

# THE EFFECT OF THERMAL TREATMENT ON INDUSTRIAL PITCH AND CARBON ANODE PROPERTIES - PART 2

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## ABSTRACT

A series of industrial-type pitches were produced in a pilot unit to simulate production processing. The feedstocks were categorized by quinoline insoluble content and aromaticity. Controlled process thermal treatment was used to increase  $\beta$ -resin and avoid the formation of mesophase. The  $\beta$ -resin effect on 6 x 9 x 12-inch vibraformed carbon anode properties is reported. (Preliminary information on this project can be found in Light Metals, 1993.)

## INTRODUCTION

In Part 1 of this series of papers, the effect of thermal treatment in producing industrial-type pitches was studied.<sup>1</sup> Thermal treatment in the 300-390°C range was used to increase  $\beta$ -resin [the difference between toluene insoluble (TI) and quinoline insoluble (QI)], without any apparent mesophase formation.

The feedstocks characterized in Table 1 represented two different aromaticity levels for the 2.5 wt.% and the 7 wt.% QI ranges. Based on the data from this study, we concluded:

1. Generally, the feedstock aromaticity was directly related to QI content.
2. The low aromatic feedstocks demonstrated a marked increase of pitch  $\beta$ -resin content with thermal treatment when compared to those produced from high aromatic feedstocks.

3. Laboratory coking value determined by the modified Conradson method was not significantly affected by  $\beta$ -resin formed during thermal treatment.
4. Viscosity increase during thermal treatment was more pronounced for high QI than low QI feedstocks.
5. At the chosen conditions, thermal treatment longer than eight hours resulted in a decreased rate of  $\beta$ -resin formation with a corresponding increase in QI content.

TABLE I. PROPERTIES OF FEEDSTOCKS SELECTED FOR THE PITCH PROCESSING STUDY

Sample ID	TI, wt. %	QI, wt. %	$\beta$ -resin, wt. %	I <sub>A</sub> IR	Ha/Hn NMR
A	4.3	2.2	2.1	2.2	3.5
C	5.4	2.7	2.8	2.8	5.1
P	9.5	6.9	2.6	3.4	5.7
Q	10.5	7.2	3.2	3.9	8.0

Pilot scale carbon anodes were produced to determine the importance of aromaticity and  $\beta$ -resin on carbon anode properties for each industrial pitch.

## EXPERIMENTAL PROCEDURE

- Employing the established guidelines and materials used in Part 1, pilot quantities of both thermal treated and untreated pitches were prepared. The four feedstocks represented low and high values of both QI and aromaticity. Three pitches of progressively increasing  $\beta$ -resin were produced from each feedstock.
- Vibroformed anodes measuring 6 x 9 x 12 inches were prepared using these pitches as binders with a sized petroleum coke blend and mix design obtained from a commercial smelter. Based upon experience with this petroleum coke mix design, binder levels were adjusted to obtain a pre-determined anode density. In general, the binder levels increased relative to QI content.
- The green anodes were packed in fluid coke and baked to 1125°C in a nitrogen atmosphere.
- Eight 50 mm (2 inches) diameter x 152 mm (6 inches) cores were cut in the molding direction from each anode.
- The cores were prepared and characterized as illustrated in Figure 1. Koppers test methods were used when ASTM and/or ISO standard methods were not available.
- The pitch and carbon anode property measurements were compared for each pitch binder.

## Experimental Results

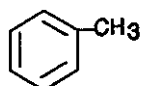
### Pitches

Pitch testing methods used in this study are listed in Table II. Pitch properties for the four trial series are summarized in Table III. As further illustrated in Figure 2,  $\beta$ -resin increases with the degree of thermal treatment for each series of pitches. The low QI, low aromatic feedstock used to prepare the "A" pitches has the greatest total increase in  $\beta$ -resin.

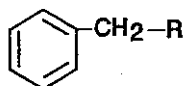
TABLE II. PITCH MEASUREMENT METHODS

Characterization	Unit	Method
Softening Pt. (sp)	°C	ASTM D 3104
Viscosity	cP	ASTM D 5018
Coking Value	wt. %	ASTM D 2416
Toluene Insoluble	wt. %	ASTM D 4072
Quinoline Insoluble	wt. %	ASTM D 4746
$\beta$ -resin	wt. %	TI less QI
Sulfur	wt. %	LECO Instrument SC-132
Primary, Secondary and Coarse QI	vol. %	ASTM D 4616
NMR Alpha Methyl Hydrogen: Alpha Methylene Hydrogen ratio *		Comparative NMR Procedure

