EVIDENCE FOR THE AGING OF WAX DEPOSITS IN CRUDE OILS BY

OSTWALD RIPENING

João A.P. Coutinho[a][*], J.A. Lopes da Silva[a], Artur Ferreira[a], Maria Rosário

Soares[a], Jean-Luc Daridon[b]

[a] CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal
[b] Laboratoire des Fluides Complexes, Université de Pau, 64000 Pau, France

ABSTRACT

The ageing of wax deposits is known to occur in paraffinic waxes forming in pipelines and storage tanks. It is characterized by a hardening of the deposit and an increase in paraffin content. A mechanism for the ageing of deposits, based on diffusion caused by temperature-concentration gradients within the wax, has been previously proposed.

This work presents evidence indicating Ostwald Ripening to be another ageing mechanism of wax deposits. Rheology of paraffinic crudes, kept isothermally at temperatures in the neighborhood of the pour point, shows a kinetic of hardening of the oil samples. The X-ray diffraction and Cross Polar Microscopy indicate this phenomenon to be caused by an increase of the

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[*] Corresponding author.

crystallites size with time. The DSC measurements support the idea that recrystallisation takes place in the wax sample. The evidence gathered shows another ageing mechanism based on the recrystallisation of the paraffins, such as Ostwald Ripening, to be responsible for the ageing of wax deposits besides the diffusion mechanism previously proposed.

INTRODUCTION

Wax precipitation and deposition occurring due to oil cooling or gas release during production and transportation of crudes is responsible for losses of millions of dollars yearly (Moritis, 2001). This problem is caused by the crystallization of paraffins on surfaces kept at temperatures below the wax appearance temperature (WAT) of the oil (a.k.a. cloud point). The deposits thus formed have a gel like structure, formed by a 3D network of interlocking paraffin crystals that creates a highly porous yet rigid structure full of entrapped oil (Singh et al., 1999). These deposits are known to undergo a change in characteristics with time becoming harder, richer in heavier paraffins and with lower amounts of entrapped oil (Creek et al., 1999; Singh et al., 2000; Cordoba and Schall, 2001, Wu et al., 2002). These aged deposits are more difficult to remove by either chemical or mechanical methods. The flow assurance teams are required to take into account not only the amount of deposit but also its physical characteristics in the planning of periodical cleaning of pipelines by pigging or any other alternative method.

The mechanism of ageing, although elusive for a long time, was eventually suggested to be based on a diffusion transport within the porous structure of the gel driven by temperature-composition gradients (Singh et al., 2000). This transport would be the responsible for the increase in paraffin content of the deposit and its consequential hardening. Although this mechanism is highly plausible it will here be shown that it is not the only mechanism responsible for the ageing of wax deposits.

This work shows that in the absence of temperature-composition gradients a hardening of the wax deposits is also observed that cannot be accounted by the mechanism previously proposed. Rheological studies done for three paraffinic crude oils, whose characteristics are summarized in Table 1, show a hardening of the wax deposit with time while the sample is kept isothermal. Images obtained by Cross Polar Microscopy (CPM) and results from X-ray diffraction indicate that this hardening is related to an increase of the average crystal size. Isothermal DSC measurements show an absence of heat effects indicating that a recrystallisation, rather than a crystallization with very slow kinetics takes place. All the evidence gathered in this work indicates that Ostwald Ripening, a mechanism by which the large crystals grow at the expenses of the melting of smaller crystals of higher energy, is also responsible for the ageing of wax deposits. This is in accordance with suggestions, not supported by experimental evidence, of Ostwald Ripening taking place in paraffin waxes by Creek and co-workers (Creek et al., 1999; Wu et

al., 2002) and with some results for the recrystallisation of n-alkanes previously reported in the literature (van Hoof et al., 1998; Hollander et al., 2001).

