

# Alcan Characterisation of Pitch Performance for Pitch Binder Evaluation and Process Changes in an Aluminium Smelter

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## ABSTRACT

Coal tar pitch is the main raw material used as a binder for anode fabrication. The characteristics of the pitch binder affect the paste plant operation and anode performance during electrolysis. Over the last two decades, the coke oven design and technology have been improved to minimise environmental emissions and to increase coke oven productivity. The properties of the coal tars used as raw materials for pitch production have been affected by this change. The pitch producer also uses more and more different tar sources. In the same period, the aluminium industry increased its requirement in terms of anode quality to improve cell control, productivity and to increase cell amperage. The impact of the pitch property evolution on paste and electrode performance has been studied. A new experimental device has been developed by Alcan to measure the pitch wetting capability for pitch binder evaluation.

## INTRODUCTION

Coal tar pitch, along with calcined coke, is one of the primary materials used for the production of carbon anodes, which are used in the fabrication of aluminium. The rheological behaviour of the carbon paste has a major impact on anode manufacturing and performance. Characterisation of this behaviour is complex and difficult to characterise by a single parameter. The pitch binder itself is a good example of a Newtonian liquid, but the anode paste coke aggregate content is too high (70 to 85%), bringing into play strike effects and frictional or granular behaviour. An appropriate characterisation of pitch and a good control of coke aggregate size distribution are required for anode manufacturing and performance.

Söderberg paste fluidity behaviour is sensitive to pitch binder property variability. The Söderberg paste binder level (25-30%) is significantly higher when compared with prebaked anodes (14-16%). The variability of the paste fluidity on the top of the Söderberg anode and the detachment of pieces of baked anode in the cell (carbon outs) can be identified as being major factors

affecting cell performance. The stability of pitch binder characteristics can be pointed out as one of the most important parameters that affect anode performance.

In the last few years, some of Alcan's smelters have been facing major problems in controlling the fluidity of the paste for Söderberg anodes and the frequency of thermal shock for prebaked anodes. The investigation on these problems has shown that the pitch binder characteristics have a significant impact on paste and anode performance.

The objectives of this work are to present an overview of some plant problems that have occurred since 1990 and to present a new experimental device to characterise the pitch flow behaviour.

## MATERIALS AND EXPERIMENTAL METHOD

Calcined petroleum coke and coal tar pitch binders used by the aluminium industry were used for this work.

The mixer used for laboratory paste production is a batch Sigma blend mixer. The plant and laboratory paste fluidity was measured using a sloped plate test. The fluidity of the paste was determined on a cylindrical sample (50 mm in length and 25 mm in diameter) by measuring the elongation of the paste after it was heated at 250 °C for 15 minutes.

The pitch wetting capability was measured by determining the contact angle and/or height of a pitch drop deposited on a coke bed by using a new device developed by Alcan laboratory (SyTac).

Several investigations were carried out in order to study pitch flow behaviour. One of the most interesting was to develop and study the interaction between pitch and calcined coke during the anode paste mixing process by using a droplet (or penetration) test to measure the pitch wetting capability [1.2].

Pitch flow behaviour represented by the droplet test depends on:

- Thermodynamic factors (contact angle on the coke and surface energy) and the rheological properties (viscosity or softening point) of the pitch drop before the onset of the penetration
- The variation of these properties during the penetration test
- The presence of fine solid or mesophase particles in the pitch

Because the anode problems in the potroom related to the pitch characteristics variability, Alcan developed a new piece of equipment (SyTac) using a droplet test to study pitch flow behaviour. Different pitch samples corresponding to the potroom anode problem were investigated by using Alcan SyTac equipment. During the test, the contact angle and height of the pitch drop on the coke bed were measured and the results are given as a function of the temperature on the graph.

The curves of the contact angle or drop height (Figure 1) can be characterised by two temperatures [1]:

- $P_1$ : is defined as the intersection of the tangent to the point of inflexion of the curve with the base line that corresponds to the coke bed
- $P_2$ : is the temperature above which the drop of pitch flowed completely through the coke bed.

The shape of the plots obtained by the droplet test can vary with temperature depending on the pitch sample used [1]. Figure 1 shows three types of pitch behaviour during the droplet test. A Type A graph corresponds to a pitch with a fast and total penetration in the coke bed ( $P_1=P_2$ ). A Type B graph corresponds to a pitch with a slow penetration. A Type C graph corresponds to an incomplete or negligible penetration with a residual tail on the top of the coke bed at the end of the test.

The temperature corresponding to  $P_1$  can be considered as the paste mixing temperatures to be used for the pitch Type A ( $\Delta P < 5$  °C) at the paste plant. For pitch Type B, the mixing temperature has to be higher than  $P_1$ . However, as shown by previous work [3] an excess of mixing temperature negatively affect the paste and anode quality.