\* Ratio of the following hydrogen types:



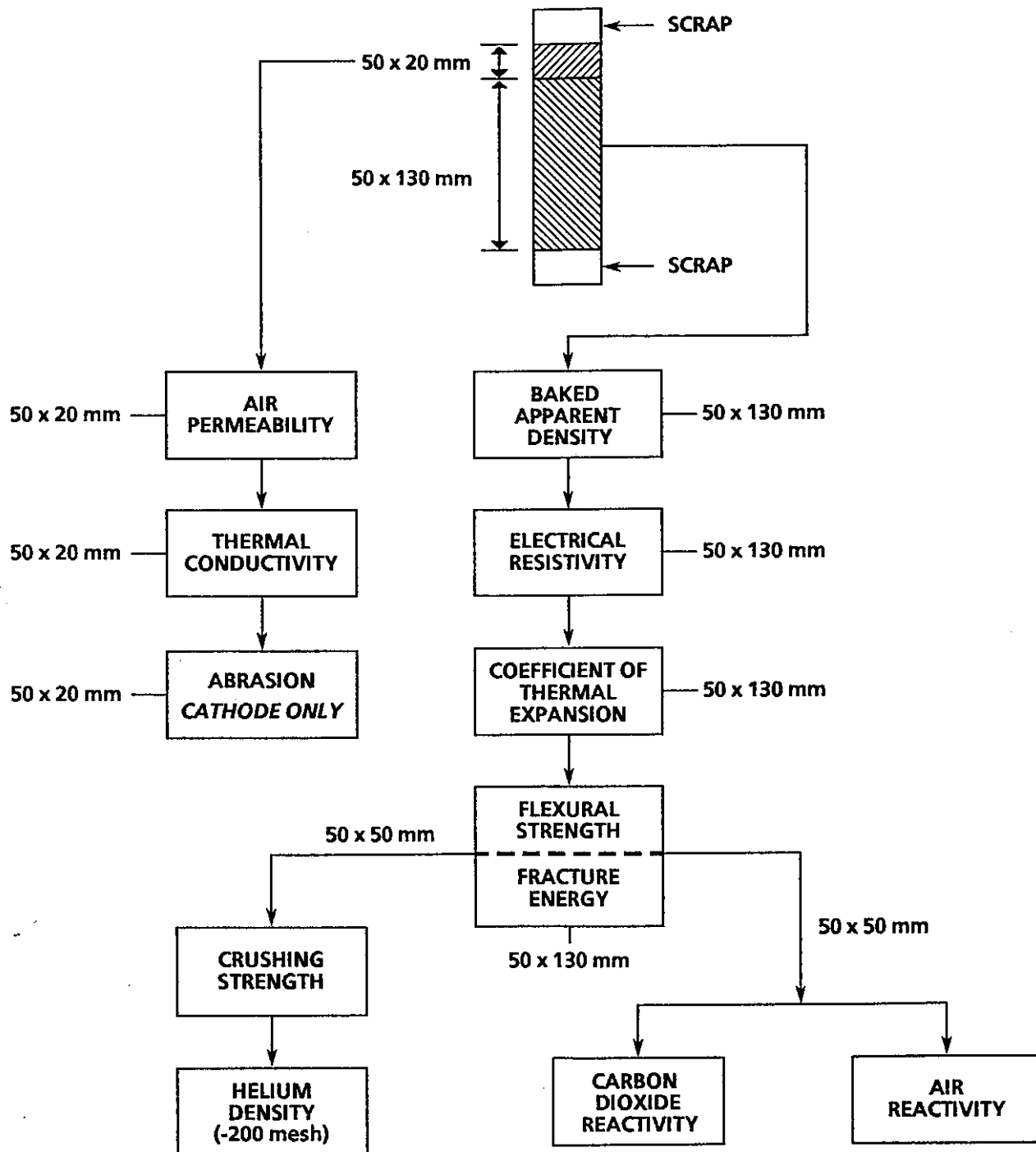
Alpha-Methyl



Alpha-Methylene

**FIGURE 1.**

**METHODS FOR THE DETERMINATION OF PREBAKED ANODE PROPERTIES**



**TABLE III. PITCH PROPERTIES FOR THERMAL TREATMENT PROCESSED FEEDSTOCK SERIES**

Feedstock	A	A	A	C	C	C	P	P	P	Q	Q	Q
Thermal Treatment	None	Mild	Severe	None	Mild	Severe	None	Mild	Severe	None	Mild	Severe
Softening Point, °C	109.2	108.0	108.2	107.5	111.8	108.1	111.7	109.7	107.7	109.7	111.0	108.8
Toluene Insoluble, %	18.1	21.4	25.9	19.3	25.0	25.8	24.0	28.7	30.8	25.3	30.3	33.5
Quinoline Insoluble, %	4.0	3.8	4.3	4.8	5.4	5.7	11.7	11.4	11.4	12.2	12.5	13.5
Beta-Resin, %	14.1	17.6	21.6	14.5	19.6	20.1	12.3	17.3	19.4	13.1	17.8	20.1
Coking Value, %	50.0	49.7	51.5	52.9	55.2	53.8	54.4	54.0	54.5	56.3	57.4	56.5
Sulfur, %	0.59	0.55	0.49	0.72	0.66	0.65	0.65	0.63	0.53	0.75	0.71	0.64
NMR, $\alpha$ -Methyl/ Methylene	2.7	3.2	3.3	1.2	1.7	2.4	2.3	2.6	3.6	1.0	1.1	2.7
Viscosity @170 °C,cP	340	450	580	410	670	560	600	650	830	660	1130	1030

Nuclear magnetic resonance (NMR) data show that cracking occurs with more extensive thermal treatment; i.e., the alpha-methyl/alpha-methylene hydrogen ratio increases with the degree of thermal treatment for each feedstock series. Only a trace of mesophase was found by photomicroscopy in the severe thermal treatment products.

Another trend observed was that sulfur content decreased as a function of thermal treatment.

#### Anodes

The green anode densities ranged from 1.60 to 1.62 g/cc and yielded baked core densities from 1.51 to 1.54 g/cc. The anode core data are presented in Table IV. Figures 3-8 illustrate selected physical properties plotted as a function of  $\beta$ -resin. The results are mixed. Generally, for high QI feedstocks, baked density, air reactivity residue and strength decrease with the degree of thermal treatment. However, for low QI feedstocks, these trends are not distinct. The non-thermal treated, high QI (P,Q) and more aromatic, low QI feedstock (C) pitches have higher density and less air

reactivity than the low QI, low aromatic feedstock pitch (A).

The high QI, low aromatic based pitch (P) improves in resistance to carboxy reactivity with thermal treatment. The non-thermal treated, high QI pitches (P,Q) have higher strength than the other pitches; moreover, the more aromatic, high QI feedstock pitch (Q) resulted in the stronger anodes.

