to –20°C and held at that temperature for one hour, then poured into a chilled funnel (vacuum) having a frit of 10–16  $\mu\text{m}$  porosity. The filter cake was rinsed with 25 cm<sup>3</sup> cold 2-butanone and the bitumen wax fraction was obtained. The chemical composition and thermodynamic properties of the isolated waxes will be reported elsewhere.

## 3. Test methods

### 3.1. Differential scanning calorimetry (DSC)

In thermal characterisation, a TA Instrument (model 2920 DSC) equipped with a refrigerated cooling system was used. For each experiment approximately 15 mg of sample was scraped from the sample container and then hermetically sealed into a DSC sample pan. A matched pan and lid were used as reference. The sample was first heated to 120°C and kept at this temperature for 15 min. The data were recorded during cooling to –80°C followed by heating to 120°C. The heating and cooling rates were 10°C/min. Wax content was calculated from endothermic peak during the heating scan. A constant melting enthalpy of 121 J/g was used as reference in the calculation. The reference enthalpy was based on a comparison of melting enthalpy determined for slack wax in bitumen and literature data for wax in bitumen.

TABLE I List of bitumen samples

Bitumen samples		Physical properties			Chemical composition <sup>b</sup>			
		Pen 25°C (0.1 mm)	Softening point (°C)	Vis. 135°C (mm <sup>2</sup> /s)	Saturates (%)	Aromatics (%)	Resins (%)	Asphaltenes (%)
Codes	Sources							
B1	Venezuelan	192	37.8	199	10	52	19	19
B2	Lab blend <sup>a</sup>	–	–	–	–	–	–	–
B3	Mixing crudes	61	49.0	468	7	47	26	20
B4	Unknown	86	46.4	181	11	55	19	15
B5	Lab blend <sup>a</sup>	–	–	–	–	–	–	–
B6	Lab blend <sup>a</sup>	–	–	–	–	–	–	–
B7	Venezuelan	214	39.1	283	7	49	23	21
B8	Unknown	64	49.4	424	5	49	27	19
B9	Mid-East	205	39.2	225	9	60	17	14
B10	AAM-1	64	52.0	569	11	52	21	16
B11	Russia	180	40.1	202	7	58	21	14
B12	Mexico	101	45.1	325	9	56	17	18

<sup>a</sup>The laboratory blends B2, B5 and B6 were prepared by mixing non-waxy bitumen B1 with 6% slack wax, 6% wax isolated from B7, and with 6% wax isolated from B9, respectively.

<sup>b</sup>Determined using thin-layer chromatography with flame ionisation detection (TLC-FID, Iatroscan) [14].

### 3.2. Polarised light microscopy (PLM)

In PLM, small amount of bitumen was placed on a clean glass slide and covered with a cover glass. The samples were prepared by first heating the bitumen at 120°C for one hour followed by homogenisation. A drop of the sample was then placed between preheated glass and cover glass. The “sandwich” was slightly squeezed to get samples thin enough, and left at room temperature (22°C) for one hour before viewing in a microscope (Nikon).

### 3.3. Confocal laser scanning microscopy (CLSM)

In CLSM (Leica TCS 4D), the light source was an argon-krypton laser using excitation 488 nm. For comparison, sample slides were prepared in the same ways as in PLM. Since the CLSM detected the reflected light (488 nm), thick samples were also investigated. In preparation of thick samples, bitumen in the tin was heated at 120°C for one hour and homogenised, after which a small amount of bitumen was placed into preheated metal cups (approximately 2 mm deep and 10 mm diameter) and covered with glasses. The samples in metal cups were left at room temperature (22°C) for one hour and then examined with CLSM.

