

## PREPARATION OF CARBON METALLURGICAL ELECTRODES FROM LOW-TEMPERATURE LIGNITE COKE AND LIGNITE PITCH BINDER

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### INTRODUCTION

Low-temperature carbonization of coal produces char and coal tar. Char is potentially useful as powerplant fuel, as smokeless fuel for domestic uses, for synthesis gas production, and for blending with other coals to make metallurgical coke. Low-temperature tar is a potential source of organic chemicals and other products, including materials for making carbon electrodes. Large quantities of carbon in the form of petroleum coke are used to make carbon electrodes for the aluminum, steel, electrochemical, and electrothermal industries.

Two methods were developed for producing carbon electrodes from low-temperature lignite tar. Electrodes were then made by these methods and evaluated by comparing their properties and performance with those of commercial grade electrodes. This paper presents preliminary results of the comparison.

### ELECTRODE PRODUCTION AND SPECIFICATIONS

Carbon and graphite manufacture was developed by the end of the 18th and the beginning of the 19th century. The earliest use of carbon in an electrical application is attributed to Sir Humphrey Davy in 1800. His carbon material was charcoal. The need for stronger carbon materials, which could resist heat and have higher electrical conductivity, enhanced the carbon industry for its manufacture. The first baked carbon composition from coke, lampblack, and sugar syrup, is credited to a French scientist, Carré, in 1876. The graphite industry started 20 years later, in 1896, with the development of the resistance type electric furnaces.

Carbon electrodes for metallurgical purposes today are made by mixing petroleum coke, graphite, anthracite, or coal with a coal pitch, placing the mix in a mold, then baking for about 24 hours to about 2,000° F. Baking converts the pitch into coke which serves as a binding skeleton between filler particles, resulting in a strong finished product (7). Theoretically, about 0.3 ton of carbon is required to produce a ton of aluminum, however in practice about 0.6 ton of carbon of which 0.2 ton is pitch is required (3, 8, 11). About 400,000 tons of coal tar pitch is used annually in the United States for aluminum production. The U. S. market for carbon electrodes is about 2.5 million tons per year.

The characteristics of the coal tar pitch determine the stability and tensile strength of finished electrodes (5). The amount of binding coke formed during the baking operation depends to a large extent on the percentage of medium molecular weight tar resins contained in the coal pitch. The higher the amount of these resins in the pitch binder, the greater will be the binding effect. Alpha resins contained in pitch have high molecular weight, however, and do not enhance

binding of the electrodes; therefore their content in the pitch should be as low as possible. Contrarily, the beta resins, being in colloidal form in the pitch, have a great binding power, so their content in the electrode pitch binder should be as high as possible. Since the value of the resins is determined by its free carbon, the free carbon characterizing the total pitch unity should be as high as possible. The pitch binder coke produced during baking is an all-important factor in bonding coke aggregate particles into an overall structure possessing high compressive strength, high apparent density, and low electrical resistivity. A good pitch binder should have a carbon-hydrogen ratio of 1.20 to 1.80, ash content less than 1%, softening point of about 105° to 120° C, and coking value of at least 60% (9). For many purposes, a density approaching the theoretical maximum of 2.6 g/cc is highly desirable, yet in practice it is difficult to exceed 2.0 g/cc (4, 6, 10).

### EXPERIMENTAL EQUIPMENT AND PROCEDURE

Materials used to produce electrodes in this investigation were derived from low-temperature lignite tar except for the petroleum coke and bituminous binder. The latter two were obtained from commercial suppliers.

Coke and binder for the electrodes were obtained from low-temperature lignite pitch by two methods--thermal cracking (1) and delayed coking (2). Both thermal cracking and delayed coking produce an oily liquid and coke. The liquid is distilled into a distillate and a residue. The residue shows suitable specifications for use as an electrode binder. Coke from both processes is leached, calcined, and screened for electrode aggregate as shown in Figure 1.

Coke is leached by digesting it in a 50% hydrochloric acid solution for 2 hours. After filtration and washing until neutral, the leached coke is dried at 212° F and then calcined for 12 hours in nitrogen atmosphere at 2,500° F. Calcination of green coke is necessary for several reasons. First, the green coke when ground cannot be bound together to give a proper density. Second, electrodes are difficult to mold or extrude from green coke. Third, the electrodes give off volatile matter during baking, thus resulting in a very porous electrode. Finally, electrodes are poor conductors and have a high resistivity when made from green coke. The green and leached coke, both calcined at 2,500° F, were analyzed for iron, sulfur, ash content, and electrical resistivity.