The characteristics of the penetration test curve can be related to paste behaviour and anode quality in the potroom:

- If  $P_1$  is high: on the top of the Söderberg anode ( $T=170-190$  °C) the paste fluidity can increase, but under the anode top surface layer ( $T > 200$  °C) the paste could become drier.
- If  $\Delta P = P_2 - P_1$  is high: the paste thermal stability decreases, the paste mixing efficiency will be reduced, and the variability in paste fluidity may increase

The great advantage of Alcan's new device (SyTac) for pitch wetting capability measurement is the precision with which it can determine  $P_2$ . Although the determination of  $P_1$  is relatively simple from the graph, the determination of  $P_2$  requires a more advanced device with good precision. Based on the Alcan investigation a pitch with a  $\Delta P$  value lower than 5 °C can be considered as a good pitch binder for the electrode.

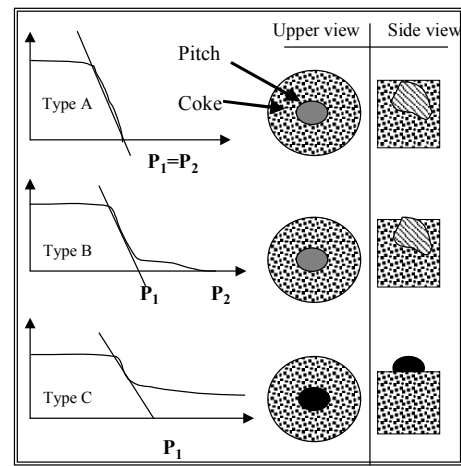


Figure 1: Schematic presentation of test results. On the graph Y-axis is contact angle and X-axis is the temperature

### **Description of Alcan's SyTac equipment for pitch wetting capability measurement**

The testing equipment developed for pitch wetting capability measurement is fully integrated and automated. It is very easy to use by laboratory personal and requires very little training to operate.

Figure 2 shows a diagram of the equipment. One of the main components of the testing apparatus is a special dual chamber furnace (2). The temperature inside each chamber is controlled very accurately. Thermocouples are carefully designed and located to provide a maximum temperature gradient of 1°C below and above the sample under test (1).

The dual chamber furnace can be opened completely to allow access to the sample. The sample is deposited on a coke bed at the center of the furnace.

A mixture of air and/or argon inside the furnace can be adjusted as required by the testing procedure. Heating elements (3) are driven by the temperature controller (4) which follows a specific heating program downloaded from the computer (8) database. Hardware and software safety protection exists to protect the operator and the equipment in case of component malfunction.

Special windows (6) and light source (7) allow the camera (5) to capture high definition video pictures of the sample in the furnace. The camera is interfaced to the computer via a frame grabber interface card. Live video is used to provide accurate sample placement on the coke bed at the beginning of the test. Once the test is started, one video frame is grabbed periodically and analyzed by the computer. The overall test bench is mounted on a vibration free table. This guarantees that any external vibration during the experiment will not affect the sample.

Comprehensive application software provides a user-friendly interface to perform the test configuration, the test supervision and the test report generation.

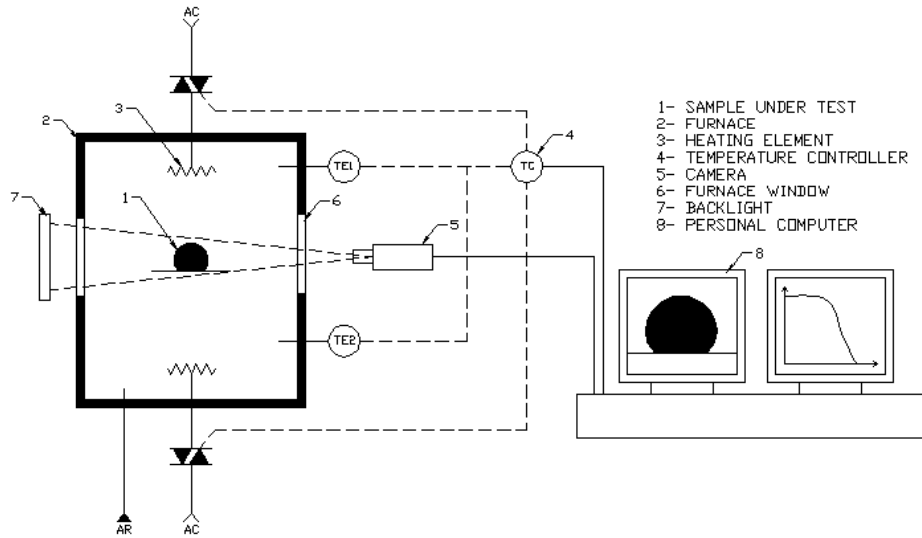


Figure 2: Diagram of the Alcan's SyTac equipment for pitch wetting capability measurement

Before starting an experiment, the operator defines a heating sequence, which is the rate ( $^{\circ}\text{C}/\text{hour}$ ) at which the pitch sample deposited on a coke bed is to be heated. He also defines the number of photos to be taken and analyzed during that experiment. Windows application software started by the operator is responsible for a pitch wetting capability measurement experiment.