### 3.4. Freeze etching (fracture) in combination with transmission electron microscopy (FF-TEM)

In FF-TEM, small amount of bitumen was placed in a gold cup made for freeze-etching/fracturing. The sample was heated at 120°C for one hour, left at room temperature (22°C) for one hour, and then frozen in liquid nitrogen (−196°C). The frozen bitumen was moved into a freeze-etching device and fractured at −150°C. The fractured surface was replicated with platinum and carbon, and was cleaned in toluene. The replica was viewed in a TEM (LEO 906E) at an accelerating voltage of 80 kV and under high magnification (35970×).

## 4. Results and discussion

### 4.1. DSC characterisation

DSC has been widely applied to characterise the thermodynamic properties of bituminous binders. In this study, DSC was used to determine wax content and wax crystallisation starting and melting out temperatures. A typical diagram is shown in Fig. 1. In the cooling cycle, an exothermic transition occurs at around +30°C which usually is interpreted as wax crystallisation. The transition continues down to the glass transition which vaguely can be seen around −30°C. In the heating cycle, there is an endothermic reaction which is interpreted as melting of the wax. The temperature at which all wax is completely melted is considerable higher than the start of crystallisation. This is probably due to super cooling effect at the cooling cycle. In Table II, the DSC results are summarised.

As indicated, the selected bitumen samples differ widely in wax content (0–6.2%), as well as in crystallisation starting temperature (18–46°C) and melting out temperature (63–92°C). For the laboratory prepared

TABLE II DSC parameters of bitumens

Bitumen samples	Wax content (%)	Wax crystallisation starting temp. (°C)	Wax melting out temp. (°C)
B1	0	–	–
B2	4.0	30	63
B3	1.9	37	90
B4	6.2	41	74
B5	1.9	28	70
B6	1.6	30	79
B7	2.4	31	72
B8	1.8	41	92
B9	4.2	39	83
B10	4.6	18	81
B11	4.1	40	87
B12	4.1	46	84

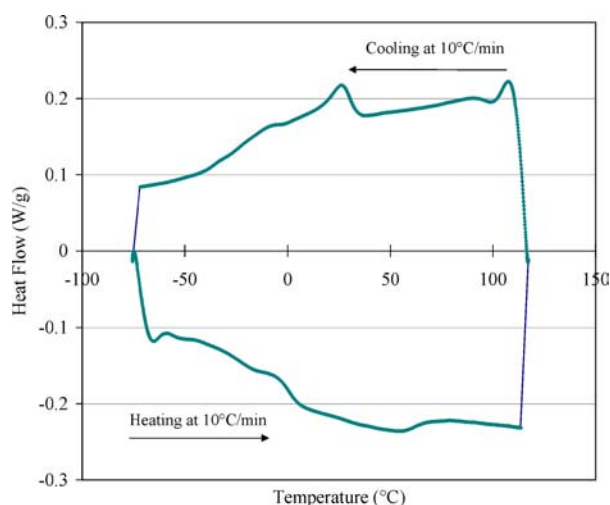


Figure 1 DSC diagram of bitumen B4 (cooling and heating scans at 10°C/min).

samples (B2, B5, and B6) with 6% slack wax or 6% isolated bitumen waxes, the measured values are lower than the added content. This is probably due to the fact that a constant melting enthalpy has been used as the basis for calculation of wax content regardless of wax type. It is however well known that the melting enthalpy for wax is different for different types of wax and also changes if interactions like for example dissolution in the bitumen take place [16]. Consequently, the wax contents as presented in Table II are primarily related to the melting enthalpies rather than true gravimetric values. From Fig. 1 it is obvious that the crystallisation takes place during a range of temperatures, indicating the presence of molecules with different crystallisation points. At lower temperatures, mobility of molecules is low compared to the cooling rate, which results in the DSC thermogram being dependent on testing conditions, such as cooling and heating rates, and isothermal storage time. The magnitude of the effects can vary with wax molecular characteristics and bitumen composition.