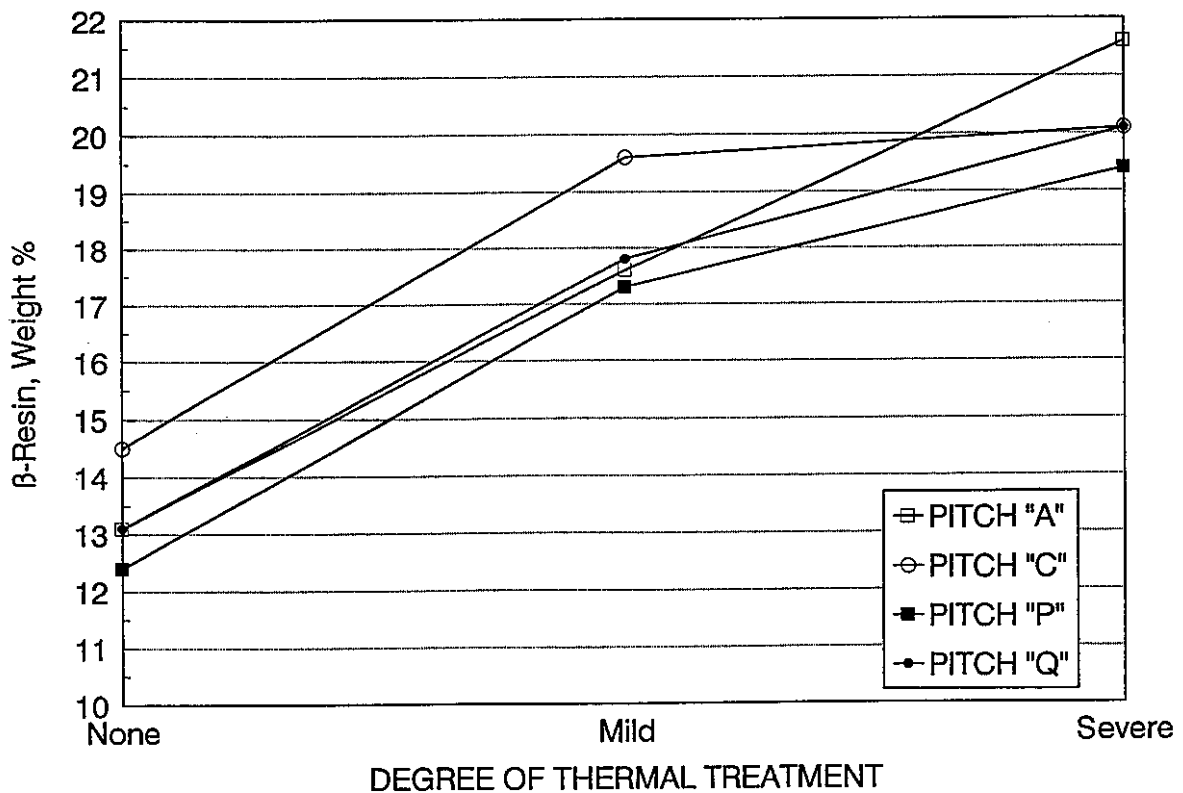
#### **CONCLUSIONS**

1. Pitch  $\beta$ -resin content increased with the degree of thermal treatment of each feedstock type.
2. The alpha-methyl to alpha-methylene hydrogen ratio, as determined by NMR, is directly related to the degree of thermal treatment within each feedstock series.
3. Generally, baked anode density, air reactivity residue and strength decreased with the increase in  $\beta$ -resin for the high QI feedstocks.