Two systems were used for making electrical resistivity measurements. A Wheatstone bridge galvanometer was capable of measuring 0.001 ohm. The other system (Figure 2) impresses a 2 ampere current through the electrode and then measures the voltage drop across a 2.01 inch length. From this measurement and the diameter, the electrical resistivity is calculated.

The preparation of test electrodes involves making the green mix (or paste), molding, and baking. The pitch is placed in an oil heated sigma-blade mixer which has been preheated to about 300° F. After the pitch has melted, the mixer is started and different size coke fractions are added one at a time, starting with the largest size (minus 10 plus 20 mesh). About 5 minutes is allowed between the addition of each size fraction (the timing of the addition is recorded) to assure wetting of the coke by the binder. When the mixing of the paste is completed, it is transferred still hot to the molds, which have been preheated to about 250° F. The paste is tamped into stainless-steel molds and pressed. At first graphite

molds were used, but later stainless-steel molds were found more practical. Two sizes of molds were used, 1-1/4 inches diameter by 5 inches long and 1-3/4 inches diameter by 5 inches long. The larger electrodes were required for use in the metallurgical reduction cell.

The upper one-half inch of the mold is filled with powdered dry coke and the molds are placed in the baking jig. The jig is then placed in a crucible type furnace and baked (in a nitrogen atmosphere) to 1,850° F at a heating rate of 90° F per hour.

After baking, the electrodes are allowed to cool in the furnace for 24 hours and then removed for testing. The density is determined by carefully measuring a section of the electrode and then weighing it. The resistivity and strength of the section are then measured and the remains are used for the reactivity test. The electrodes were also evaluated in an electrical reduction cell used for reduction of alumina.

## RESULTS AND DISCUSSION

**Calcination.** A study on the effect of calcination of coke at different temperatures on the electrical resistivity and density gave interesting results, as shown in Table 1. Calcination causes shrinkage with the expulsion of volatile matter and effects an increase in the specific gravity or real density of the electrode. The photomicrographs (Figure 3) compare the appearance of coke particles after calcination at increasing temperatures from 1,850° to 4,800° F. The particles calcined at 1,850°, 2,500°, and 3,000° F show little change in appearance from the original coke. At 3,175° F the appearance begins to change from the asymmetric oblong grains to the irregular grains with rough edges that are highly branched and are the predominant shapes of the particles calcined at 4,800° F.

Table 2 shows the analytical differences between the green and the leached coke, which influence the qualitative specifications of a carbon electrode. The green coke showed a much higher electrical resistivity and iron content than the leached coke.

**Product Specifications.** When a coke is mixed with a binder and the mix extruded or molded, a structure is formed that is similar in many aspects to a compressed powder. During the mixing of the pitch with the coke, the degree of wetting is of considerable importance, because it is desirable to obtain nonporous and very compact electrodes of low specific resistivity, high compressive strength, low reactivity, and low ash and sulfur content. Low electrical resistivity avoids waste of electric power, which is one of the largest costs in electrolytic processes. High compressive strength requires that the electrodes be sturdy when subjected to tension, compression, and shear and twist; otherwise they fail, disrupting furnace and cell operation and increasing overall cost. High reactivity destroys the electrodes by oxidation. Some elements in the ash, for example, iron, vanadium, boron, and alkalis, by acting as catalysts, can affect the reactivity of the electrode with certain gases present during operations. Ash is especially undesirable in electrolytic operations that use consumable electrodes, since the ash can contaminate electrolyte and, in some operations, can be reduced and contaminate the product. For applications where these conditions apply, the ash content of binder pitches and electrode aggregates should be as low as possible. A high

sulfur content in pitches used for electrodes can contribute to the formation of a layer of iron sulfide on the metallic contact pins, thus changing the electrical resistance at the interface. Sulfur can have harmful effects on carbon products during graphitization. The fumes of sulfur are also objectionable. The sulfur content of most coal tar pitches ranges from 0.35 to 0.50 percent.

The pitch binder has a tendency to penetrate deep into the voids of the coke aggregate. Photographs of the electrode sections (Figure 4) show the poor condition that occurs inside some of the electrodes and serve as the first step in photomicrographic studies to determine wetting of the coke by the binder and the quality of calcination during the baking cycle. All the electrodes shown in Fig. 4 were made with about the same amount of binder, except the one labeled "thermally cracked lignite binder," having 25% of binder. The preferred weight-percentage of low-temperature lignite pitch binder for the green mix was found to be 25 to 27%, varying in relation to the density of the calcined coke. The higher the calcination temperature, the higher is the density of the coke, as shown in Table 1, consequently the amount of binder should be proportionately increased to avoid higher porosity of an electrode.

