

## TEMPERATURE STABILITY OF SØDERBERG ANODE PITCH

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A number of quality conditions must be met in a good Søderberg binder, both with respect to cell operation and potroom working environment. Among the more important are low evaporation loss of pitch, acceptable rheological properties which are maintained over a wide range of temperatures, and good enough quality of the binder coke to avoid problems in the baking and consumption zones.

Mild heat treatment of several Søderberg pitch binders used in industry revealed large differences in their thermal stabilities and hydrocarbon emissions. Evaporation losses from pitch surfaces may vary by one order of magnitude and changes in viscosity by a factor >1000 after the same mild heat treatment. Variations in pitch viscosity over ten orders of magnitude are well described by a simple empirical equation that utilizes the softening point of the pitches in a reduced temperature expression.

Introduction

Demands for a better environment in the potrooms and new regulations concerning anode emissions have caused several aluminium smelters to modify their operation towards anodes with colder tops and drier paste. However, the use of less binder in the paste may make the anode operation critically sensitive to pitch quality, a problem compounded by the fact that compromises are necessary. A good control with the flow properties of the green paste is important for the whole anode operation. The amount of fine filler particles is crucial to the flow and segregation behaviour of the molten paste [1]. The quinoline insoluble (QI) fraction of the binder pitch may act as solid particles in this respect, requiring this component to be considered along with the finest coke filler fractions.

Apart from small amounts of coal dust and ash carry-overs, the QI in coal-tar pitches usually contains two different kinds of particles. One is "natural" QI (also called "primary" QI), made up of spherical particles formed during severe vapour phase cracking (1000 °C and more) of tar vapours in the coke oven [2]. These solid pyrolysis particles are small, usually less than 1 µm in diameter, and have an atomic carbon to hydrogen (C/H) ratio between 3.5 and 4.0 [3]. The second type of particles often found in anode pitches are mesophase spheres, comprising the "secondary" QI or "thermal" QI. The mesophase is an anisotropic liquid crystal phase which forms and separates from the isotropic pitch during heat treatment. The frequently observed spherical shape is caused by surface tension phenomena. Average mesophase diameters are usually much larger than primary QI diameters and values ranging from optically observable (approximately 1 µm) to >100 µm are common. Since the mesophase is a liquid phase, its C/H ratio is considerably less than that of primary QI; a ratio of about 2 - 2.5 has been indicated.

The mesophase content in coal-tar pitch has been the subject of much discussion in recent years. It has been claimed [4] that the mesophase acts as solid particles in the green paste stage and therefore does not contribute to the properties of the binder. Another report [5] maintains the conflicting view that the mesophase spherulites are destroyed upon mixing and adhere to the filler particles, thus decreasing the wettability of coke particles by the pitch. The mesophase may form a very viscous envelope around the filler particles and this envelope may cause an increase in the viscosity of the green paste. A high paste viscosity is believed to be undesirable [2], as more pitch is needed to correct this deficiency.

Søderberg anode pitches

The three pitches used in the present laboratory investigation are industrially used coal-tar based binders for the vertical stub Søderberg anodes. Table 1 contains some analysis data for the pitches, lettered A, B, and C. Flowability characteristics of the pitches in mixtures with fine coke were all typical of the Søderberg-type binders.

Pitches A and B are extremes with respect to mesophase content (Figure 1). Pitch A contains no observable mesophase (optical microscopy, >1 µm diameter), whereas more than 50 % of the QI material in pitch B is optically quantifiable mesophase spheres up to about 40 µm in diameter. Pitch C is a more "typical" Søderberg anode binder, whose mesophase content constitutes only a minor part of the total QI fraction.

Table 1. Properties of pitch binders studied.

