

Coal Tar/Petro Binder Studies,
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I. INTRODUCTION

A. HISTORICAL STATEMENT

Some 40-60 years ago the petroleum materials available as binder for carbon products would have been asphaltic. Typical properties of these asphalts would be a 1.0 specific gravity and a 35 percent coking residue, which would yield only a 1.35 g/cc baked carbon density. These values compare to typical coal tar pitch properties of 1.30 specific gravity, 56% coking residue and a baked carbon density of 1.58 g/cc.

In the 1960's more aromatic, high specific gravity petroleum pitches were developed. Various feedstocks such as catalytic cracker bottoms, thermally cracked materials, and ethylene cracker residues were additionally processed by cracking and/or distillation to produce these improved petroleum pitches. Many evaluations of these new pitches were performed.^{1,2,3} The most extensive test was at the Reynolds, Jones Mills Reduction Plant.⁴ By reducing the petroleum pitch percentage 1.5% from the normal coal tar pitch level in 250 lb. anodes, comparable performance was obtained. The binder level adjustment relates to specific gravity and quinoline insoluble differences in the two pitches.

Table 1. Comparison of Coal Tar and Petroleum Pitches

	Coal Tar <u>Pitch</u>	Petroleum <u>Pitch</u>
Softening point, °C	106	120
Specific Gravity	1.34	1.23
Quinoline Insoluble, wt. %	15	0.8
Coking Value, wt. %	58	50

In subsequent larger size anode evaluations, petroleum pitch has not provided acceptable performance. The typical evaluation has reported uneconomical carbon consumption for petroleum pitch binder.

There are adequate worldwide supplies of coal tar for the required pitch requirements. However, the required feedstock supply is not always available in all geographic areas. Because of environmental and economic reasons, many USA coke plants have closed in the past decade. North America is presently a net importer of coal tar feedstock and pitch. The economic and quality effects of imported coal tar materials vs. domestic petroleum materials in feedstock must be studied. We believe there are potential techniques to produce a coal tar and petroleum material combination that will result in acceptable carbon binder performance. This paper will report the status of our coal-tar/petro pitch development program in cooperation with a number of customers.

B. APPROACH

We approached the development of a coal-tar/petro pitch by building on the positive characteristics of each component, possible synergisms and new process design. For

a discussion of pitch properties, see my paper at the Fourth Australasian Smelter Technology Workshop.⁵

1. BASIC PITCH PROPERTIES

(a) Softening Point and Viscosity

At the same softening point, most petroleum pitches have a lower viscosity than coal tar pitches, consequently, petroleum pitch is usually marketed at 10-20°C higher softening point than coal tar pitch. The higher softening point for petroleum pitch still results in a reduced coking value difference when compared to standard coal tar pitch.

(b) Aromaticity, Coking Value and Specific Gravity

There are structural characterization differences between coal tar and petroleum pitches.⁶ Consequently, the lower aromaticity and carbon content of petroleum pitch results in lower coking value and specific gravity than coal tar pitch.

(c) Pitch Insoluble (Quinoline Insoluble or QI)

In North America the typical coal tar pitch binder has a QI content of 10-15%. Usually 90-98% of the QI is natural and the remainder is a mixture of cenospheres, coke, coal, and mineral matter. The variety of coke oven designs and operation around the world results in QI levels from 2-20%. The typical petroleum pitch has no QI. QI results in 95-100% coking value.

(d) Beta-Resin

β -resin is the mathematical difference between toluene insoluble and QI and represents a large polynuclear molecular weight portion in pitch. Normal coal tar pitch binder has 10-18% β -resin compared to 3-7% for petroleum pitch.

(e) Metals

The metals in coal tar pitch relate to the coal source and process additives. Some tar distillers add sodium hydroxide to neutralize potential tar acid corrosion which can result in excessive sodium in the pitch product. Since petroleum pitches are usually produced from distillates, feedstock metals are low; however, catalyst from a cracking operation is a potential impurity.