EXPERIMENTAL STUDIES

The samples were studied isothermally by four different techniques: Rheology, X-ray diffraction, Cross Polar Microscopy (CPM) and Differential Scanning Calorimetry (DSC). In all the cases no temperature gradients exist across the sample and the aliquots studied are closed systems, thus no external influx of material exists. Assays were carried during long periods of time, typically between 15 and 40 h, to allow the ageing effects to develop. Although some assays could be carried for longer periods of time, the costs of extending the measurements at low temperatures would not be compensated by additional information. Even if the ageing was not carried to completion within the period of time studied, the goal of this work was to show that it could occur under isothermal conditions and the results obtained clearly illustrate the presence of isothermal ageing in wax deposits, as shown below.

Crudes

Three crude oil samples, a gas condensate and two black oils, obtained directly from oil companies were used in this study. A summary of their characteristics is reported in Table 1.

Rheology

Rheological measurements were performed on a controlled stress rheometer (AR1000, TA Instruments) fitted with a parallel plate measuring system (steel rough plate, 40 mm diameter, gap 1 mm). Crude samples were kept in the rheometer measuring geometry at 20 °C above the WAT temperature during 15 min previously to the tests to ensure complete melting of the waxes. Samples were quenched to the desired temperature at 1°C/min. Then, time sweep oscillatory experiments at constant temperature and low strain amplitude (0.3%) were used to follow the variation of the elastic modulus with time (1 Hz oscillatory frequency).

X-Ray Diffraction

Crystallites larger then 0.1 μm have a sufficient number of planes to allow the diffraction peak at θ to display its inherent Darwin width, additionally broadened by instrumental effects. Small crystallites (smaller then 0.1 μm) cause the effect of 'particle size broadening' of the diffraction lines.

For the gas condensate, where the crystals forming had sizes below 0.1 μm it was possible to observe the narrowing of the paraffin wax diffraction peak around $2\theta = 21.2°$(for Cu target wavelength) with time, and to study the kinetic of the crystal growth by x-Ray crystallite size determination.

X-ray diffraction 'in situ' at 10°C was performed in a Philips X'Pert equipment with a low temperature Anton-Parr TTK450 chamber cooled by liquid nitrogen. A heat program was accomplished with dwells at t = 0.25h, 0.92h, 3.33h, 4.92h, 12.05h, 17.47h and 22.27h for diffraction measurements. Diffraction data was

collected in a 2θ range from 4-75° with a step of 0.02 and a time per step of 2s with incident and diffracted beam anti-scatter slits of 1º, divergence slit =1º, receiving slit = 0.1mm and curved graphite diffracted beam monochromator.

Diffraction patterns showed the presence of solid paraffin wax (JCPDS 14-763) and were analytically treated to determine the width (B) and position (θ) of the diffraction peak around 2θ = 21.2º. Analytical treatment was performed in Profit® and involved background subtraction, $k\alpha_2$ stripping and peak fitting to Pseudo-Voigt function. The peak position (θ) and width (B) was though obtained. The intrinsic values of diffraction peak broadening (β) were calculated subtracting to B the instrumental contribution (b) determined in the same conditions for the 2θ =21.43º peak of the LaB6 NIST 660a standard powder (b = 0.142º).

Cross Polar Microscopy

Aliquots of the oils were placed between two glass blades and inserted on the chamber of a Linkam TP 93 hot stage coupled to an Olympus BX 50 microscope. The microscope was equipped with a 10× magnifying objective and eyepieces with 12.5× magnification giving a limit of resolution of about 1 μm. The hot stage peltier device allowed for a temperature control better than +/-0.1 K. The observations were conducted under transmitted light through crossed polarization lens. The digital images were taken by means of a SANYO Color CDD Video Camera, High Resolution model VCC 2972 connected to a PC where they were captured using Studio DC10PLUS (v. 1.04.5, The Pinnacle Systems Company). Image Processing Toolbox (Matlab v. 6.1, The Mathworks Inc.) was used for

image treatment and feature analysis. A binarization step was conducted (threshold equal to 0.45) permitting to label the objects and to determine its number and total area.

Differential Scanning Calorimetry

The calorimetric measurements were performed on a Shimadzu DSC-50 with the sample chamber purged with dry nitrogen. The DSC-50 has a minimum detection sensitivity of 10 µW. Samples of crudes, sealed in aluminum pans, were first heated to 100 ºC and kept at this temperature for 30 minutes to ensure complete dissolution of paraffin crystals and then cooled to the required temperature at 3 ºC/min. The sample was subsequently kept at that temperature for 12 h and the heat effects registered.