Pitch	A	B	C
Softening point (Mettler) °C	120.7	113.4	105.6
Density, 20 °C kg/m <sup>3</sup>	1326	1315	1317
QI %	10.4	11.9	11.9
TI %	32.0	32.9	34.0
β-fraction %	21.6	21.0	22.1
Coking value (Alcan) %	59.2	57.5	56.8
Mesophase %	0.0	6.0	3.5
(C/H) <sub>QI</sub>	3.89	2.59	2.98

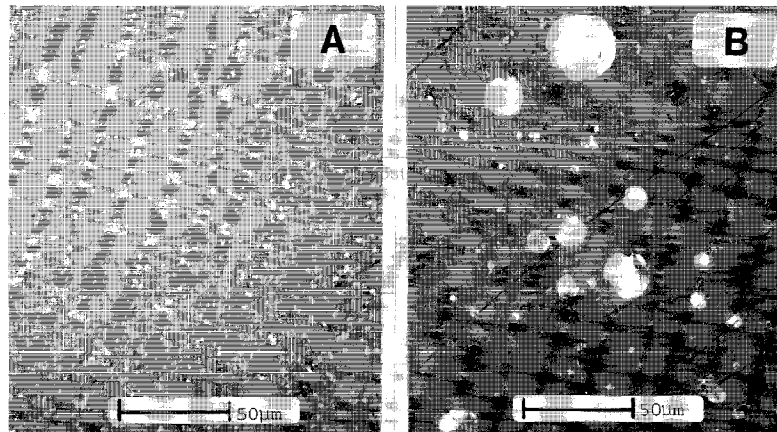
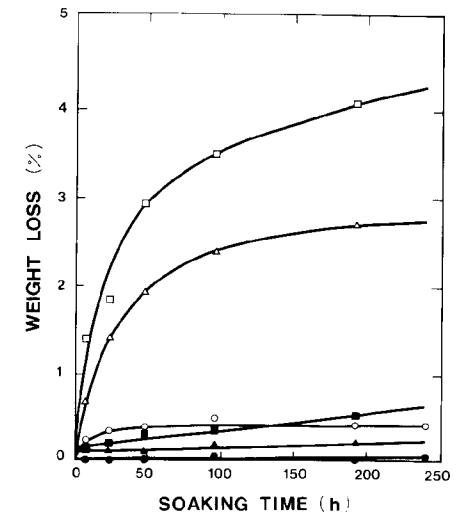


Figure 1 - Microphotographs of pitch A and pitch B show their difference in QI matter. Pitch C has a visual QI appearance between these extremes.

The mesophase content reflects partly the thermal treatment which the binder has been subjected to during the tar distillation process. In order to achieve an acceptable QI content, pitch B has apparently been subjected to the most severe heat treatment resulting in 6.0 % optically identifiable mesophase; pitch C has received a somewhat less severe treatment (3.5 % mesophase), whereas pitch A has been given a mild heat treatment so that no mesophase can be optically determined. The atomic C/H ratio of the QI fraction (C/H)<sub>QI</sub>, verifies this, and is 2.59, 2.98, and 3.89 for pitches B, C, and A, respectively. The β-fraction which is the difference between TI (toluene insoluble) and QI fractions and often believed to indicate carbonization and mesophase forming properties of pitches, differs with only about 1 %.

Heat treatment is also used by tar distillers to increase the softening point of the binder. An alternative way to achieve this is to concentrate the heaviest fractions by a vacuum treatment of the straight-run pitch. This may be the reason why pitch A simultaneously has a high softening point and zero mesophase content. The removal of low boiling compounds may also contribute to the higher coke yield and density of pitch A (Table 1).

Figure 2 - Pitch weight loss from evaporation at constant temperature 200 °C. Open symbols: pitch surface exposed to surrounding air (open system). Closed symbols: Aluminium foil tightly fitted around crucible top to protect pitch surface (semi-closed system)  
 o, ●: pitch A; Δ, ▲: pitch B;  
 □, ■: pitch C.



Evaporation loss from pitch surfaces

The weight loss during mild heat treatment of pitches A, B, and C showed large individual differences. In each experiment a container with 60 g pitch was used with an exposed pitch surface area of 18 cm<sup>2</sup>. Figure 2 shows weight loss curves for the three anode pitches held at 200 °C for various lengths of time. Open symbols represent experiments where the molten pitch surface was exposed to the surrounding air. Closed symbols represent a "semi"-closed system where an aluminium foil was tightly fitted around the upper rim of the container. The foil allowed for vapour pressure equilibration with the surrounding atmosphere but also for diffusion of minor amounts of pitch vapour components out of the system. In contrast to the former case, no pitch vapour transport due to air convection above the pitch surface, could take place.