### 4.2. Wax morphology

#### 4.2.1. Comparison of methodology

A number of samples (B1, B2, B3 and B4) containing about 0–6% wax were investigated for comparison of different microscopy techniques (PLM, CLSM,

and FF-TEM) as well as different procedures of sample preparation. By applying these techniques to a set of non-waxy bitumen, waxy bitumens and laboratory blended samples, wax crystals have been confirmed and characterised at different length scales.

For detecting wax crystals, PLM is probably the most common technique. PLM distinguishes between isotropic and anisotropic materials, and detects birefringent areas that appear bright in micrographs. When PLM uses transmitted light, which is the case in this study, sample has to be thin enough to permit transmission of light through the highly absorbing bitumen sample. For non-waxy bitumen B1, as well as

B3, no structure pattern (wax crystals) was detected by PLM.

In CLSM, sample specimen is illuminated and scanned by a laser beam, and the reflected or fluorescent light from the specimen is focused onto a small aperture (pinhole) in front of the detector. The combination of point illumination and point detection improves resolution. When recording images on bitumen samples (thin or thick), the reflected light was captured, which means light with the same wavelength (488 nm) as the illumination was detected. When the two preparation techniques were compared, it became evident that in thick samples (2 mm in metal cups) the size of the wax

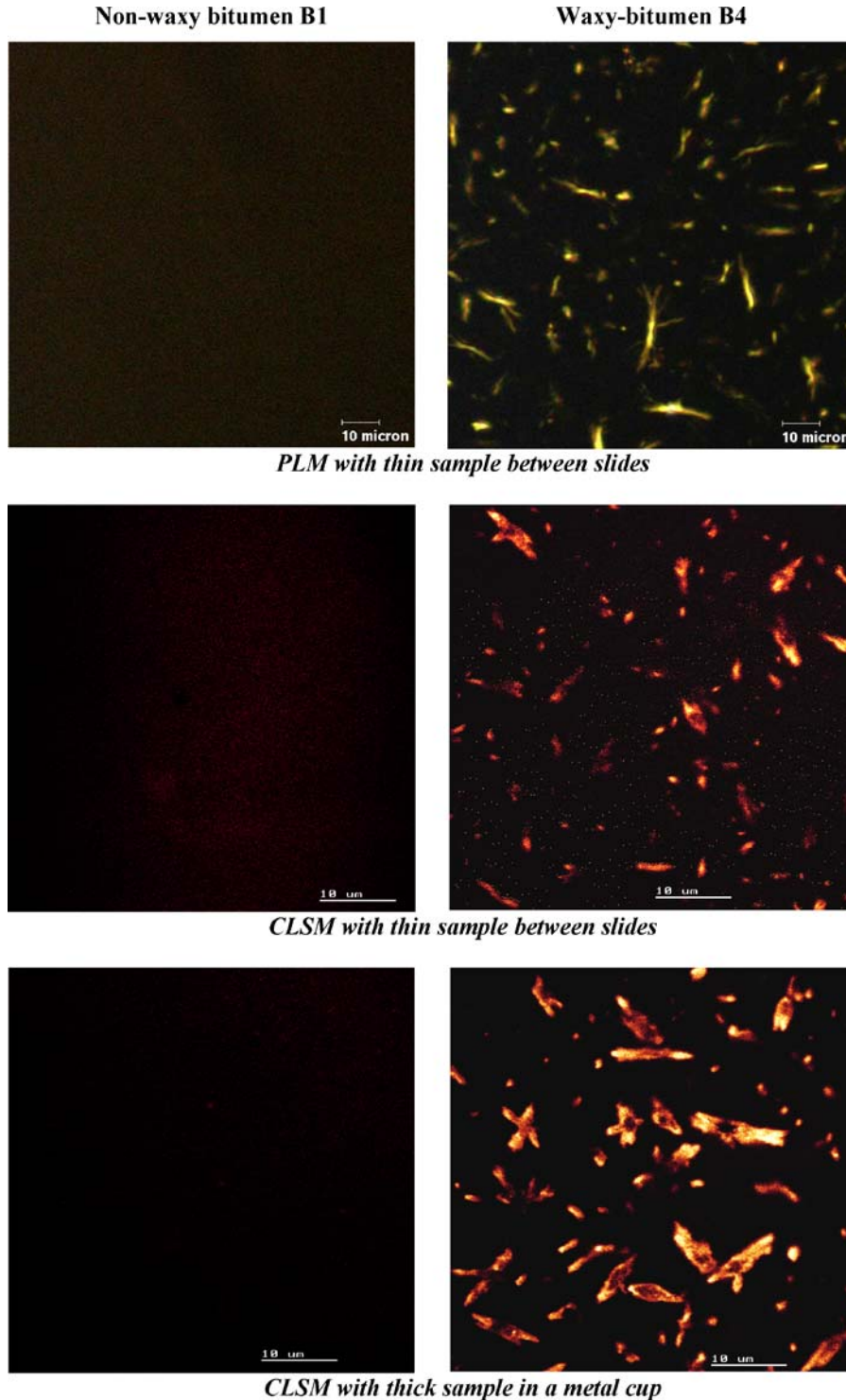


Figure 2 Comparison of PLM and CLSM for non-waxy (B1, left column) and waxy bitumen (B4, right column).