(f) Sulfur

Sulfur content in coal tar pitches is usually in the 0.45 to 1.0% range. With the increased usage of more sour crude, petroleum pitch sulfur can be in the 2-3% level.

- (g) Polynuclear Aromatic Hydrocarbons (PAH)
Typical benzo(a)pyrene [B(a)P] equivalent of a coal tar pitch is 27,500 ppm.^{7,8} Using the same HPLC procedure, typical petroleum pitch has a 8000 ppm B(a)P equivalent level.

2. TYPICAL PETROLEUM FEEDSTOCK PROPERTIES

We began our study by characterizing some 75 petroleum materials. Typical characterization included:

- (a) Infrared index (I_A) which is the ratio of the absorbencies of the aryl and alkyl CH groups.
- (b) Nuclear magnetic resonance (NMR) to compare ratio of the aromatic hydrogen to aliphatic hydrogen and other relationships.
- (c) The relative distillation and reactivity properties.
- (d) Carbon yield.
- (e) Sulfur level.

After selecting the more promising petroleum materials for the program, we explored techniques for combining them with coal tar materials. The direct blending of feedstocks prior to pitch production was the most logical process. We have now developed proprietary processing to further enhance the pitch properties for binder application.

In order to study a variety of pitch and carbon product properties we selected two ranges of petroleum content in the trial pitches:

<u>Type</u>	<u>Petroleum Material, percent</u>
A	≤ 15
B	≤ 40

II. DEVELOPMENT

Pitch development began at the bench and pilot scale level. However, we soon learned that our flexible production processes allowed us to produce 100 - 200 ton batch sizes. These potential shipment quantities permitted us to propose trial evaluations with our customers.

A. PRODUCTION TYPE A PITCH EVALUATED IN PILOT SCALE CARBON ANODES

In the first quarter of 1994, a 200-ton Type A coal-tar/petro pitch was prepared in one of our production plants for evaluation (see Table 2).

Properties	Trial Pitch	Control
Softening Point, °C	110.5	110.2
TI, %	26.4	27.2
QI, %	12.1	13.2
Beta Resin, %	14.3	14.0
Coking Value, %	55.8	57.1
Ash, %	0.22	0.19
Density, %	1.32	1.33
Sulfur, %	0.76	0.61

At this level of petroleum material, the property differences between coal-tar/petro and the coal tar pitch control are minimal.

Vibroformed anodes measuring 6 x 9 x 12 inches were prepared using these pitches as binders with sized, calcined, petroleum coke and butt material. The mix design was provided by a major USA smelter. The green anodes were packed in fluid coke and baked to 1125°C in a nitrogen atmosphere.

Eight 50mm diameter x 152mm cores were cut in the molding direction from each anode. The anode core properties are compared in Table 3.

Table 3. Pilot Scale Anode Core Properties Comparing Production Scale Type A Pitch to Control Coal Tar Pitch										
Koppers Pitch Sample	Type A Test Pitch					Control Pitch				
	Count	Min.	Max.	Avg.	Std. Dev.	Count	Min.	Max.	Avg.	Std. Dev.
Baked Apparent Density, g/cc	115	1.52	1.57	1.54	0.01	112	1.53	1.60	1.55	0.01
Electrical Resistivity, $\mu\Omega\text{m}$	115	60	77	66	3	112	57	78	64	3
CO ₂ Reactivity, % Residue	59	91.0	95.7	93.6	1.1	56	89.9	95.2	93.6	1.0
CO ₂ Reactivity, % Dust	59	0.2	1.9	0.8	0.4	56	0.3	1.7	0.7	0.3
Air Reactivity, % Residue	55	77.0	90.1	84.7	2.9	55	79.1	90.9	86.2	2.8
Air Reactivity, % Dust	55	0.2	5.1	2.3	1.2	55	0.1	4.7	1.7	1.1
Air Reactivity, % Loss	55	9.7	17.9	13.0	1.7	55	9.0	16.6	12.1	1.7
Air Permeability, nPm	115	0.33	0.88	0.47	0.09	112	0.30	1.23	0.46	0.14
Thermal Conductivity, W/mK	115	2.28	3.13	2.70	0.16	112	1.87	3.20	2.64	0.23

The binder in-situ coking value calculated during the baking process was 68.7% for type A and 69.4% for the control. The air reactivity measurements show the only significant difference between the trial and control material. As a result of this trial, we began to make additional changes to our process and to closely monitor carbon air reactivity.