As shown in Figure 2, the evaporation loss of pitch C is 10 times larger than pitch A both in a system exposed to the surrounding atmosphere and in a semi-closed one. Evaporation from the exposed surface of pitch A reaches a constant value of 0.4 % after a period of about 50 h at 200 °C, while weight losses in pitches B and C continue for the duration of the experiment. Due to the limited pitch reservoir, the evaporation rate is continuously reduced as the melts are depleted of their low boiling compounds. Keeping in mind that the measurements were performed with small pitch volumes, the calculated pitch losses are 130, 900, and 1400 g/m<sup>2</sup> pitch surface during a 200 h period for pitches A, B, and C, respectively. In the same order the pitch evaporation rates are 0, 4.8, and 6.4 g/m<sup>2</sup>h, and 0, 0.4, and 1.5 g/m<sup>2</sup>h, at 50 and 200 h, respectively.

Weight loss curves for pitches B and C in the semi-closed system appear to intercept the y-axis above zero. This value corresponds to the moisture content in these two pitches which were flash evaporated at the beginning of each experiment. Pitch A does not contain water in detectable amounts. The major part of the evaporation loss is thus caused by loss of organic pitch components. Identification of pitch vapour components has not yet been performed, but all three pitches are highly aromatic coal-tar pitches; consequently low pitch evaporation losses, like those found for pitch A, can contribute to improved working conditions in the Søderberg potrooms.

Changes in pitch properties during mild heat treatment

The observations described above are probably functions of process variables in the tar distillery and also reflect the quality of the coal-tar precursor. Pitch properties change somewhat during the isothermal heat treatment at 200 °C. As one might expect, the pitch softening point increases (Figure 3). The increase is largest for pitch C which has the lowest softening point to start with (Table 1). An increase of about 16°C is observed in this pitch over a period of 200 h, while the softening point of pitch A only increases about 3°C under the same conditions.

No significant softening point differences or trends are, however, observed for pitches which have been exposed to the surrounding atmosphere during the isothermal heat treatment and pitches which have been heat-treated in the semi-closed system described above, although the difference in loss of volatiles is as much as 3.5 wt % in the case of pitch C. Prolonged soaking times eventually give pitch B a higher softening point than pitch A (Figure 3).

Figure 3 - Changes in pitch softening point (Mettler) during isothermal heat treatment at 200 °C. See Figure 2 for symbol explanation.

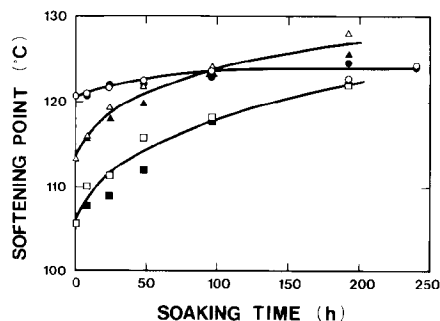
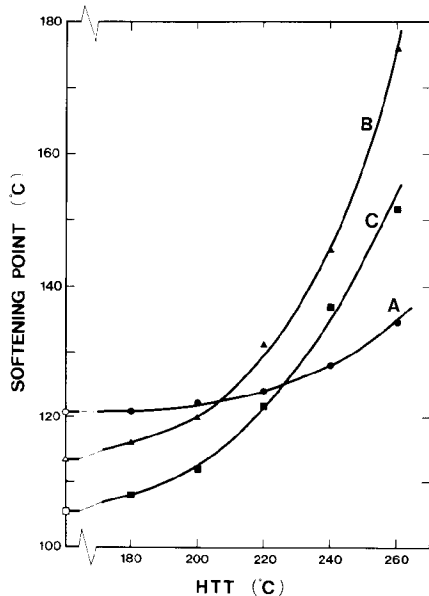


Figure 4 - Pitch softening point (Mettler) as a function of heat treatment temperature (HTT) in semi-closed system. Open symbols are softening points of untreated pitches (starting values).



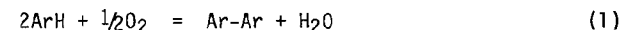
Changes in QI content at 200 °C is almost zero for all three pitches, while the total content of TI material increases about 1.5 - 2 %. There is no significant discrepancy between TI values measured in pitch contained in an open crucible, or a semi-closed one, in accordance with the observations for the softening point.