RESULTS

This work is the result of rheological studies carried in paraffinic crudes which attempt to establish the nature of the gel formed by paraffinic deposits and to obtain a relation between the rheological gelling point, defined as the temperature for which the elastic modulus, G', becomes larger than the storage modulus, G'', and the ASTM pour point (D-97) (Singh et al., 1999). Experiments on the kinetics of gelling, just below the gelling temperature, showed the solid like character of the deposit, as expressed by the elastic modulus, G', having an increase of almost an order of magnitude within 14 h of its formation as presented in Figure 1 for Oil A. While ageing of wax deposits was well described in the literature (Creek et al.,

1999; Singh et al., 2000; Cordoba and Schall, 2001, Wu et al., 2002), this result was surprising as no previous result of ageing of waxes under isothermal conditions had been reported and the proposed mechanism for gel ageing, caused by thermal gradients within the wax deposit, could not explain the hardening of the wax observed under isothermal conditions.

A study trying to determine the mechanism for the ageing of the wax deposit under isothermal conditions was thus undertaken and is here described. An evaluation of the change on the size of the wax crystallites was carried on to establish its influence on the observed hardening. Two techniques were used to evaluate this change: X-ray Diffraction and Cross Polar Microscopy (CPM). Both techniques were applied to the three crudes.

For the x-ray diffraction, the particle size broadening of the diffraction lines is limited to the detection of growth of crystallites under 0.1 μm as discussed above. This technique could only be applied to the gas condensate sample A. For the oils the size of the crystallites at the temperatures of interest was already larger than that value as manifest on the CPM images with a resolution of 1 μm. According to the Sherrer relation (Jenkins and Snyder, 1996)

$$r = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

the crystallite size, r, is inversely proportional to the peak breadth, β. As shown on Figure 2 a plot of the $2\theta = 21.43°$ peak breadth as a function of time at 10 ℃

reveals a kinetic of crystal growth of the type $r^n-r^n_0=k\ t$, typical of crystals undergoing Ostwald Ripening (Ryum and Hunderi, 2001).

The Cross Polar Microscopy can detect only crystals larger than 1 µm and was thus appropriate to follow the growth of crystals for the black oils under isothermal conditions. Results for oil B are presented on Figure 3. Images taken in the neighborhood of the pour point, at 40 ºC, at various times up to about 110 h of ageing display a clear increase in the size of the crystals as obtained by image analysis and reported on Table 2. The kinetic of crystal growth obtained for this system was of the same type obtained for oil A by x-ray diffraction indicating that the same mechanism was driving the maturation of the deposit. The growth of the large visible crystals, possibly by recrystallisation of smaller, non-visible, crystals, fitted well into the Ostwald Ripening hypothesis for the mechanism of wax ageing.

To make sure that a recrystallisation was taking place, and not just a very slow crystallization kinetics that the previous experience of the authors with paraffin crystallization seemed to preclude, DSC measurements were performed. Samples of oil were subjected to a similar temperature program used by the other techniques: heating above the WAT to completely melt the wax crystals, slowly cooling down to the neighborhood of the pour point after which the sample was kept at constant temperature for a long period of time. Any kinetics crystallization, albeit slow, would be detected as the amount of crystals forming, as revealed by the CPM images, was very important and the heats of

crystallization of paraffins are very large. The thermograms obtained, an example of which is presented in Figure 4 for oil C, do not show any detectable heat change under isothermal conditions at 40 ºC. This can only occur in a system without changes or when the heat of crystallization released is used by the melting of an equivalent mass of crystals. Knowing from the results previously presented that an increase in the size of crystallites was actually occurring this result proves that recrystallisation was taking place in the system kept at constant temperature and thus confirming that a mechanism such as Ostwald Ripening was the responsible for the ageing of wax deposits under isothermal conditions.

