**EVALUATION OF PITCHES AND COKES
FROM SOLVENT-EXTRACTED
COAL MATERIALS**

FINAL REPORT

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I. SUMMARY

Three initial coal-extracted (C-E) samples were received from the West Virginia University (WVU) Chemical Engineering Department. Two samples had been hydrogenated to obtain pitches that satisfy rheological requirements. One of the hydrogenated (HC-E) samples had been extracted by toluene to remove ash and higher molecular weight aromatic compounds.

We were unable to measure the softening point and viscosity of the non-hydro treated solid extract sample. Positive characteristics in the HC-E materials were softening points of 113-119°C, low sulfur and ash. The oxygen and nitrogen content of the HC-E samples may limit future usage in premium carbon and graphite products. Coking values were similar to petroleum pitches.

Laboratory anode testing indicates that in combination with standard coal-tar pitch, the HC-E material can be used as a binder pitch.

II. INTRODUCTION

The closure of by-product coal coking oven batteries has resulted in up to a 3% per annum reduction in domestic coal-tar production during the middle of the 1990's. This source reduction has affected industrial capability to produce quantities of quality of binder and impregnating pitches used in the aluminum and commercial carbon and graphite industries. The objectives of this research are to develop dependable domestic coal-based raw materials for the production of: binder pitches for aluminum cell anodes and commercial carbon and graphite products; impregnating pitches for commercial carbon and graphite products and specialty materials; oils for wood treatment and carbon black production; and metallurgical and foundry grade cokes.

We reviewed the processing and product properties of the coal extract materials prepared by WVU. The WVU coal extraction process coupled with hydrogenation yields materials that have potential binder and impregnation application.

We performed standard characterization of small-scale extracts. This information was shared with our Carbon Products Consortium (CPC) partners (Alcoa, Amoco, Conoco, FMI, UCAR and WVU). We also formed small carbon artifacts to demonstrate the binding capability of the laboratory-extracted pitches.

Our studies are summarized in the following sections of this report.

III. EXPERIMENTAL PROCEDURES

- A. Pitch property measurement methods as measured by Koppers are listed in Table I.

Table I
Methods for Measuring Pitch Properties

Characterization	Unit	Method
Softening Point (sp)	°C	ASTM D 3104 (Mettler)
Viscosity	cP	ASTM D 5018
Toluene Insoluble (TI)	wt. %	ASTM D 4072
Quinoline Insoluble (QI)	wt. %	ASTM D 2318 or D 4746
β-Resin (β-R)	wt. %	TI - QI
Modified Conradson Carbon Coking Value (MCC)	wt. %	ASTM D 2416
Density, 25°C	g/cm ³	ASTM D 71 (Water) or D 4892 (Helium)
Ash	wt. %	ASTM D 2415
Carbon and Hydrogen	wt. %	LECO CHN Analyzer
Elemental Analysis	ppm	Atomic Absorbtion (ASTM Draft Method)
Sulfur	wt. %	LECO Sulfur Analyzer
Thermogravimetric Analysis (TGA)		UCAR, using TA Instruments Model 951 Module (10°C/min. in inert atmosphere)

B. Bench-Scale Anode Production

1. Raw Materials
 - a) Sized petroleum coke provided by a commercial aluminum smelter.
 - b) Experimental and commercial pitches.
2. Mix Design as Provided by a Commercial Smelter.
3. Forming Conditions (50 mm-diameter mold)
 - a) 185°C mixing temperature
 - b) 105°C molding
 - c) 7500 psi molding pressure
4. 1150°C Maximum Baking Temperature
 - a) 10°C/Hr 0-600°C
 - b) 25°C/Hr 600-1150°C
 - c) 13-Hour hold at 1150°C(Inert gas purge throughout baking and cooling cycle.)

C. Anode Testing

Carbon anode testing methods at Koppers are detailed and supported by established quality control procedures. Koppers is directly involved in establishing carbon testing methods in ASTM and ISO; consequently, these methods or methods-under-development are used wherever possible. Statistical process control is used at each test station. A list of our typical testing methods with units is summarized in Table II.