At the beginning of the experiment, the sample has a cylindrical shape and is at room temperature. The Windows application:

- Shows the sample picture in real-time
- Downloads the heating sequence to a temperature controller that will take care of the heating sequence, until it is stopped by the same Windows application
- Takes a first picture that is analysed by the Alcan image analysis software using the VISILOG commercial package. This first analysis saves the temperature, the initial height measured and the Left/Right angles in a text file.

During the experiment, the temperature increases and the sample shape changes (Figure 3). Each time a photo is taken and analysed by the Alcan software:

- Left/Right contact angles are evaluated, the height of the drop is measured and the results are stored in text files
- Two real-time graphs are displayed on the screen: these graphs show the Temperature vs. Time and also the % of Initial Height and Angles vs. Temperature

When the experiment time has elapsed, the Windows application will stop the temperature controller and close the result files. At any time after the test, the operator can produce graphical results of the experiment by using the Excel automated procedure. The graph of the contact angle vs. temperature can be characterised by two temperatures ( $P_1$  and  $P_2$ ). The  $P_1$  was determined on the graph.  $P_2$  is obtained by clicking on the selected point of the graph on computer the screen and the photo of the pitch drop corresponding to a temperature appears on the screen.

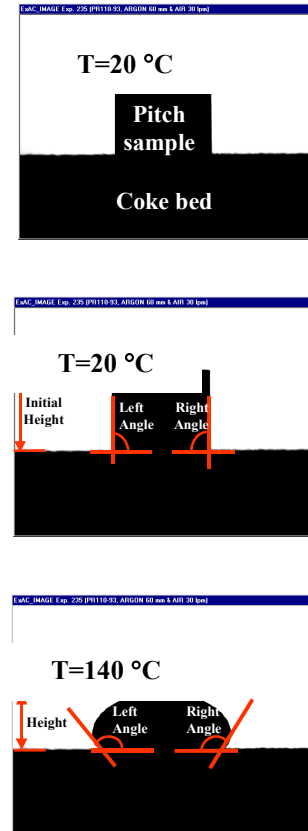


Figure 3: Pitch sample shape evolution during droplet test

## RESULTS AND DISCUSSIONS

Since 1990, some anode and process control problems have been observed at some Alcan plants using Söderberg and prebaked anode technologies. After investigation on raw materials (coke and pitch) and production parameters at anode plants, these problems were very often associated with pitch binder characteristics. It is particularly interesting to mention that the problems occurred between consecutive pitch shipments, despite the fact that the pitch seems to show no variability according to the request specifications. In one case, the problem occurred at the same time in the prebaked and Söderberg potrooms when two coal tar pitches with the same specifications were blended.

A Söderberg anode is more sensitive to the raw materials (coke and pitch) quality variability and the variability in paste manufacturing process parameters than prebaked technology.

In Söderberg smelters paste pitch content is typically controlled to an elongation target, or to a constant anode top condition target. One of most common problems observed in Söderberg plants was that paste fluidity changes greatly on the top of the anode for a given pitch content as one changes from one pitch shipment to the next, while meeting the same specifications. Another problem observed was an increase in the number of carbon outs in the potroom, and in some cases this problem was related to the specific pitch shipment.

### Overview of anode problems in plants related to the pitch

In 1992, it was observed, at the Söderberg Plant-A, using a pitch with a softening point of 132 °C, that the binder content for the paste had to be increased significantly in order to reach the paste fluidity target (Figure 4). The results of the investigation showed that in the same period, the pitch TI (toluene insoluble) content increases in order to meet the specification for beta-resin content. During this period, the laboratory work carried out on pitches from the same source having the same softening point and the same QI (quinoline insoluble) content, showed the effect of increasing TI content on the paste binder demand (Figure 5). Because of the fluidity control problems, that occurred at this plant, the maximum TI limit for this pitch was fixed at 34% to prevent this problem.