B. PILOT SCALE TYPE B PITCH EVALUATED IN PILOT SCALE CARBON ANODES

A Type B coal-tar/petro pitch was prepared in the pilot plant for evaluation (see Table 4).

Table 4. Properties of Pilot Scale Prepared Type B Pitch Compared to Control Coal Tar Binder Pitch		
Pitch Type	B	Control
Softening Point, °C	109.4	111.3

Toluene Insoluble, %	24.4	28.1
Quinoline Insoluble, %	10.2	11.9
Beta-Resin, %	14.2	16.2
Modified Conradson Carbon, %	54.0	55.7
Ash, %	0.16	0.21
Volatility at 350°C, %	2.0	2.1
Specific Gravity, 25/15°C	1.30	1.33
Sulfur, %	1.2	0.6
Viscosity, centipoise at:		
150°C	2835	3010
160°C	1260	1300
170°C	650	680
180°C	350	375

The Type B material reflects the expected lower insolubles, higher sulfur, etc. by incorporating petroleum.

Vibroformed anodes measuring 6 x 9 x 12 inches were prepared using these pitches as binders with sized petroleum coke blend and mix design obtained from a commercial smelter. The green anodes were packed in fluid coke and baked as described in Section A.

The anode core properties are compared in Table 5.

Pitch	Binder wt. %	In-Situ Coking Value, Wt., %	N	Baked Density g/cc	Elect. Resist. $\mu\Omega\text{m}$	Air Perm. nPm	Air React. Residue wt. %	Crush Strength, MPa	Flex. Strength, MPa	CTE $\times 10^{-6}/^\circ\text{C}$	Thermal Cond. W/mk
Control	17.1	67.7	24	1.53	63	0.54	64	38.9	7.1	3.65	2.9
Type B	17.1	66.2	24	1.53	66	0.56	60	35.0	5.7	3.58	2.7
Type B	16.7	68.4	16	1.52	64	0.87	59	40.2	6.7	3.49	2.8

These properties show that the binder level for Type B pitch must be adjusted to obtain optimum anode properties. The laboratory coking value advantage for the control pitch did not translate to the reduced binder level baked anodes.

C. PRODUCTION TYPES A AND B PITCHES EVALUATED IN PILOT SCALE GRAPHITE ELECTRODES

In mid-1994, samples of both production scale Type A coal-tar/petro pitch and Type B coal-tar/petro pitch were supplied to UCAR Carbon Co. for evaluation in

pilot scale graphite. UCAR provided the following data for pitches used in their trial. These Type A and B pitches are different design than used in the previous trials.

Pitch Type	A	B	Coal Tar Control	Petroleum Control
Softening Point, °C	113.4	112.0	112.0	122.5
TI, %	28.4	23.0	27.8	4.5
QI, %	13.9	10.7	12.3	<0.1
Beta-Resin, %	13.0	12.3	15.5	4.5
Modified Conradson Carbon, %	57.9	55.5	57.7	50.6
Ash, %	0.22	0.09	0.22	0.0
Viscosity, cP at:				
150°C	3100	2800	3000	6800
160°C	1400	1200	1300	2300

UCAR prepared blends with each of these pitches using commercial mix designs and then extruded each into 6-inch diameter electrode stock. The stock was first baked to about 850°C and then graphitized to about 3000°C. Properties of the graphitized electrodes are compared in Table 7.