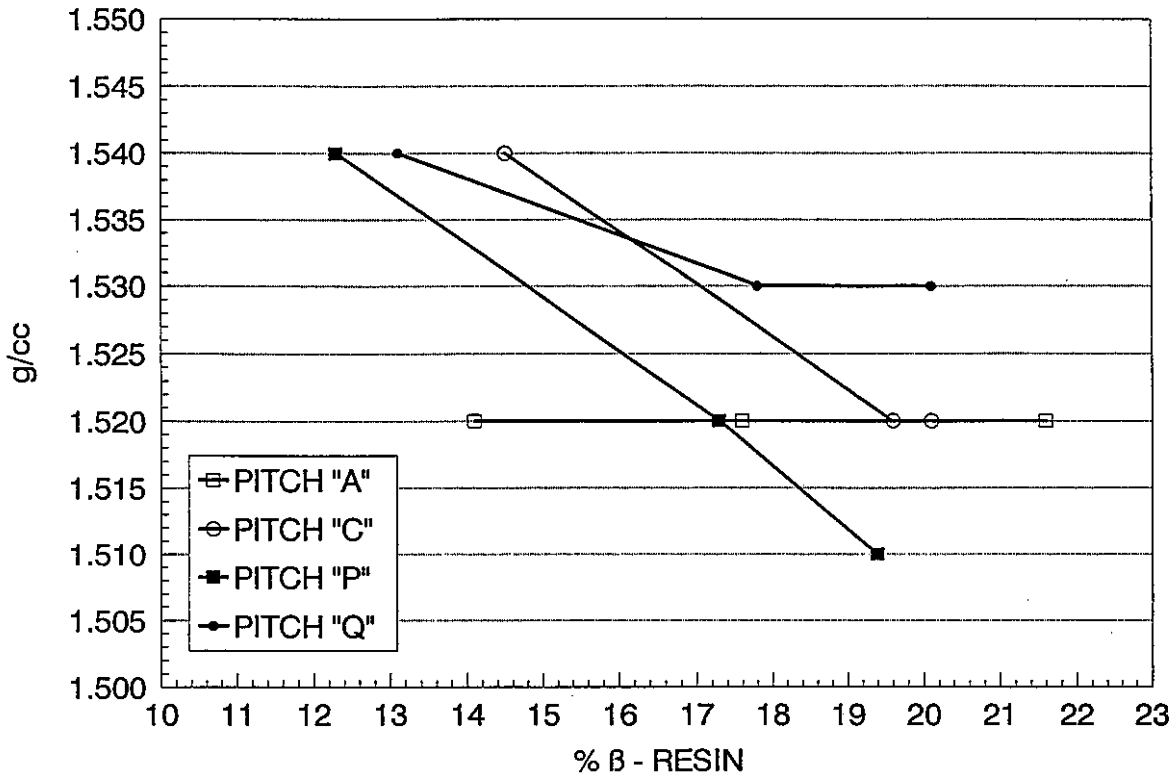
TABLE IV. CARBON ANODE CORE AVERAGE PROPERTY COMPARISON

Pitch	Baked Apparent Density (g/cc)	E.R., $\mu\Omega\text{m}$	Air Perm., nPm	CO Reactivity, % Residue	Air Reactivity, % Residue	Crush Strength, MPa	Flexural Strength Stress, MPa	CTE Avg. Alpha (E-6/ $^{\circ}\text{C}$ @300 $^{\circ}\text{C}$ )	Thermal Conduct W/mK
"A", No Thermal Treatment	1.52	63.8	0.80	84.7	69.7	30.74	7.36	3.61	2.95
"A", Mild Thermal Treatment	1.52	62.5	1.01	84.8	65.5	33.18	7.26	3.61	2.83
"A", Severe Thermal Treatment	1.52	61.5	1.02	86.2	65.8	34.76	7.38	3.62	2.82
"C", No Thermal Treatment	1.54	61.2	0.67	86.2	66.6	35.72	8.17	3.74	2.98