Some results showing that n-alkane crystals forming in solution undergo recrystallisation to minimize the surface energies were reported by Hollander et al., (2001). They show how tricosane and pentacosane suffer post-growth shape transitions to minimize their surfaces. Van Hoof et al. (1998) have also shown, both experimentally and using Monte-Carlo simulations, that at low saturation thin orthorhombic tricosane crystals dissolve, whereas thicker crystals grow within close vicinity. Both these results support our findings that wax deposits forming in crudes suffer recrystallisation leading to larger crystals and stiffer gels.

The mechanism for gel ageing here proposed to explain the experimental observations does not preclude that under non-isothermal conditions a mechanism of the diffusion type, driven by a temperature gradient may take place. Nevertheless it shows that diffusion alone cannot explain the ageing of the deposits since the ageing is also caused by an Ostwald Ripening of the paraffin

crystals. Further studies to individualize the two contributions in the ageing and the influence of the average chain length on the recrystallisation are required.

CONCLUSIONS

The results reported on this work show that ageing of wax deposits takes place even for samples kept under isothermal conditions. The diffusion mechanism driven by temperature-composition gradients proposed by Singh et al. (2000) cannot thus be the only mechanism responsible for gel ageing. The broadening of peaks on x-ray diffraction and the CPM images showing an increase in the crystallites size, together with the DSC thermograms obtained under the same conditions without detectable heat effects associated to this change, indicate that wax deposits in crudes suffer recrystallisation and thus Ostwald Ripening is also a mechanism responsible for the ageing of wax deposits.

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Table 1- Characteristics of the oils studied

	Oil type	WAT (ºC) (CPM)	Pour Point (ºC) (ASTM D97)
Oil A	Gas condensate	45	<0
Oil B	Microcrystalline oil	57	40
Oil C	Paraffinic oil	73	40

Table 2- Increase of the crystals as obtained by analysis from the CPM images.