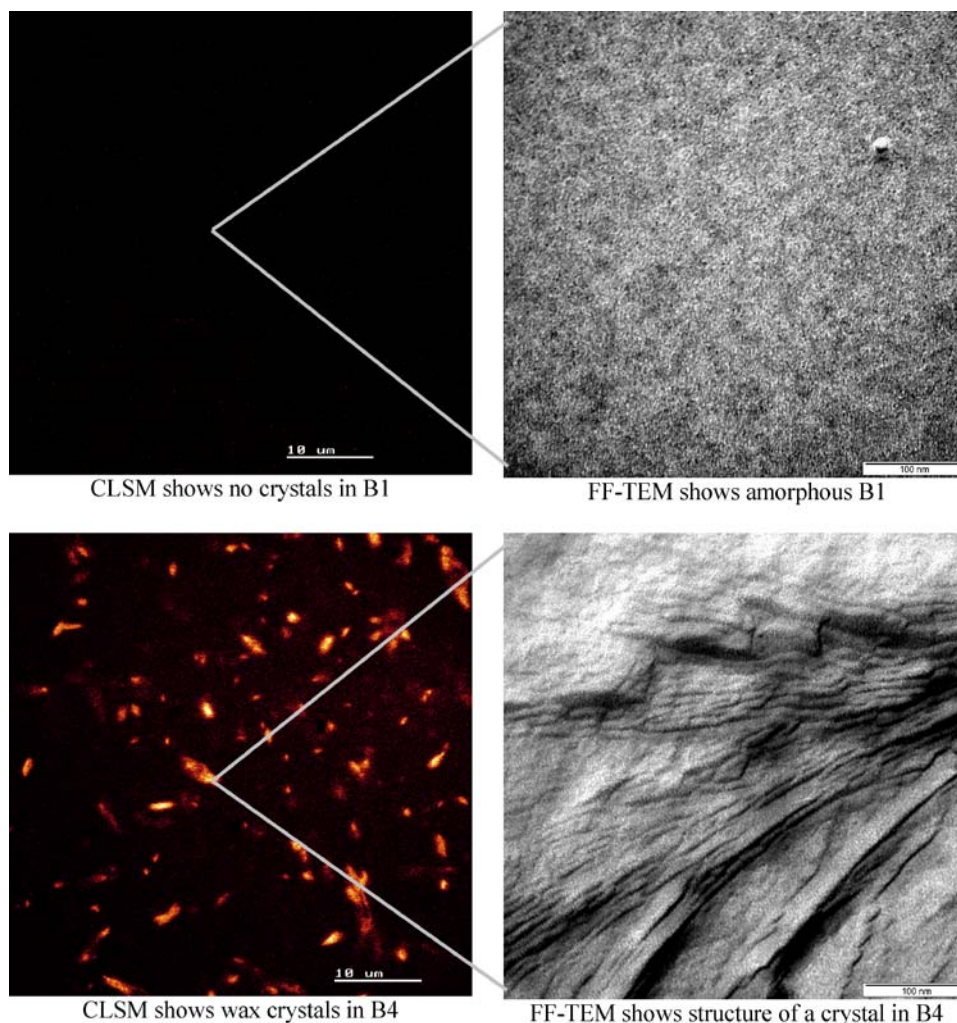


Figure 3 CLSM and FF-TEM images of bitumens with and without wax (scale: 10  $\mu\text{m}$  in CLSM and 100 nm in FF-TEM).

crystals seemed to be larger. Even in bitumen B3, which did not show any crystals in PLM, fine wax crystals (about 1  $\mu\text{m}$ ) were observed.

Thick samples in metal cups were believed more representative of bitumen in bulk. Thus, CLSM with thick sample preparation was used in further investigations with regard to effects of bitumen, isothermal time/temperature and thermal cycling on wax morphology. A comparison between PLM and CLSM with thin and thick samples of the non-wax bitumen B1 and waxy bitumen B4 is presented in Fig. 2.

The third technique applied to confirm wax crystals in bitumen is freeze-etching (fracture) in combination with transmission electron microscopy (FF-TEM). Using this technique, wax crystals are recognised by their repeating and well-organised structure. Examples of TEM images are shown in Fig. 3. Notice that the magnification used in the TEM images is 100 $\times$  larger than in the CLSM images. The TEM image of bitumen B1 is a magnification of a random spot, while the TEM image of bitumen B4 is a magnification of one of the light spots seen in the CLSM images. It was found that, of the four bitumen samples studied, B2 and B4 show an internal structure of wax crystals (layers building up the crystals), while no crystalline structures were visible in B1 and B3. The observations confirm that the particles visualised in PLM and CLSM are true wax crystals.

The presence of wax crystals in bitumen B4 was also confirmed by X-ray diffraction (WAXD results are not presented in this paper). For B3, which has exhibited fine particles in thick sample with CLSM, the absence of crystalline layers in the freeze etched sample could be due to the fracture properties of the frozen bitumen, i.e. the fracture plan did not go through wax crystals, or alternatively that the particles consist of other structures than crystals.

#### 4.2.2. Classification of wax morphology using CLSM

As mentioned earlier, CLSM with the thick-sample preparation in small metal cups was used in all further experiments. In Fig. 4, typical micrographs for 12 samples are illustrated. As can be seen, the non-waxy bitumen (B1) gives no pattern in CLSM, while waxy bitumens (B3, B4, and B7–B12) display an evident pattern with differences in size and shape. By adding 6% slack wax or waxes isolated from waxy bitumens B7 and B9 to the non-waxy bitumen B1, crystallised wax phase appears in CLSM (Cf. B2, B5 and B6 in Fig. 4). Moreover, by comparing B5 and B7, as well as B6 and B9, one can see that the isolated waxes display similar morphology as in the original bitumens when blended in the non-waxy bitumen. Thus we may conclude that