Binder Type	A		B		Coal Tar Pitch Control	Petroleum Pitch Control	
Binder level, pph	25	26	25	26	26	24.5	25
Density, g/cm ³	1.62	1.62	1.59	1.60	1.61	1.57	1.56
Electrical Resist. $\mu\Omega\text{m:wg}^*$	6.85	6.80	7.14	6.98	6.94	6.73	6.81
ag*	11.09	11.15	11.57	11.83	11.15	11.47	11.71
Moduli Elasticity, psi $\times 10^6\text{wg}$	0.94	0.95	0.93	0.97	0.91	0.87	0.87
ag	0.49	0.49	0.49	0.48	0.47	0.43	0.42
Flexural Strength, psi:wg	958	1008	872	1050	923	889	861
ag	645	665	678	676	641	485	474
Coefficient of Thermal Expansion, $\times 10^{-6}/^\circ\text{C:wg}$	0.19	0.21	0.23	0.19	0.19	0.29	0.27
ag	1.27	1.26	1.33	1.38	1.25	1.39	1.38

* wg = with grain, ag = against grain

These results show that the required binder level must be determined for each pitch type in order to obtain the optimum graphite properties. The coal-tar/petro binder systems provide equivalent graphite quality to that produced using the standard coal tar pitch.

III. CARBON ANODE PRODUCTION TRIALS

A. Production Type A Pitch Evaluated in Production Scale Prebaked Carbon Anodes

Over a period of 14 months, 16,700 tons of Type A coal-tar/petro pitch was evaluated as a binder (see Table 8). This binder was used in the production of 47.25 x 23.4 x 31.5 inch vibrated anodes with an average weight of 2000 lbs.

Pitch Type	A	Control
Softening Point, °C	110.5	110.5
Toluene Insoluble, %	32.0	31.4
Quinoline Insoluble, %	14.7	13.9
Sulfur, %	0.62	0.55
Iron, %	0.022	0.024
Silica, %	0.039	0.037

During this trial period a 15% binder level resulted in a normal green density of 1.59 g/cc for 115,250 anodes.

There were no discernable differences during the baking operation. Pottlines ran at a typical amperage of 153.3 KA with 4365 cells running. The 68-shift anode pattern resulted in a butt weight of 514 lbs and net carbon consumption of 0.435 lb/lb of aluminum. There was no observable change in airburn between the trial and control pitch anodes.

The overall conclusion is that there was no significant difference in anode quality or performance between the trial and control binder pitches.

B. Production Type B Pitch evaluated in Production Scale Prebaked Carbon Anodes

In this trial 520 tons of Type B coal-tar/petro pitch was evaluated as binder in 2100 anodes each weighing approximately 1800 lbs. The formulations, process and control factors were not adjusted from the control coal tar pitch anode production.

The trial anodes were processed and used in aluminum cells without any significant problems. The average anode density and carbon consumption were marginally lower for the trial anodes. However, it is anticipated that properties will be normal with binder level optimization.

C. Production Type B Pitch Evaluated in Production Scale Soderberg Carbon Anodes

A Soderberg Aluminum cell trial is in progress using Type B coal-tar/petro pitch binder. This Type B pitch was designed to have a significant reduction on the B(a)P equivalent level (see Table 9).

	Typical Coal Tar Pitch	Type B Pitch
B(a)P	9,800	5,900
B(a)P Equivalent	27,500	15,000

An acceptable Soderberg anode is being produced. This initial one-year trial period will be completed by the end of 1995.

IV. SUMMARY

- A. Acceptable Type A and Type B coal-tar/petro binder pitches have been produced for both aluminum anode and graphite electrode applications.
- B. Binder level optimization is required for coal-tar/petro binder pitch to obtain acceptable product properties.
- C. Our concentrated development effort has been to decrease sulfur and toxicity levels in the pitch systems and air reactivity in the carbon anodes.

V. 1996 ACTIONS

- A. Develop laboratory anode testing to accurately predict air reactivity for different binder systems.
- B. Control sulfur to a maximum of 1.0% in both Type A and B pitches.
- C. Develop Type B pitches with a 60-80% reduction in toxicity from typical coal tar pitches.
- D. Continue development of improved coal-tar/petro pitch properties
- E. Expand production scale testing to provide customer confidence in use of coal-tar/petro pitches.

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