The temperature stabilities of the anode pitches, as well as their relative differences, are better illustrated in Figure 4 where the softening point is plotted as a function of heat treatment temperature (HTT) at constant soaking time 48 h. These experimental values are from the semi-closed system only. Pitch A, which at the start has the highest softening point, is exceeded by pitch B at a HTT less than 210°C and by pitch C at HTT less than 230°C. Total changes in softening points at HTT 260°C are 14, 62, and 46°C for pitch A, B, and C, respectively. The pitch evaporation losses are 0.30, 0.84 and 1.71 %, in the same order as above.

Changes in both QI and TI take place rapidly above 200 °C. In the semi-closed system, a soaking time of 48 h at 260 °C increases the QI content in the pitch to 39.3, 50.4, and 46.6 % for pitches A, B and C, respectively, taking into account the weight loss due to evaporation of low-boiling pitch components.

Obviously, the above changes in pitch properties are not primarily caused by the removal of "solvent" compounds of low boiling points and low molecular weights. It is known [6-8] that the changes in pitch properties will not take place at such low temperatures if oxygen is excluded. This was verified with pitches A and B which were sealed into quartz glass ampoules under an argon atmosphere and kept at 240 °C for 48 h. No significant change in pitch softening points could be measured. If, however, oxygen is present, changes in pitch properties have been reported [6] to start above 200 °C.

The observed changes in softening point, QI, and TI may therefore be the result of reactions with atmospheric oxygen. As previously discussed, no significant differences in pitch properties could be observed in experiments where the surrounding air had free access to the pitch surface and in cases where the supply of oxygen was restricted (semi-closed system). It seems therefore likely to assume that oxygen may initiate pitch polymerization or condensation reactions without being consumed in significant quantities. Published studies [9] of mild air oxidation of pitch, at comparable temperatures, show that this treatment leads to increased average molecular weight without oxygen being chemically bonded to any significant extent in the product. The reported results were consistent with an oxidative mechanism involving dehydrogenative condensation of high molecular weight aromatic components (ArH) in the pitch:



The organic reaction products are larger and higher in molecular weights and, are thus likely to increase softening points and QI and TI fractions of the pitch.

It is not realistic to assume that thermal pitch reactions which take place above the baking zone in dry top Søderberg anodes proceed without any access to oxygen. Air is always present in pores in the paste and will follow the flow of paste down towards the baking zone. These pores can always be seen when samples from the upper part of the anode are examined. The access of small amounts of air will therefore give a more realistic environment for studying the low temperature thermal reactions which take place well above the baking zone, than performing similar experiments under

an inert atmosphere.

The observed increase in QI content with HTT is not followed by a simultaneous increase in observable mesophase. In the case of pitch A, no mesophase is observed by optical microscopy after heat treatment at 200°C, although the QI content increases from 10.4 to 14.7 %. In pitches B and C an increase in mesophase content is observed, but not nearly enough to account for the increase in QI fraction. Figure 5 shows the deviation between QI analysis and optical mesophase content,

$$\Delta QI = QI_{total} - \text{Mesophase}, \quad (2)$$

plotted as a function of HTT. The loss of volatile compounds has been taken into account. It is shown that the rate of deviation increases most rapidly for the most reactive, or thermally least stable, pitch B.

It should be possible to spot any growth of existing optical mesophase upon heat treatment by a microscopic point counting technique. This is confirmed to some extent with pitches B and C, but as Figure 5 shows, the optically quantifiable mesophase cannot account for the total increase in QI. Excluding any new quinoline insoluble phases it seems likely that the difference consists of mesophase particles too small to be identified in the optical microscope ( $< 1 \mu\text{m}$ ). A mild heat treatment may thus not only result in growth of existing mesophase spherulites, but also in the nucleation of new ones. Although discussions involving mesophase spherulites most often are concerned with particle sizes that can be identified by optical microscopy, it has been shown [10] that in the early stages of formation the particles can only be observed by transmission electron microscopy techniques.