In 1993, at Plant-B, producing the anode paste for both Söderberg and prebaked technologies, it was decided for logistic reasons to blend two coal tar pitches produced by two suppliers. Line-1 produced the paste with pitch-X for Söderberg anodes and Line-2 used pitch-Y for prebaked anodes. Both single-source pitches met the same specifications. As soon as the use of this blend of the two pitches was implemented, it was observed:

- That the Söderberg paste fluidity was significantly affected, and it affected the behaviour and performance of the Söderberg electrolysis cell operation
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- That there was at the same time a thermal shock problem in the prebaked potrooms with the use of prebaked anodes made with this pitch blend

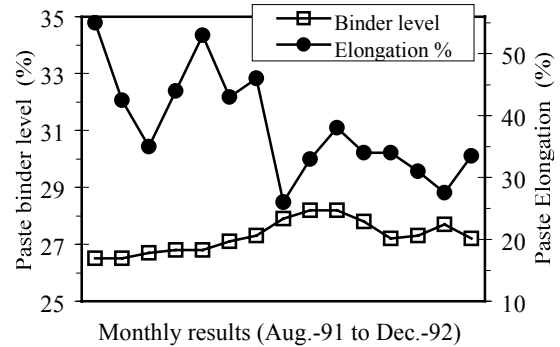


Figure 4: Paste binder content and fluidity variation at Plant-A from one shipment to the next

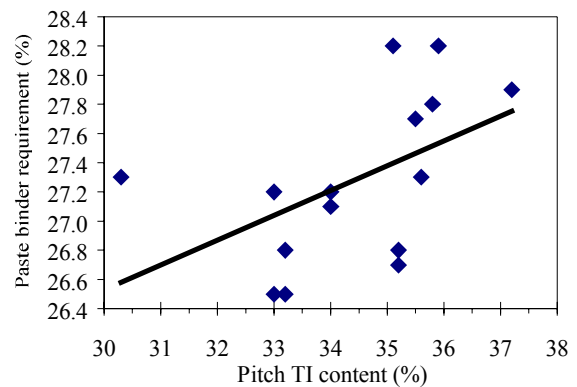


Figure 5: Effect of pitch TI content on paste binder requirement (Plant-A)

In order to understand the Söderberg fluidity problem occurring in the potrooms, a comparative study was carried out in the laboratory.

The laboratory work was performed on single source pitches and on the blended pitch. The X and Y pitches were blended in laboratory-controlled conditions with a ratio X/Y = 50/50 (%).

Three different laboratories were investigated on the single and on the blended pitches. The results of these evaluations have shown that some of the blended pitch characteristics (Table 1) are not representative of the single-source pitches.

The fluidity behaviour of the pastes produced in the laboratory with the single-source and blended pitches was also compared (Figure 6). These results show that at lower binder content the fluidity behaviour of the paste made with blended pitch is not representative of pastes made from single-source pitches.

Table 1: Single source and blended pitch characteristics (Plant-B)

Properties		Pitch-X	Pitch-Y	Blend X-Y
TI	%	31.8	30.4	33.2
Viscosity	mPa.s			
220		33	45	80
°C		75	130	240
200		260	390	700
°C		1200	1350	2600
180		6500	7530	15000
°C				
160				
°C				
140				
°C				

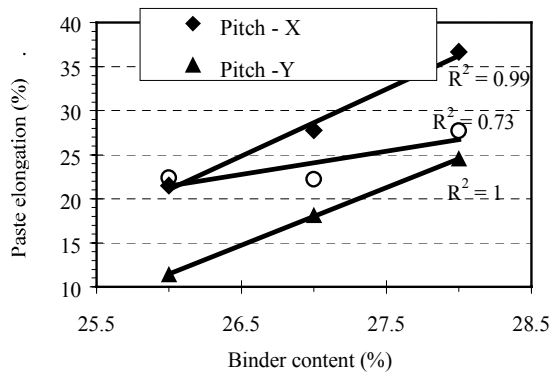
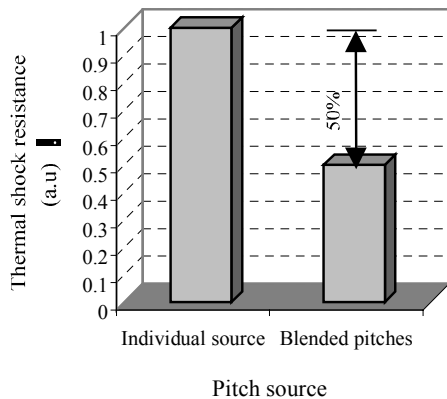


Figure 6: Paste fluidity behaviour with single-source and blended pitches (Plant-B)

During the thermal shock crisis at Plant-B, the prebaked anodes made with blended pitches (both Söderberg and prebaked anodes used same blended pitches) were sampled for a comparative laboratory study with anodes made from each of two sources. The thermal shock resistance was measured and the results presented by Figure 7 show that the thermal shock resistance of the prebaked anode using blended pitch is significantly lower when compared with one of the anodes using each pitch source Figure



7: Thermal shock resistance results of the prebaked anode (Plant-B) separately. The laboratory results confirm the thermal shock problem observed in the potroom with anodes made with blended pitch.

Based on potroom observations at plant-B with the Söderberg and prebaked anodes and on laboratory results, it was concluded that, given the complexity of the chemical composition of pitch and the difficulty of evaluating pitch compatibility:

- It is not recommended to blend pitches from different suppliers
- It is not recommended to blend pitches from different manufacturing processes.