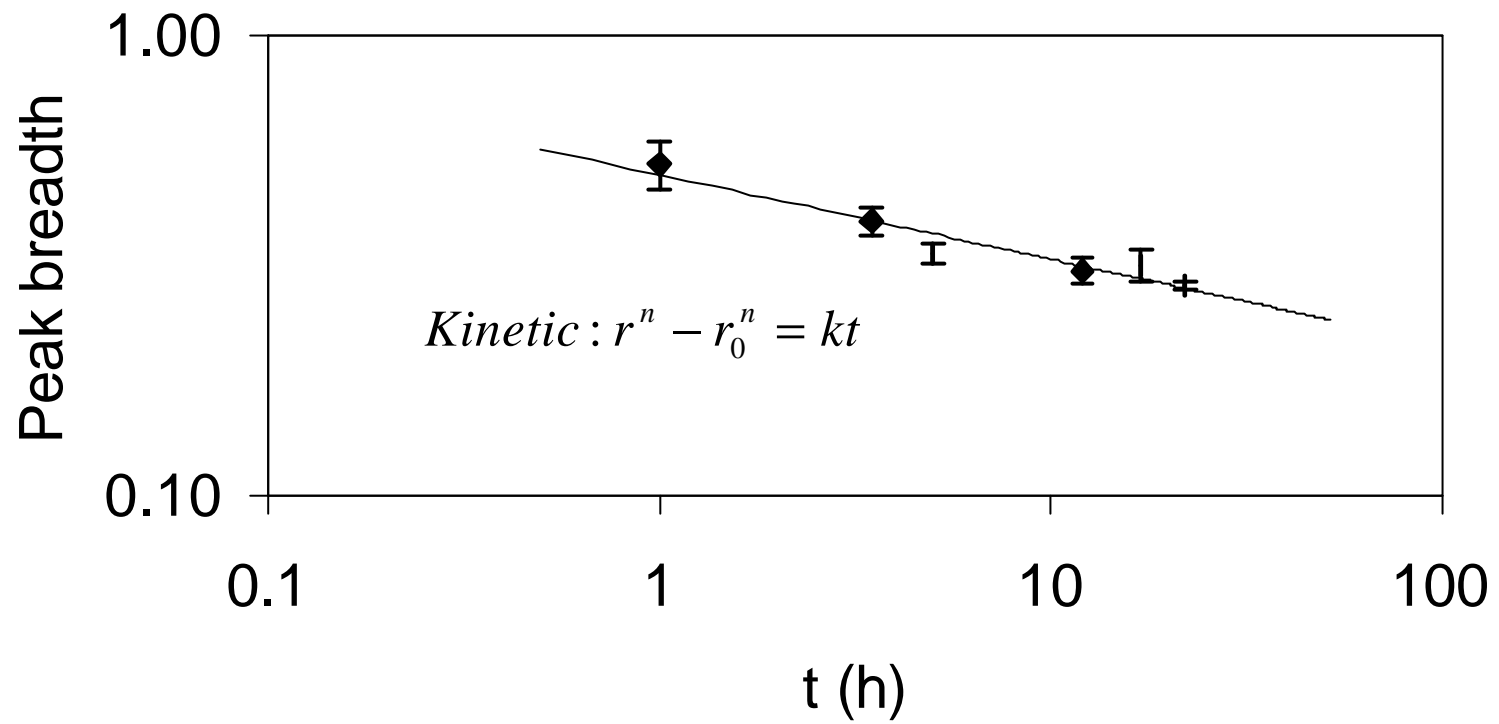| Time (min)	0	840	2340	6600
Fraction of image occupied by crystals	6.4%	11.9%	13.3%	15.3%
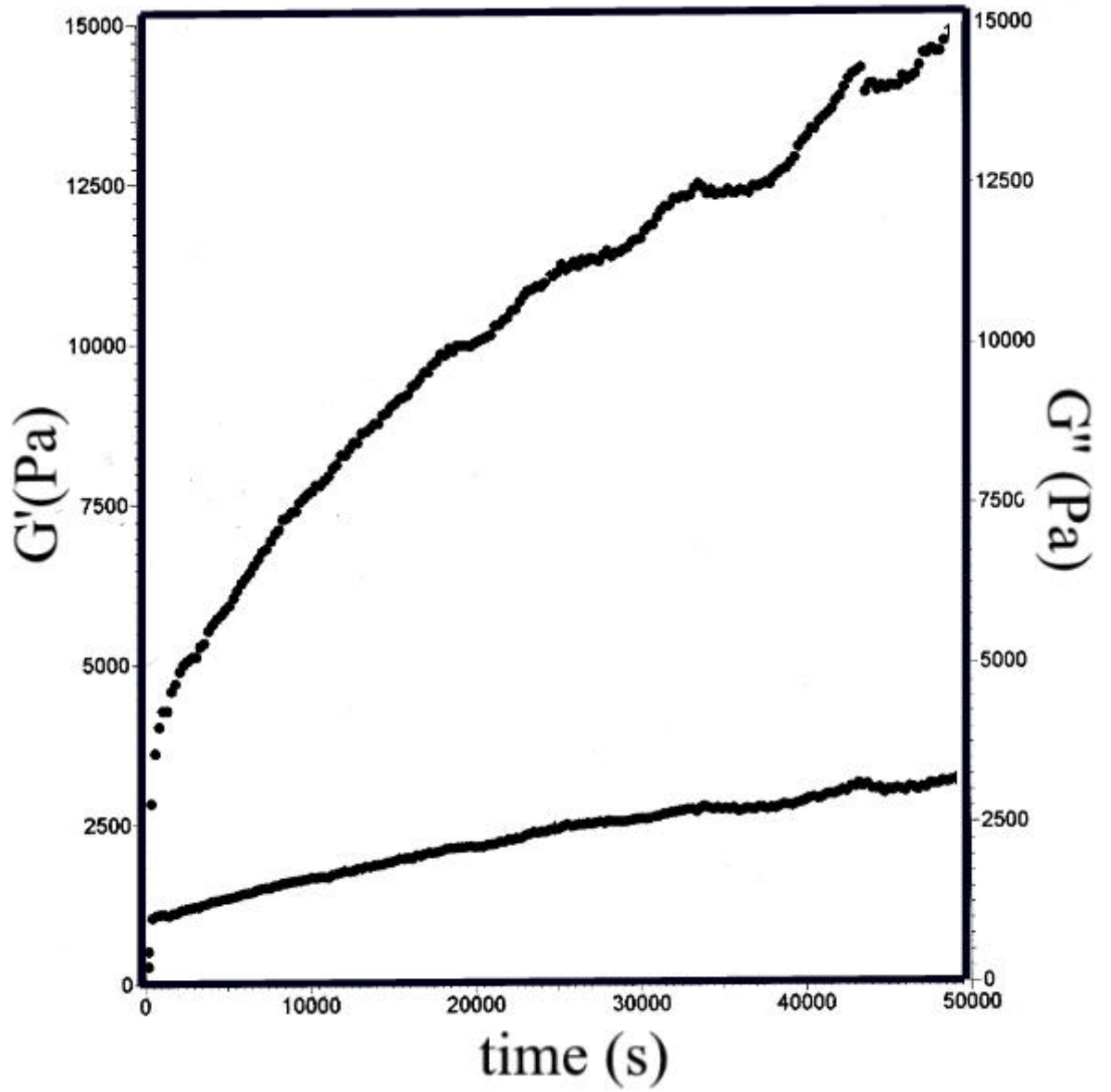
Figure 1- Elastic and loss modulus for oil A at 20 ℃