The quinoline extraction and mesophase point counting techniques have their limitations. The room temperature microscopic techniques are only strictly valid for measuring the observable anisotropic phase present at the solidification temperature of the pitch; extrapolation of these results to molten pitch temperatures should be done with great care [11]. The ani-

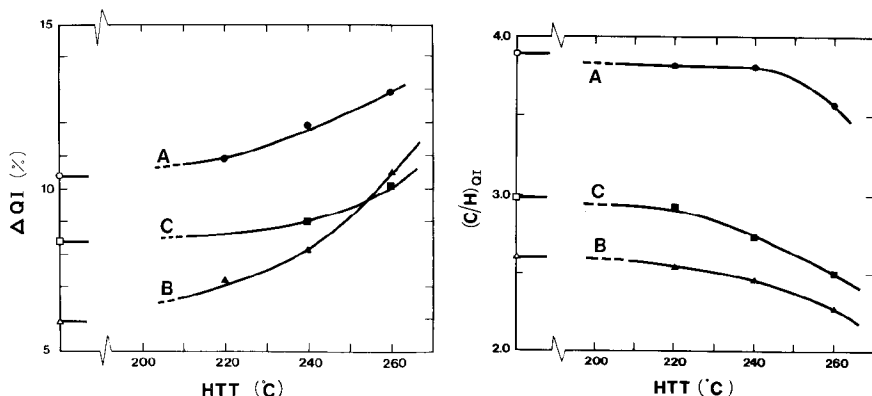


Figure 5 - The difference between QI content and optically observable mesophase in original and heat treated pitches (semi-closed system).

Figure 6 - Atomic C/H ratio of QI fraction of original and heat treated pitches (semi-closed system).

sotropic mesophase has no uniform molecular composition, but contains components over a wide range of molecular weights. It has been found [4] that for certain pitches the mesophase content can partly be dissolved in quinoline, thus making the QI content an underestimate of the total particle content in the pitch. In terms of thermodynamic considerations it will be expected that the smallest mesophase particles also will be those most easily dissolved in the quinoline solvent.

Changes in atomic C/H ratios of the quinoline insolubles as a function of HTT (Figure 6) also illustrate the increased content of secondary QI material. The positioning of the curves relative to the y-axis serves as an indication of their content of mesophase in the QI fraction.

### Viscosity measurements

The pitch viscosities, before and after heat treatment, were measured in the temperature range 60.5-203°C. These measurements, which covered viscosities from far below the softening point to the liquid low viscosity range, were all performed on a viscometer built at Elkem a/s, R & D Center [12]. The instrument is a parallel plate compression viscometer on-line interfaced to a microcomputer for automatic data acquisition and evaluation of absolute viscosities. Experimentally, the plate separation is measured at a given temperature as a function of time [13].

The measuring range of the instrument covers viscosities differing by 10 orders of magnitude, from as low as 0.1 Pas to as high as 1,000,000,000 Pas (Figure 7). Coal-tar pitches behave more like super-cooled liquids than solids below their softening temperatures, and viscosities may thus be determined at temperatures well below their normal fluid range.

Arrhenius plots of logarithmic viscosity vs. 1/T (Kelvin) for untreated pitches A, B, and C, as well as plots of the same pitches heat treated at 260°C (48 h), are shown in Figure 7. The untreated pitch A was most thoroughly examined and shows a near constant activation energy for viscous

Figure 7 - Viscosities of untreated binder pitches (open symbols) and the same pitches heat treated at 260°C for 48 h (filled symbols).  
o, ●: pitch A; Δ, ▲: pitch B;  
□, ■: pitch C.

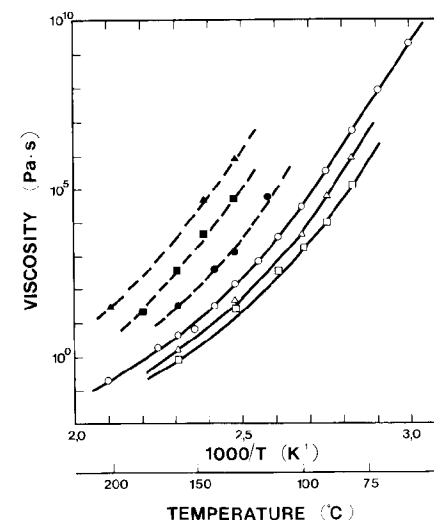


Figure 8 - Plot of binder pitch viscosities at 150 °C vs. HTT. Values on ordinate corresponds to untreated pitches.