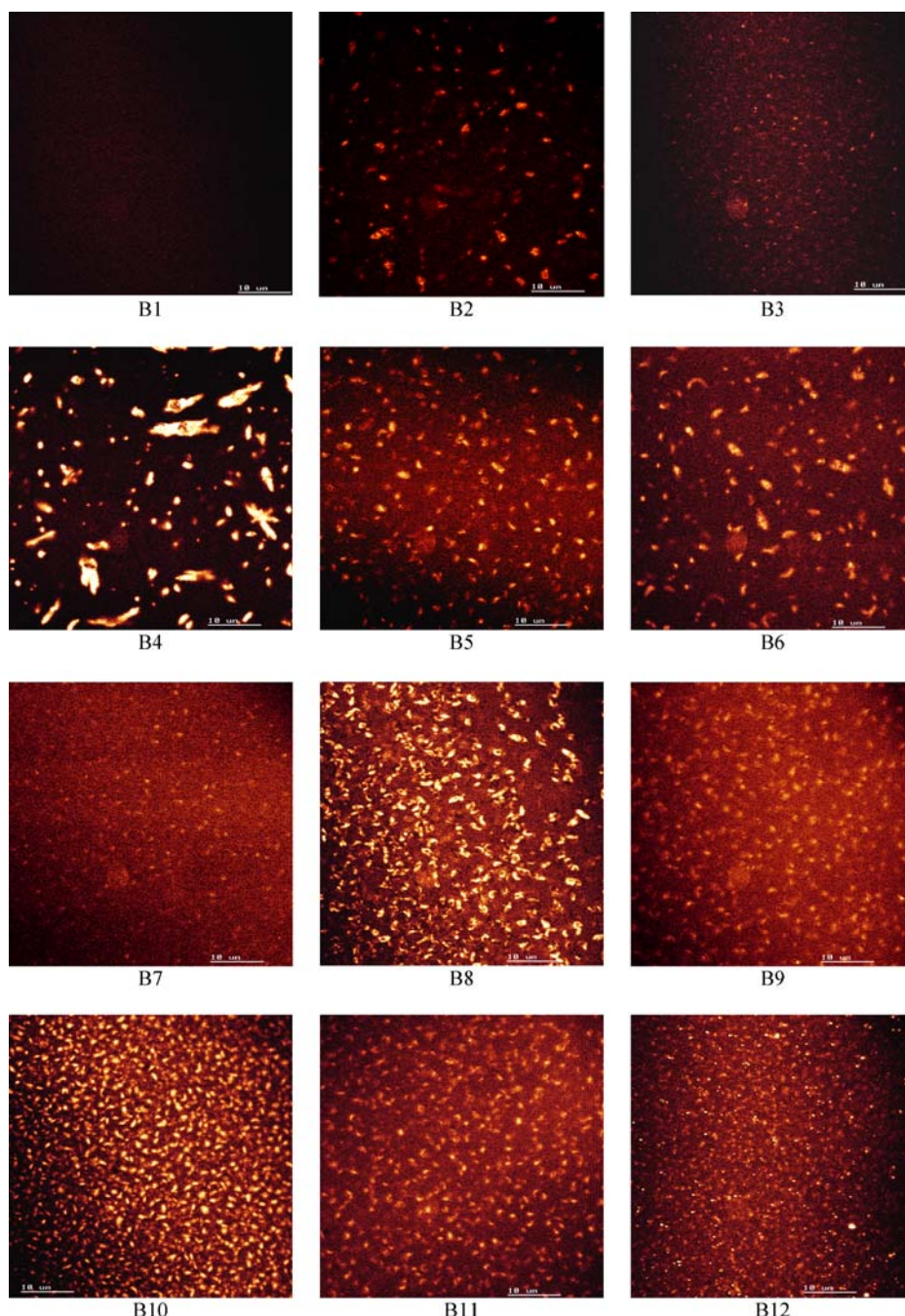


Figure 4 CLSM micrographs of bitumen samples (scale: 10  $\mu\text{m}$ ).

the pattern visualised in CLSM mainly consists of wax like material defined as non-interacting molecules in SEC which precipitates upon cooling. It is not likely that a precipitate obtained by this procedure should contain substantial amounts of asphaltenes (defined as n-heptane insoluble fraction of bitumen) although we can not completely rule out the possibility that some of the precipitate may have an amorphous structure rather than crystalline. This is also indicated by an attempt to classify the wax crystals shown by CLSM:

- Slightly elongated shape with size about 1–2.5  $\mu\text{m}$  in B2, B5 and B7
- Crescent shaped particles with size about 2–5  $\mu\text{m}$  in B6, B8, B9 and B11
- Flakes with about 1  $\mu\text{m}$  wide and 2  $\mu\text{m}$  long in B10 and B12; spot-like crystals in B12

- “Unique structures” in B3 and B4, which do not fit into any groups above: very small and fairly indistinct crystals or particles in B3 (Note that this bitumen did not show crystals with the thin samples prepared in slides); very large crystals (about 10  $\mu\text{m}$ ) in B4

Examples of non crystalline structures might be evident in the crescent shaped particles in B6, B8, B9 and B11 as well as in the fairly indistinct particles in B3. It is also evident that the shape and size of wax crystals have no relation to the wax contents determined using DSC. It should be pointed out that, for thick samples, wax crystals form randomly in three dimensions. This implies that small spots in micrographs could be either small crystals or larger crystals protruding perpendicular from the viewing plan. It is therefore difficult to

estimate the volume fraction of waxes by using two-dimensional CLSM images.

#### 4.2.3. Effect of crystallisation time and temperature

In studying the effects of time and temperature on wax morphology, bitumen samples B4, B7 and B9 were used. CLSM micrographs were taken after sample specimens (in metal cups) being stored at  $-19^{\circ}\text{C}$ ,  $0^{\circ}\text{C}$ ,  $22^{\circ}\text{C}$ , and  $40^{\circ}\text{C}$  for 1 h, 4 h and 24 h. For each temperature-time combination, a new sample was prepared. Samples were prepared by pouring bitumen which had been heated to  $120^{\circ}\text{C}$  for 1 h into metal cups, kept at room temperature for 1 h and then adjusted to storing temperature. The temperatures used for taking micrographs were the same as the storage temperatures. Examples of micrographs are shown for B4 in Fig. 5.

Generally, at lower temperatures (especially at  $-19^{\circ}\text{C}$ ), the time for visible wax crystals to appear was longer and the crystals were smaller compared to wax crystallisation at  $22^{\circ}\text{C}$ . For bitumen B7 and B9, at  $-19^{\circ}\text{C}$ , no wax crystals were detected even after 24 h storage. This could imply that the increased viscosity and reduced mobility of the molecules at low temperature prevent wax crystallisation. At high temperature ( $40^{\circ}\text{C}$  in this case), a few crystals with large size were detected. For all the testing temperatures, the wax crystals became more distinct with increasing storage time.

The bitumen source dependence of wax crystallisation/melting was also demonstrated in experiments with temperature cycling between  $-15$  and  $60^{\circ}\text{C}$ . For bitumen B7, wax crystals started to disappear as temperature increased to  $40^{\circ}\text{C}$ . However, for B4 and B9, wax crystals existed at a temperature as high as  $60^{\circ}\text{C}$  (the highest temperature used in CLSM). An additional test made for B4 showed that the wax crystals were