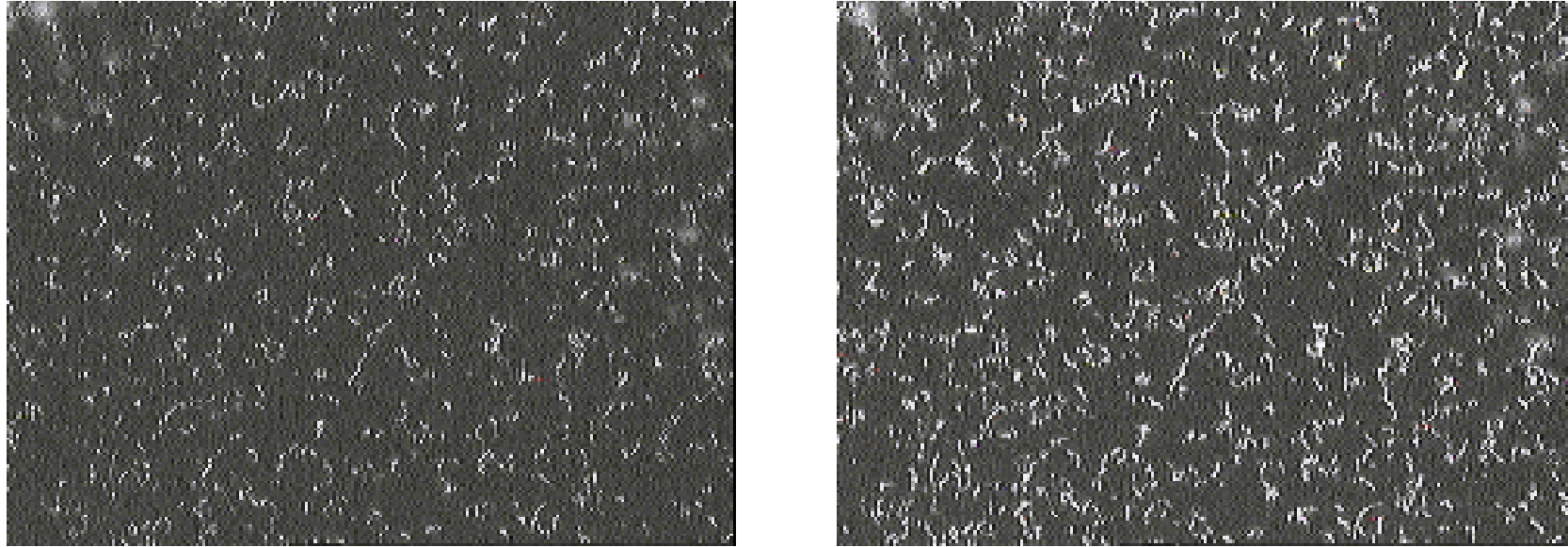Figure 2- Kinetic of crystal growth for Oil A from X-ray diffraction analysis at 10 °C.