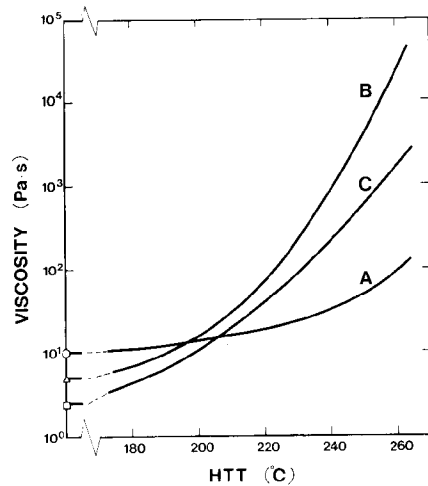


Table 2. Parameters in 3rd order polynomial fit of log(viscosity) [Pas] vs.  $T/T_s$  (equation (3)).

A(0)	A(1)	A(2)	A(3)	Std.error
292.22	-729.96	617.60	-177.22	0.23

flow at temperatures below its softening point and a small monotonous decrease in the activation energy at temperatures above. It can also be seen that the activation energy for viscous flow of pitches B and C does not differ much from what is observed in pitch A as the curves have a near parallel displacement determined by the difference in their softening points. The same is also valid for the heat treated pitches shown in Figure 7.

Plots of log(viscosities) vs. HTT yield curves which qualitatively are very similar to those presented in Figure 4. This is shown in Figure 8 with viscosity values interpolated at 150°C. It might thus be possible to calculate the viscosities of any examined pitch at any temperature provided that its softening point is known. This is demonstrated in Figure 9 where all experimentally determined viscosities have been plotted against the reduced temperature  $T/T_s$ , where T is the temperature at which viscosity was measured, and  $T_s$  is the softening point (Mettler) of the pitch in degrees Kelvin. A 3rd order polynomial may satisfactorily be fitted to these values:

$$\log(\text{viscosity}) = A(0) + A(1) \frac{T}{T_s} + A(2) \left(\frac{T}{T_s}\right)^2 + A(3) \left(\frac{T}{T_s}\right)^3 \quad (3)$$

The parameters for calculating pitch viscosities (in Pas) are given in Table 2.

The softening point (Mettler) viscosity calculated from Equation (3) is 435 Pas. The Mettler method gives a somewhat higher softening point than

the often quoted Ring and Ball (R & B) method. A careful examination of both methods with several coal-tar pitches gives the following relation between the softening points ( $t_s$ ) in °C

$$t_s(\text{Mettler}) = t_s(\text{R \& B}) + 4.7 \quad (4)$$

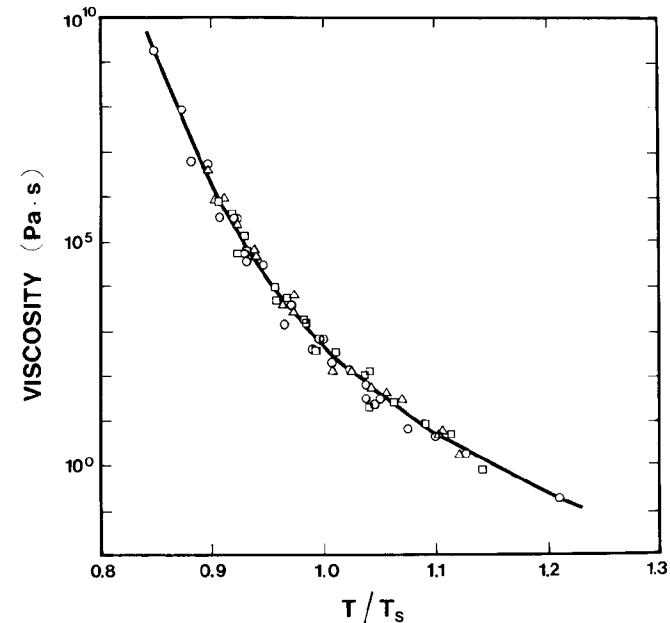


Figure 9 - Viscosities of all untreated and heat treated binder pitches plotted as a function of the reduced temperature  $T/T_s$  (in K). The curve corresponds to the least square 3rd order polynomial fit equation (3), Table 2. o: pitch A; Δ: pitch B; □: pitch C.

in the softening point range 105-120°C (Mettler). The viscosity at the R & B softening point of a 110°C Mettler softening point pitch will according to Equations (3) and (4) be 950 Pas. This is in good agreement with the expected value of about 800 Pas [14].