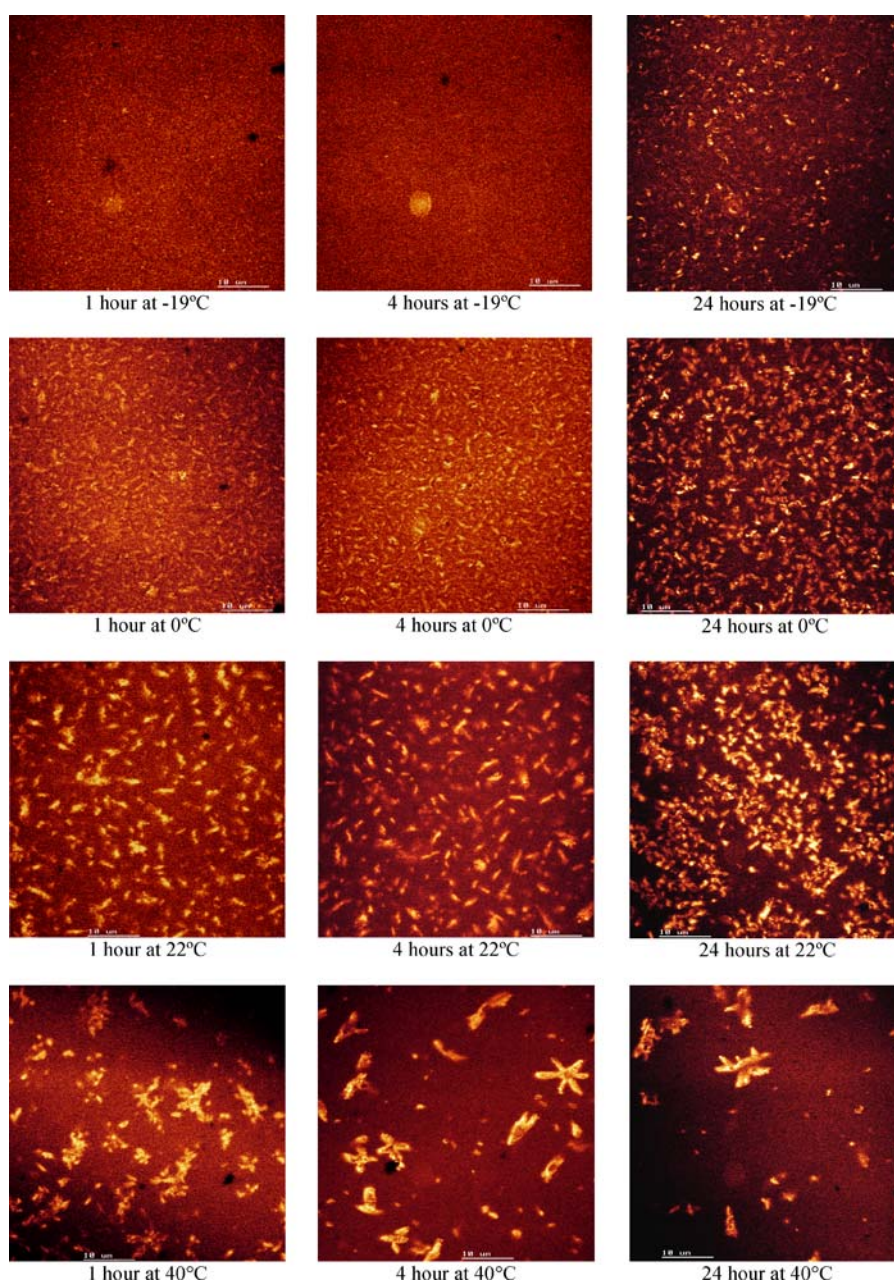


Figure 5 Effects of time and temperature on wax crystallisation in bitumen B4 (scale:  $10\ \mu\text{m}$ ).

completely melted when the specimen was heated at 80°C for 15 min. These observations agree with the DSC tests which show the wax melting out temperatures for B4 and B9 are much higher than 60°C while that for B7 is below 40°C.

## 5. Conclusions

By using different microscopy techniques, wax morphology in bitumen has been characterised at different length scales. PLM and CLSM give information about size and shape of wax crystals in bitumen, while FF-TEM shows the internal structure of wax crystals (layers building up crystals). It has been shown that:

- Non-waxy bitumen displays no structure or crystals neither in PLM, CLSM or FF-TEM;
- Waxy bitumens from different crude origins display a large variation of structures. They vary from tiny needles, elongated needles, flakes and even crescent shaped structures;
- The morphology of the wax crystals is highly dependent on crystallisation temperature as well as temperature history;
- Wax which has been isolated from waxy bitumen and mixed into non-waxy bitumen displays similar morphology as the wax in the original bitumen;
- Bitumen wax usually melts at lower temperatures than 60°C although in one case a temperature of 80°C was needed until complete melting of the wax.

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