"C", Mild Thermal Treatment	1.52	58.2	1.34	87.6	67.7	38.11	9.13	3.61	2.87
"C", Severe Thermal Treatment	1.52	60.1	1.34	85.7	66.1	33.51	12.37	3.61	2.83
"P", No Thermal Treatment	1.54	59.7	0.62	83.4	70.6	40.65	9.02	3.75	3.04
"P", Mild Thermal Treatment	1.52	60.5	0.91	87.8	65.5	37.18	7.93	3.71	2.90
"P", Severe Thermal Treatment	1.51	60.6	0.94	89.4	66.6	35.79	8.09	3.75	2.93
"Q", No Thermal Treatment	1.54	56.8	0.61	87.9	69.9	45.25	10.73	3.77	3.13
"Q", Mild Thermal Treatment	1.53	61.5	0.64	88.3	68.7	41.87	7.27	3.63	2.91
"Q", Severe Thermal Treatment	1.53	63.1	0.56	87.5	68.3	40.34	7.56	3.60	2.85

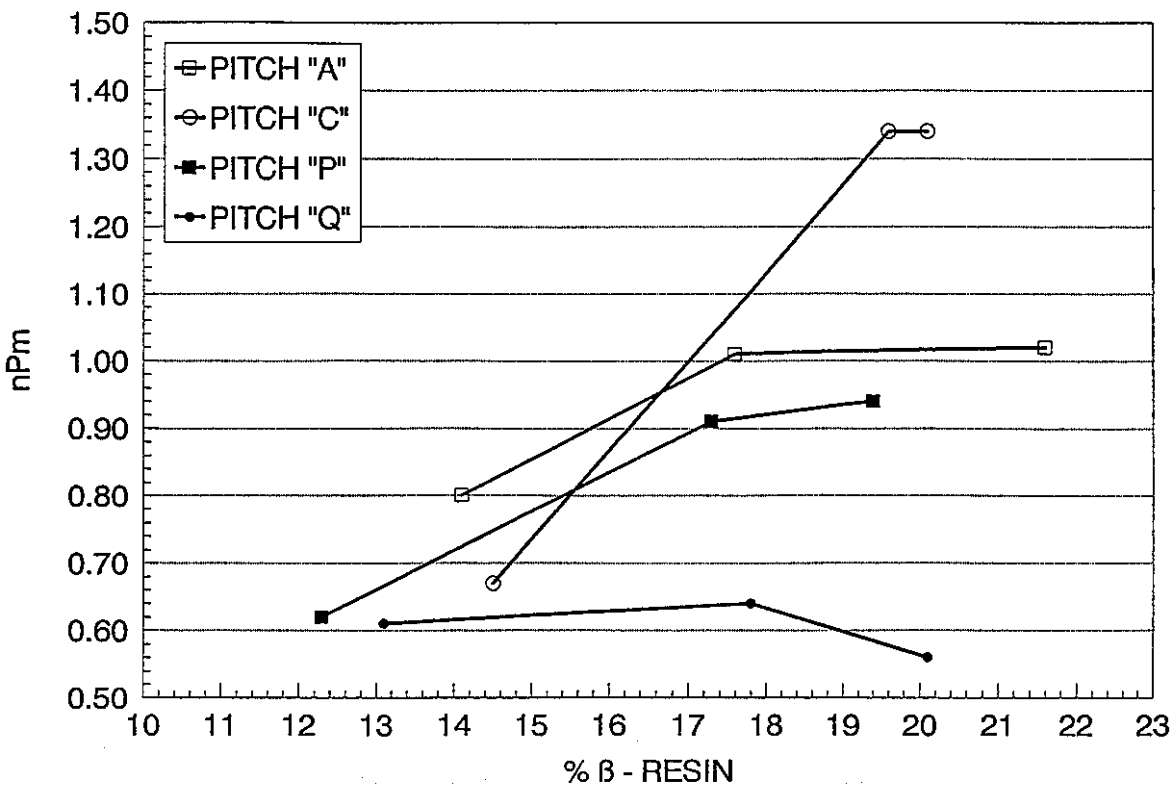
Figure 2 - The Effect of Thermal Treatment on Pitch  $\beta$ -Resin