In 1993 it was observed in the Söderberg potrooms at Plant-C, that the fluidity of the paste suddenly dramatically changed on the top of the anode when the paste plant started to use a new shipment of pitch. Laboratory investigation on the pitch samples shows that it is two different groups of pitch for this period (Figure 8). It can be seen from the graph that paste binder requirement increases significantly from the Group-1 to Group-2 shipment in order to reach the elongation target. The slope of the curve on Figure 8 also shows that the fluidity of the paste made with Group 2 pitch is less sensitive to the paste binder level variability. This phenomenon can cause more difficulty in using elongation measurements to predict the fluidity behaviour of the paste on the top of the anode.

This variability in pitch quality causes the anode problem in the potrooms and requires more process adjustment in the paste plant in order to reduce the magnitude of anode problems in the potrooms.

Three years later, the same smelter experienced another serious anode problem at the beginning of 1996. It was found that big part of this problem could be traced to a specific pitch shipment, and more particularly to large degrees of variability in pitch quality between pitch shipments.

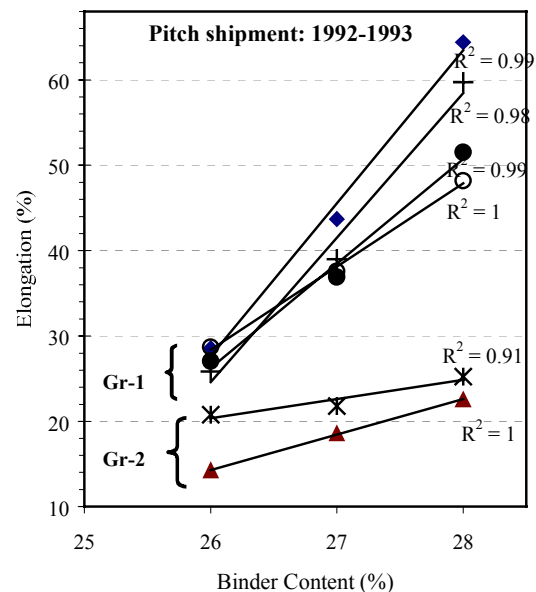


Figure 8: Variation of paste fluidity at different binder level for different pitch shipment (Plant-C)

The variability in paste fluidity at the top of the anodes between consecutive shipments occurred again despite the fact that the pitch seemed to show no variability according to the required specifications. It can be seen from Figure 9 that paste fluidity, as measured by paste elongation, changes significantly as a function of paste binder content for various pitch shipment. It can also be observed that some pitch shipments, gave particularly high elongation numbers for a given paste binder content.

More recently, in 1999, at another Söderberg plant (Plant-D), it was observed that the paste binder requirement had to be increased by 1.5% in order to reach the paste fluidity target. Use of this paste in the potroom caused very serious operational problems. The carbon dust generation and the number of carbon outs increased dramatically in the cells and, consequently, some Söderberg anodes were lost. The weakness in the pitch quality was identified as the main source of anode problems in the potroom.

All of the anode problems described in this paper pointed to pitch as the cause. However, it is particularly interesting to remember that in the majority of the cases, the problems occurred in the potroom between consecutive pitch shipments, despite the fact that the pitch showed no variability according to the required specifications. In order to face these problems and keep high anode performance in the potroom, Alcan decided to develop, in partnership with the smelters, R&D activities to study the factors affecting pitch quality variability.

**Pitch flow behaviour study and the relationship with plant anode problems**

For a given coke and optimum paste-making parameters, the anode paste fluidity is affected by:

- Flow behaviour of the pitch (viscosity, wetting angle, surface energy and mesophase)
- Variation of these properties with temperature during pitch storage, paste mixing and paste baking on the top of the anode (in the Söderberg case) or in the baking furnace for prebaked anode
- Quantity and volume of pitch between the coke aggregate

The pitch characteristics as received in the smelters are related to tar characteristics, the tar distillation process, pitch storage and handling conditions.

Pitch wetting capability results for Plant-C pitch shipment are presented in Figure 10. Figure 11 gives the anode problem in the potroom in terms of carbon outs. The results in Figure 10 show a large variability in wetting capability (P<sub>1</sub> and P<sub>2</sub>) and also a poor wetting quality (high ΔP value) from one shipment to the next. These results were shared with Alcan's pitch supplier and much effort has been made to decrease variability in the P<sub>2</sub> value and also decrease the ΔP below 5 °C. This effort results in a positive impact in the potroom as shown in Figure 11. In fact, as we can observe in this graph, the number of carbon outs decreased in the potroom in same period as pitch wetting capability behaviour stabilised and ΔP decreased below 5 °C.