#### Carbonization behaviour of heat treated pitches

Pitch A yields a near constant coking value (corrected for pitch volatilization during heat treatment) independent of soaking time (200 °C), while pitches B and C show an increase in coke residue under similar conditions, yet without reaching the value found in pitch A (Table 1) for the duration of the experiment. Contrary to what was found for changes in softening point, QI, and TI upon heat treatment time, the coking values from open and semi-closed systems differ appreciably for pitches B and C, yielding lower increases in coke residues in the open system. This may either be caused by the rapid evaporation loss of low boiling reactive pitch components, which otherwise might increase pitch polymerization rates at elevated temperatures, or by higher oxygen concentrations which in these

melts result in formation of more CO<sub>2</sub> during coking.

Coking values at different HTT follow qualitatively a similar pattern as the softening points (Figure 4), QI, and TI. Pitch A, which originally has the highest coking value is at HTT 220 - 260 °C surpassed by pitches B and C which show a much more rapid increase in carbonization rate at elevated temperatures (180 - 260 °C).

The final carbon residue of the coked binder pitch in the baked Søderberg anode is, however, what is most important with respect to anode quality and operation. Possible anode reactivity and dusting problems are believed mainly to be determined by the binder coke quality [15], which again is closely related to the coking behaviour of the pitch.

The apparent lower coking values obtained with pitch A at HTT's >220 °C do not imply that it will give a lower amount of fixed carbon in the baked anode, only that the carbonization reactions are shifted to higher temperatures compared to pitches B and C. This is seen in Figures 10 and 11 where the coking values, corrected for pitch volatilization losses, are plotted as a function of softening point (Figure 10) and TI (Figure 11). Both the softening point and the TI fraction may serve as a measure for the extent of carbonization or polymerization in the pitch prior to the standardized coking procedure. An increased yield of binder coke will tend to lower the microporosity of the baked anode and may thus reduce the dusting problem [15].

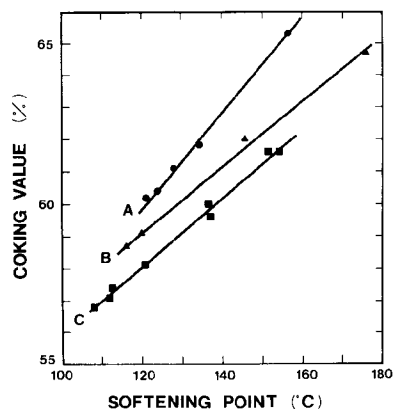


Figure 10 - Coking value (Alcan) of heat treated binder pitches vs. their softening points (Mettler).

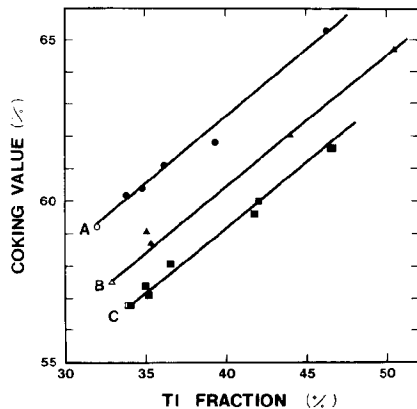


Figure 11 - Coking value (Alcan) of untreated (open symbols) and heat treated (filled symbols) pitches vs. TI fraction.

#### Concluding remarks

As the preceding discussion shows, thermal reactivity and carbonization behaviour can vary considerably between typical Søderberg binders. The pitches pass through polymerization and mesophase forming stages during the carbonization process and it is reasonable to believe that the rate at which these reactions take place may severely influence their properties as binders both in the viscous and the baked part of the anode. Especially,

the type of QI material may play an important part in pitch binder performance in the anode. It seems that a large content of primary QI retards the mesophase forming and coalescing reactions, thus shifting the rapid increases in viscosity to higher temperatures. It has been claimed [16] that binders which undergo minimal changes in viscosities, when subjected to heat treatment, are required for good anode operation. Tests for viscosity stability may thus be helpful in defining more accurately the quality of a given pitch. As binder quality and properties are related to the quality of the pitch precursor, as well as to process variables in the tar distillery, a more complete knowledge is needed to better understand and specify optimum binder properties for the Søderberg anode.

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