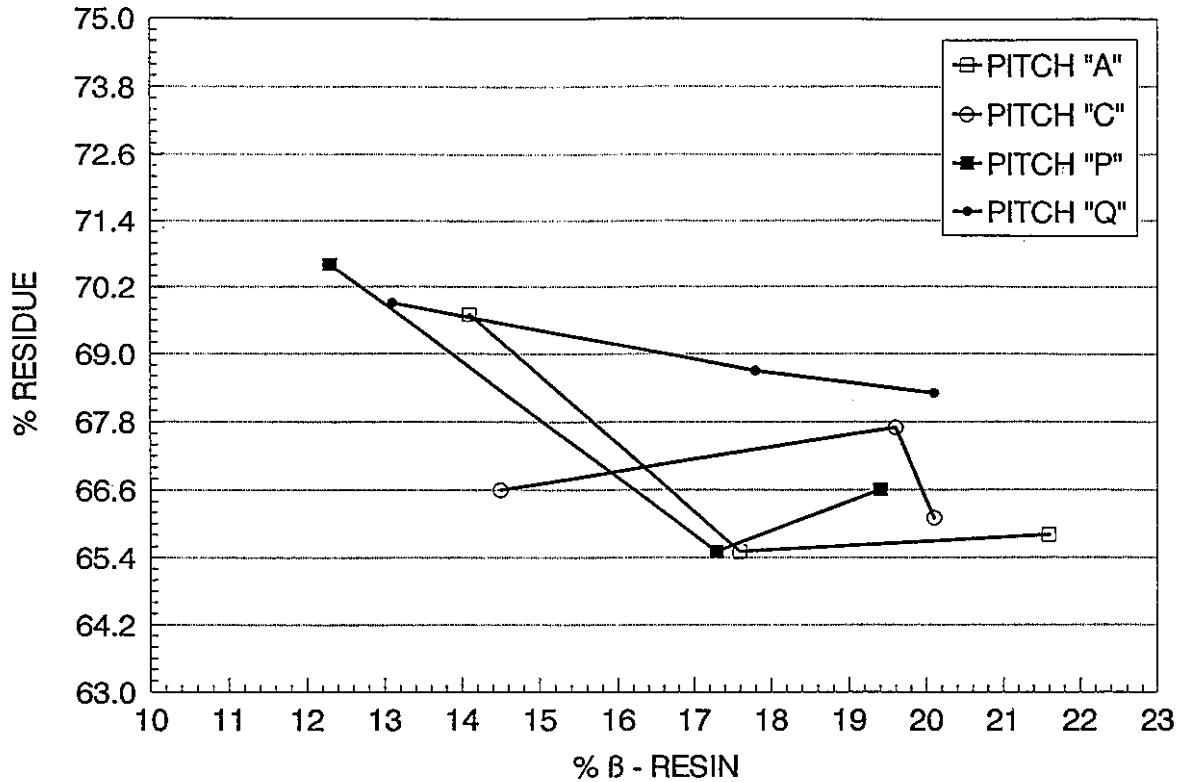
# FIGURE 3 - BAKED APPARENT DENSITY



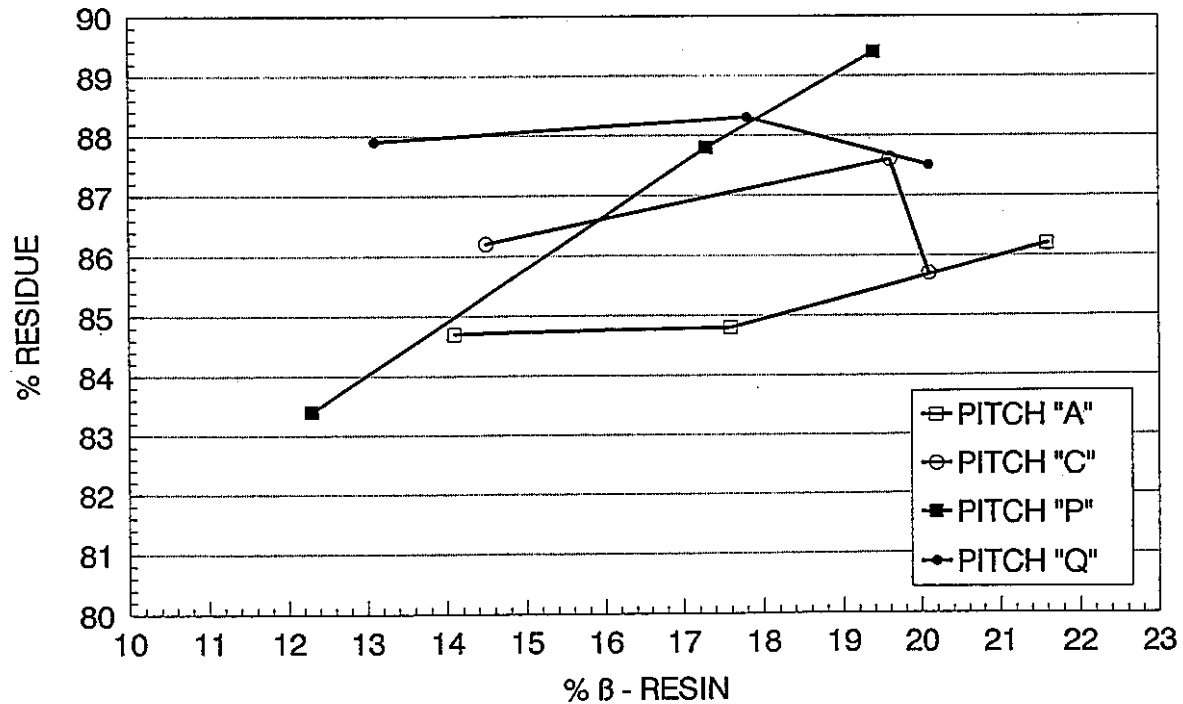
# FIGURE 4 - AIR PERMEABILITY



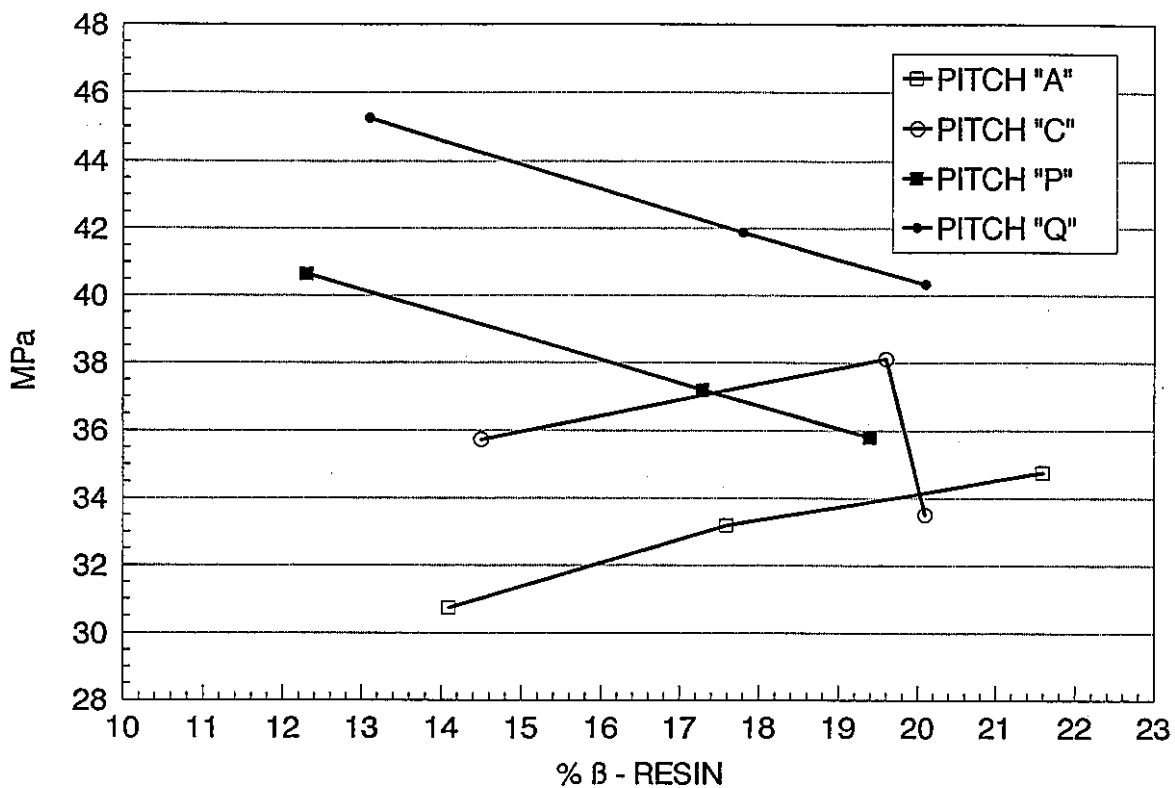
# FIGURE 5 - AIR REACTIVITY



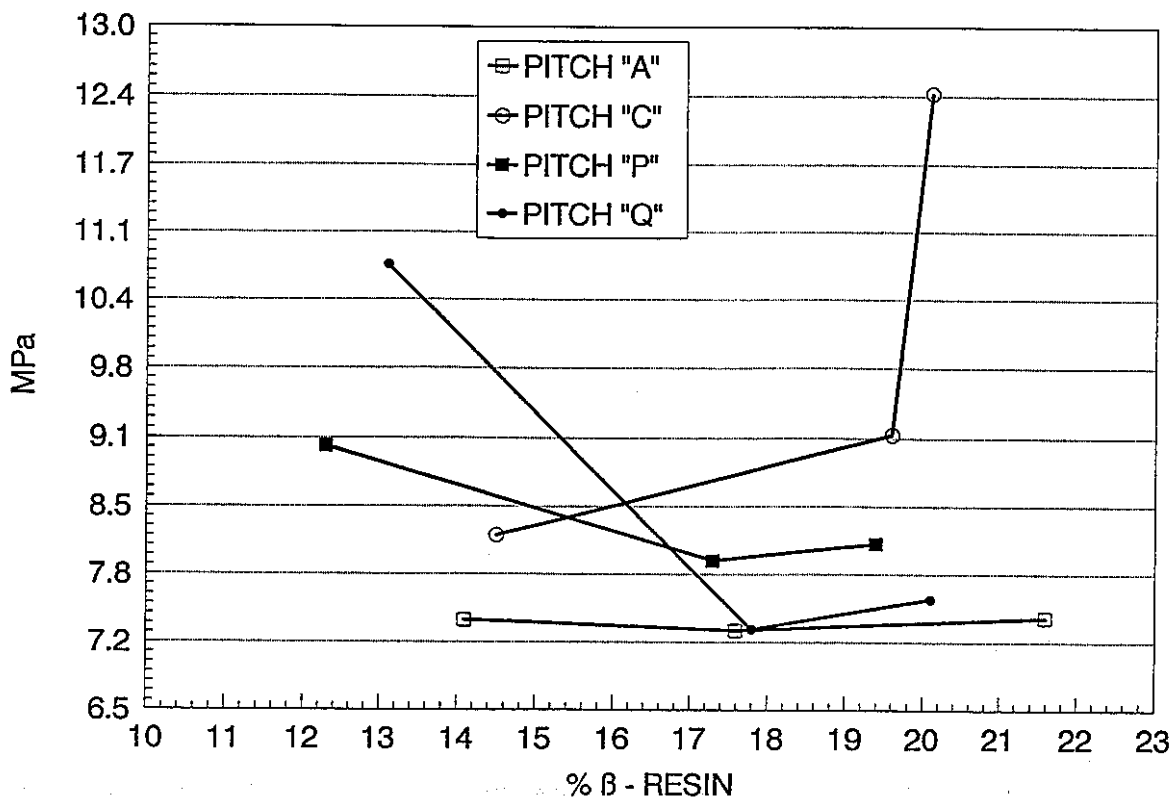
# FIGURE 6 - CO2 REACTIVITY



# FIGURE 7 - COMPRESSIVE STRENGTH



# FIGURE 8 - FLEXURAL STRENGTH



4. Anode property data for the low QI feedstock pitch series did not display specific trends as a function of  $\beta$ -resin.
5. In this study, there is not an improvement in carbon anode properties for an increase in binder  $\beta$ -resin.
6. The high QI non-thermal treated feedstock pitches resulted in anodes with the highest strength in this study.

#### **ACKNOWLEDGEMENT**

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#### **References**

1. McHenry, E., R., Baron, J. T. and Saver, W. E., "The Effect of Thermal Treatment on Industrial Pitch and Carbon Anode Properties - Part 1," Light Metals 1993, pp. 663-668.