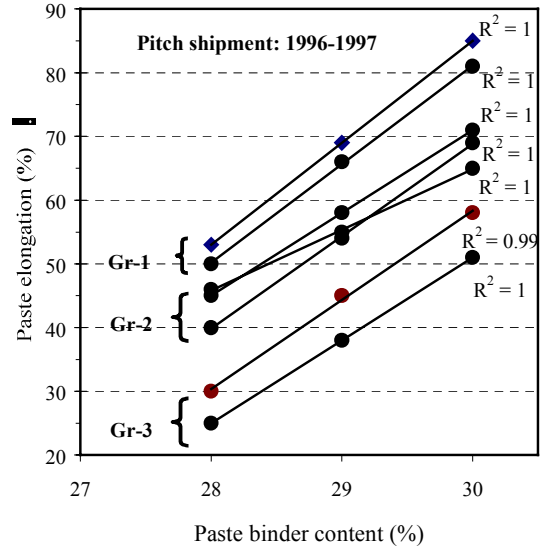


Figure 9: Variation of paste fluidity at different binder levels for different pitch shipments (Plant-C)

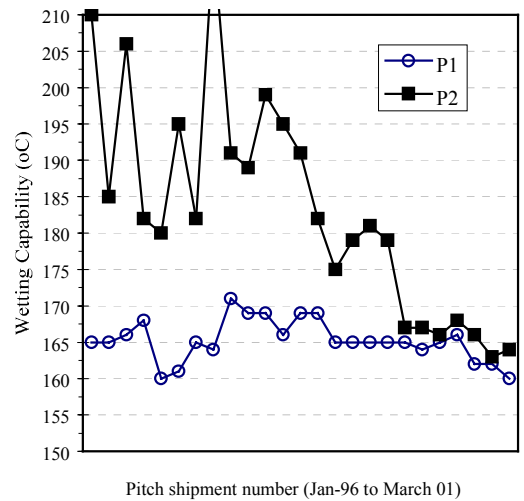


Figure 10: Plant-C pitch wetting capability evolution

Based on this investigation, it was observed that the variability in pitch wetting behaviour and especially a high value in ΔP (higher than 5 °C) was one of the main causes of the anode problem in the potroom.

The investigation on the wetting capability of the pitch used by Plant-D corresponding to the period of the anode problem showed that the fluidity problem occurring in this plant was caused by poor pitch wetting capability (Figure 12). In fact the pitch used by this plant had a wetting behaviour Type C (Figure 1). On Figure 12 incomplete penetration of this pitch drops and a significant residue tail at the end of the droplet test can be seen.

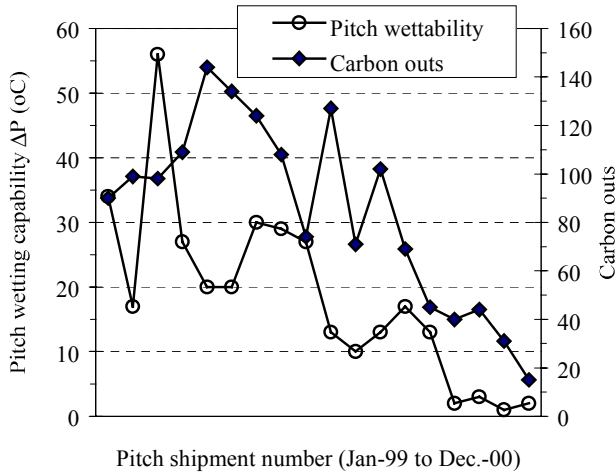


Figure 11: Number of anode carbon outs in the potroom related to the pitch wetting capability (Plant-C)

The microscopic analysis (Table 2) of this pitch sample resulted in identifying the presence of a significant amount of very fine mesophase in the pitch used during the anode problem in the potroom. The presence of the fine mesophase promotes thermal instability of the pitch and paste and also affects the paste mixing efficiency.

Table 2: Pitch sample mesophase content during anode problem at Plant-D

Pitch Mesophase size (%)		
1-3 μm	3-10 μm	> 10 μm
0.50	1.65	0.67

In the year 2000 it was decided to change the pitch source for prebaked Plant B and to use a pitch with a good wetting capability ( $\Delta P < 5^\circ\text{C}$ ). Figure 14 shows the impact of using pitch with good wetting capability on the anode baked density. At the same time the anode binder requirement decreased by about 1%. From Figure 11 it can be established clearly that using a pitch with good wetting capability ( $\Delta P < 5^\circ\text{C}$ ) has a beneficial impact on anode performance in the potroom. The number of anode problems decreased significantly in the potroom since anodes made with good pitch wetting capability have been in use.