Table II
Carbon Anode Property Measurements

Characterization	Unit
Apparent Density	g/cm ³
Electrical Resistivity	μΩm
Air Permeability	nPm
Compressive Strength	Mpa
Coefficient of Thermal Expansion to 300°C	10 ⁻⁶ /°C
Thermal Conductivity	W/m-°K

IV. EXPERIMENTAL RESULTS

A. Initial WVU Coal Extract Sample Study

Three initial coal-extracted samples were received from WVU. The first extract sample was hydro-treated to form Sample No. 2. Sample No. 3 represents the toluene-extract from Sample No. 2. Our analyses are summarized in Table III.

Table III**Analyses of Three Coal Extract Samples from WVU**

Sample No.	1	2	3
	Solvent Extracted Residue from Coal	Hydrogenated Sample 1	Toluene-Extracted Material from Sample 2
SP, °C	Not Analyzed	119.2	112.8
TI, wt. %	92.7	11.5	1.3
QI, wt. %	2.4	0.5	0.02
β -R, wt. %	90.3	11.0	1.28
Density (25°C) g/cm ³	1.272	1.206	1.217
Ash, wt. %	.25	0.07	0.0
MCC, wt. %	NA	50.7	44.8
C/H, wt. %	1.35	1.31	1.23
C, wt. %	89.97	89.57	88.84
H, wt. %	5.88	5.72	6.04
N, wt. %	2.09	2.04	1.72
O, wt. %	1.32	2.06	2.67
S, wt. %	0.74	0.37	0.42
Viscosity, cps:			
@150°C	Not Analyzed	12,160	2395
@160°C	Not Analyzed	2,430	909
@180°C	Not Analyzed	430	209
@200°C	Not Analyzed	150	72

Sample Nos. 2 and 3 have softening points and viscosities that will enable use as binders or impregnants. The sulfur, ash and QI are sufficiently low for use as an impregnant. The coking value reflects the low QI levels and aromaticity. The oxygen and nitrogen levels are higher than desirable; however, these levels are lower than in most mild gasification pitch type materials.

The TGA data in Figures 1 and 2 were measured by our CPC partner, UCAR. These results are similar to earlier samples produced at WVU for a UCAR study.¹ This illustrates repeatable bench-scale production at WVU.

B. Bench-Scale Anode Study

Because we only had about 500 grams each of the HC-E pitches, it was decided to perform a limited bench-scale anode forming study. We used 110°C sp coal-tar pitch (P-1) and petroleum pitch (P-2) as controls. The primary trial pitch was the No. 2 HC-E 119°C sp sample and was labeled P-3.

In order to explore an alternate approach of the trial material, a 20% HC-E P-3 pitch blend was made with the standard coal-tar pitch. The analyses of the control and trial binder pitches are compared in Table IV. With the 20/80 P-4 blend we have achieved typical binder pitch properties.

Following the guidelines outlined in the Experimental Procedure Section, 50 mm diameter x ~120 mm anodes were formed with the four pitches. Because this was new molding equipment, optimum binder levels were unknown. The trial pitch quantities only permitted the forming of a single anode at each different binder level. Two anodes were formed at each binder level for the control pitches.

The baked carbon test data are summarized in Table V and Figures 3-9. The optimum binder may have been obtained for the petroleum pitch via the 15-16% range; however, the other three pitches require more anode forming at higher percentage levels. The baked density and other properties show that more work is required to complete this study. The property trends provide encouragement for additional larger-scale anode evaluations.

¹I. C. Lewis, R. T. Lewis and H. K. Mayer, "Coal Precursors for Production of Carbon and Graphite Products - Final Report" Subcontract 62X-SR928C, WBS Element - UCAR-3, April 8, 1996.

Sample: R95-1498 (D057-2)

A96-00891

TGA

File: C: 96030401A.03

Size: 25.3470 mg

Operator: gfl

Method: 10C/MIN

Run Date: 5-Mar-96 12:56

Comment: ARGON 100CC/MIN Pt PAN TGA #5904

Sample: R95-1499 (D057-3)