Figure 3- Wax crystals observed by CPM for Oil B at 40 ℃. At the start (left) and after 39 h of ageing (right)
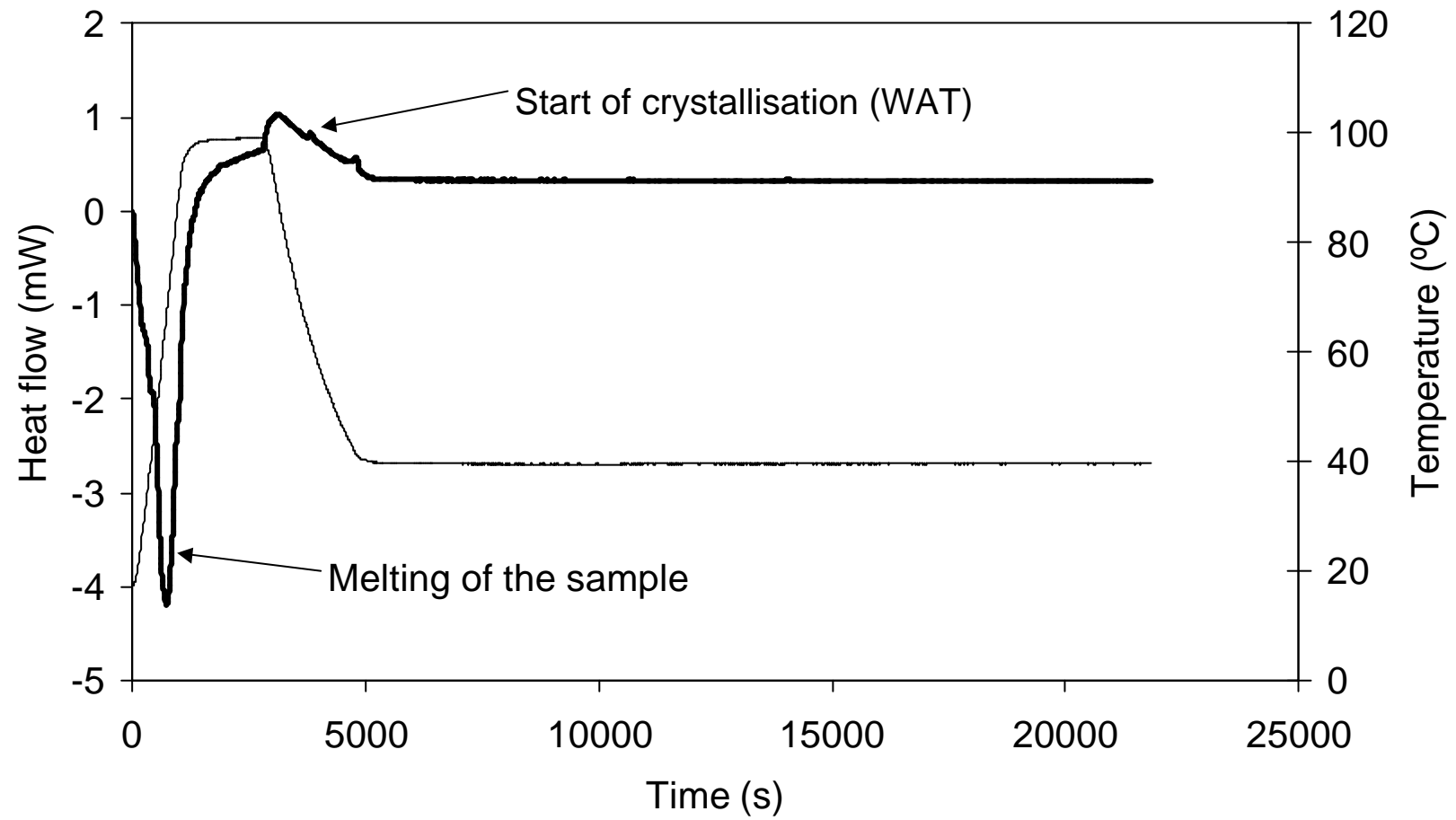
Figure 4- Thermogram for Oil C (thick line). The isothermal region above 5000 s shows that there are not detectable heat effects related to the ageing of the wax.