As previously mentioned determination of  $\Delta P$  with a good precision is a key factor for pitch characterisation. Investigations have been carried out in order to establish the relationship between pitch characteristics and pitch wetting capability. Figures 15, 16 and 17 show the results of these investigations. From Figure 15 it can be seen from that the inflexion point of the contact angle curve ( $P_1$ ) depends on the pitch softening point, whereas, Figure 16 shows that is not any clear relationship between  $P_2$  and any other pitch characteristic (QI, TI, beta-resin, etc.) presented in these figures.

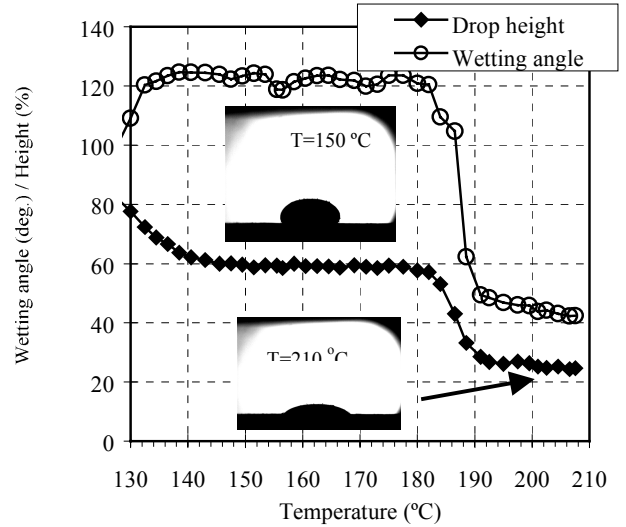


Figure 12: Plant-D pitch sample wetting capability measurement

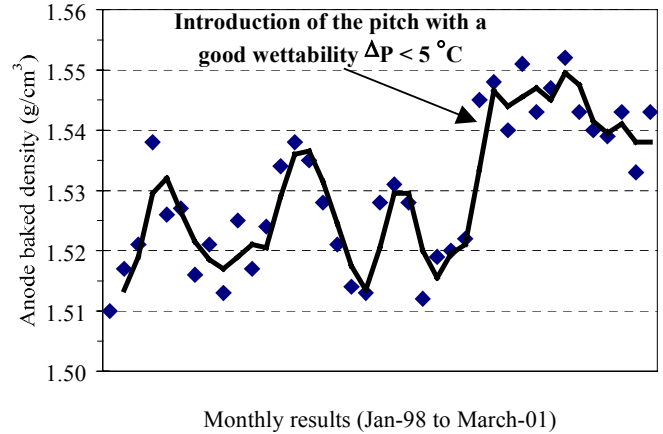


Figure 13: Impact of using of a pitch with a good wetting capability on prebaked anode density (Plant-B)

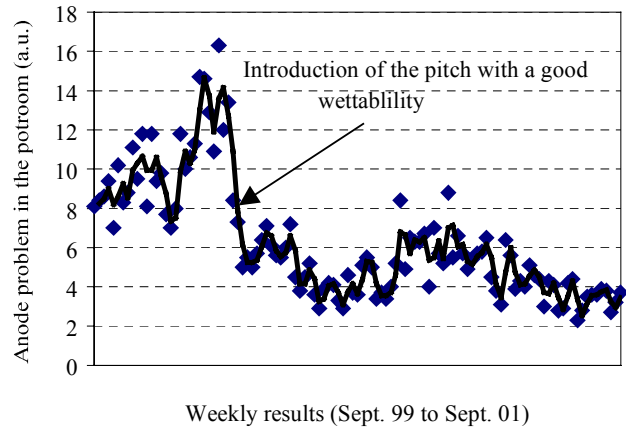


Figure 14: Impact of using of a pitch with a good wetting capability on potroom anode problems (Plant-B)

However, Figure 17 shows pitch wetting capability ( $\Delta P$ ) as a function of pitch TI content for the pitch samples with the same softening point, beta resin and produced by the same supplier. From this graph it can be seen that the pitch TI content seems to have an impact on pitch wetting capability.

A tight control of tar selection and the control of TI formation during tar distillation seem to help to improve the pitch wetting capability.