A96-00892 TGA

File: C: 96030401B.02

Size: 25.1250 mg

Operator: gfl

Method: 10C/MIN

Run Date: 5-Mar-96 08:27

Comment: ARGON 100CC/MIN Pt PAN TGA #5904

Table IV

**Analyses of Pitches Evaluated in 50 mm
Diameter Molded Anodes**

Number	P-1	P-2	P-3	P-4
Type	Coal Tar Standard	Petroleum Standard	Hydrogenated Coal-Extract	20% P-3 80% P-1
SP, °C	111.6	112.0	119.2	114.5
TI, wt. %	30.3	3.2	11.5	26.5
QI, wt. %	14.7	0.1	0.5	11.9
β -R, wt. %	15.6	3.1	11.0	14.6
MCC, wt. %	57.8	46.9	50.7	57.3
Density, g/cm ³	1.33	1.22	1.21	1.31
Ash, wt. %	0.24	0.03	0.07	0.20

Table V**Control and Trial Pitch Baked Anode Characterization**

Sample No.*	Core GAD (g/cc)	Core Baked Apparent Density (g/cc)	E.R. ($\mu\Omega\text{m}$)	Air Perm. (nPm)	Crush Strength (Mpa)	CTE Avg. Alpha (E-6/ $^{\circ}\text{C}$ @ 300 $^{\circ}\text{C}$)	Thermal Conductivity (W/m- $^{\circ}\text{K}$)	In-Situ Coking Value (wt. %)
P-1-13	1.556	1.501	97.9	4.82	16.44	3.996	1.86	63.1
P-1-14	1.626	1.553	67.1	1.09	33.59	3.655	2.27	57.5
P-1-15	1.613	1.538	74.2	2.22	26.31	3.976	2.20	61.8
P-1-16	1.633	1.561	65.7	1.56	34.40	3.877	2.23	62.6
P-1-17	1.659	1.571	61.7	0.55	40.92	3.865	2.37	62.4
P-2-13	1.603	1.511	77.6	1.65	22.83	3.845	2.23	50.6
P-2-14	1.621	1.527	71.0	1.45	26.32	3.830	2.15	51.9
P-2-15	1.643	1.540	65.7	0.89	28.87	3.816	2.33	53.6
P-2-16	1.648	1.535	62.5	1.31	28.89	3.738	2.29	52.7
P-3-14	1.553	1.480	89.3	8.38	12.94	3.616	2.02	59.9
P-3-15	1.581	1.498	85.2	9.05	14.22	3.938	1.96	57.2
P-4-15	1.588	1.502	82.3	4.82	18.49	3.926	2.03	60.1
P-4-16	1.625	1.538	69.6	1.31	27.69	4.189	2.25	60.7

*Sample No. shows the pitch type and the binder level in percent.
The two control pitch sample Nos. (P-1 and P-2) are the average of two 50 mm diameter anodes. The trial pitch samples (P-3 and P-4) are single anodes.

V. CONCLUSIONS

- The HC-E pitches have softening points and viscosities that will enable application as binders or impregnants. The low insolubles assure impregnating capability.
- An increase in coking value and a decrease in oxygen and nitrogen contents in the HC-E pitches are required for binder and impregnant applications.
- Because of insufficient sample, only two binder levels (14 and 15%) were investigated for the HC-E experimental pitch in the bench-scale anodes; consequently, the optimum anode binder level could not be determined. Nonetheless, preliminary results are promising.
- The quantity of 20% of HC-E pitch blended with 80% of standard coal tar pitch also only permitted two binder levels (15 and 16%); again, the optimum binder level was not obtained. The performance of the blend pitch is projected to be almost as good as 100% coal tar pitch.

VI. RECOMMENDATIONS FOR FUTURE WORK

- Obtain sufficient quantities of HC-E samples to enable the forming of vibrated 4-inch diameter anodes at a minimum of six binder levels.
- Larger samples will also allow preparation of several blends of HC-E pitch and coal-tar pitch for optimization study.
- Extract hydro treatment optimization as related to anode properties should be studied.
- The initial evaluation of extract and HC-E materials as feedstocks for other binders, oils and cokes should be performed.

E. R. McHenry

FIGURE 3
GREEN APPARENT DENSITY

FIGURE 4
BAKED APPARENT DENSITY

FIGURE 5

ELECTRICAL RESISTIVITY

FIGURE 6

AIR PERMEABILITY

FIGURE 7
COMPRESSIVE STRENGTH

FIGURE 8
COEFFICIENT OF THERMAL EXPANSION

FIGURE 9
THERMAL CONDUCTIVITY

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