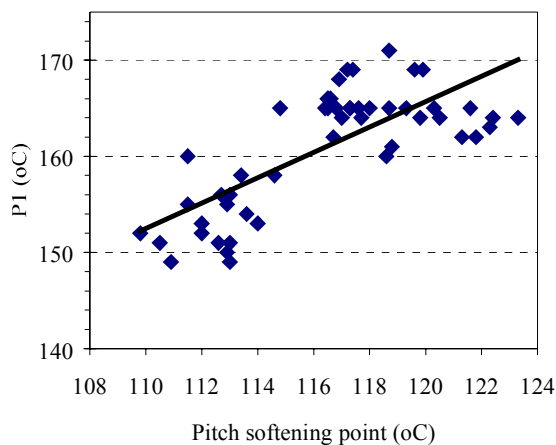


Figure 15: Impact of pitch softening point on pitch P1 point

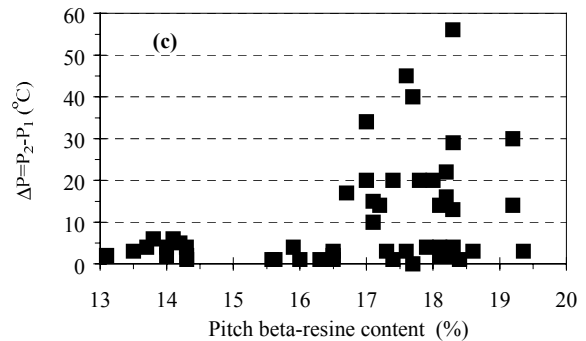
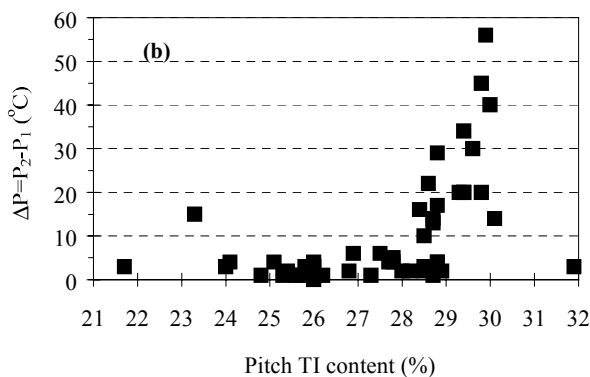
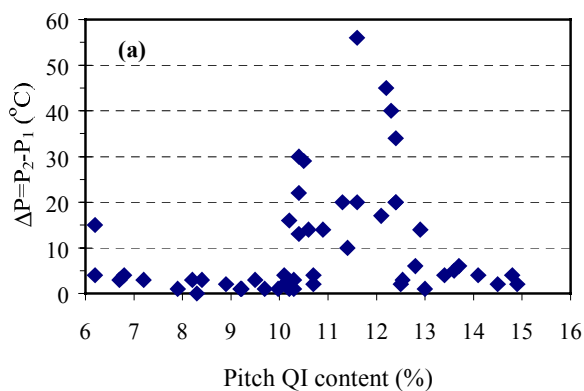


Figure 16 (a,b,c): Impact of pitch characteristics (QI, TI, beta-resin) on pitch wetting capability

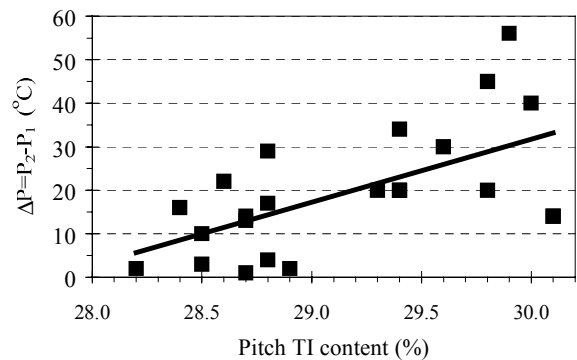


Figure 17: Impact of pitch TI on pitch wetting capability for pitch samples with the same softening point, beta resin and produced by the same supplier

## CONCLUSIONS

Based on this investigation, it has been clearly established that the pitch wetting capability characterised by  $\Delta P$  has a significant impact on paste fluidity and anode performance during cell operation.

The prebaked and Söderberg anode problem decreased in the potroom by using the pitch with a  $\Delta P < 5^\circ\text{C}$ .

Using a pitch with  $\Delta P$  less than  $5^\circ\text{C}$  improves the prebaked anode density and decreases the binder requirement.

The presence of a residue tail on the top of the coke bed after the droplet test can indicate the presence of fine mesophases in the pitch, which are not detectable by mesophase measurement according to the ASTM method. A higher value of  $P_2$  can be an indication of the presence of this fine mesophase in the pitch but, based on this investigation,  $P_2$  does not depend only on the pitch solid particles or the mesophase content.

$P_1$  value depends to the pitch softening point whereas pitch TI content seems to have an impact on the  $P_2$  value (or  $\Delta P$ ).

There is no correlation between pitch QI level and pitch wetting capability.

Using a pitch with a  $\Delta P$  less than 5 °C (according to the Alcan method) improves Söderberg paste fluidity control and the performance of the anode in the potroom.

Alcan's wetting capability measurement device (SyTac) allowed the pitch  $P_2$  value to be determined with good precision.

### ACKNOWLEDGEMENTS

The authors wish to recognise the contribution of the Alcan Primary Metal group smelter staff. We are grateful to Mr. André Proulx and Mr. Raymond Peterson who participated in many useful technical discussions. Furthermore, we acknowledge the Alcan pitch suppliers for very useful discussions in order to have a better understanding of the pitch production process and the efforts that they made to improve the quality of pitch for Alcan smelters.

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