Calcined coke prepared by thermal cracking of lignite is compared with petroleum coke in Figure 5. The coke particles differ, lignite particles being much more angular in appearance than the petroleum particles that have a more uniformly rounded appearance. The wetting property of the binder is of equal value using both cokes. The finished baked electrodes using lignite coke have more and larger void spaces than the ones using petroleum coke. Sections of coke particles exposed in the baked electrode show the lignite coke to be denser in appearance with thicker cell walls, whereas the petroleum coke has a more striated appearance in section.

Electrodes having about  $400 \text{ kg/cm}^2$  of compressive strength and  $0.007$  to  $0.009 \text{ ohm/cm}^3$  of electrical resistivity, Table 3, have been prepared totally from materials derived from lignite tar.

The characteristics of the binder pitch are given in Table 4. The better electrodes were prepared with a binder content less than 27%, and a binder having a hydrogen content less than 5%. The effect of the coking value and the benzene- and quinoline-insoluble contents are completely overshadowed by the large variation in binder percent in the electrodes.

Product Evaluation. Results of tests performed on our electrodes at the College Park Metallurgy Research Center showed that the surface of anodes prepared from our electrodes, Figure 6, after electrolysis were very similar to anodes made from commercial materials. The surfaces were uniformly eroded and the electrolyte covers the entire surface, indicating good wettability.

## CONCLUSIONS

Results of replacing petroleum coke with lignite coke to produce an entire lignite electrode were very encouraging. Lignite coke produced from thermal cracking and delayed coking of lignite pitch was calcined at  $2,500^\circ \text{ F}$  in a nitrogen atmosphere. This coke, after being calcined to  $2,500^\circ \text{ F}$ , showed a density of  $1.96 \text{ g/cc}$  and an electrical resistivity of  $0.045 \text{ ohm/in}^3$ .

Evaluation of electrodes (prepared from lignite coke and lignite binder) in an alumina reduction cell, showed them to be more susceptible to the Boudouard reaction ( $C + CO_2 \longrightarrow 2CO$ ) than electrodes made from bituminous binder and petroleum coke, resulting in higher anode consumption. However, electrodes with higher compressive strength and higher densities were found to be less reactive.

Many factors affect the characteristics of electrodes, and it is difficult to isolate any one factor as being most important in regard to performance of electrodes in reduction cells. However, two factors seem to be involved more than others noted. Coke that had been calcined to 3,175° F, as opposed to the usual 2,500° F, performed best in a reduction cell. Also, binder with a hydrogen content of less than 5 percent gave a higher compressive strength and lower porosity.

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#### REFERENCES

1. Berber, John S., Richard L. Rice, and Delmar R. Fortney. Thermal Cracking of Low-Temperature Lignite Pitch. *Ind. Eng. Chem., Prod. Res. Develop.*, v. 6, No. 3, September 1967, pp. 197-200.
2. Berber, John S., Richard L. Rice, and Robert E. Lynch. Delayed Coking of Low-Temperature Lignite Pitch. *Preprints, Am. Chem. Soc., Div. of Fuel Chem.*, v. 12, No. 2, March 31-April 5, 1968, pp. 47-55.
3. Domitrovic, R. W., R. M. Stickel, and F. A. Smith. Rapid Test Method for the Determination of the Benzene- and Quinoline-Insoluble Content of Pitches. *Symp. on Tars, Pitches and Asphalts. Preprints, Am. Chem. Soc., Div. of Fuel Chem.*, Sept. 9-14, 1962, pp. 54-64.
4. Hoiberg, Arnold J., ed. *Bituminous Materials, Asphalts, Tars and Pitches. Vol. III, Coal Tars and Pitches.* Interscience Publishers, New York, 1966, 585 pp.
5. Jones, H. L., Jr., A. W. Simon, and M. H. Wilt. A Laboratory Evaluation of Pitch Binders Using Compressive Strength of Test Electrodes. *J. Chem. Eng. Data*, v. 5, No. 1, January 1960, pp. 84-87.
6. Kuvakin, M. A., and N. D. Bogomolova. New Types of Coke for Carbon Electrodes. *Coke Chem. (USSR) (English Transl.)*, No. 12, 1965, pp. 23-28.

7. Lauer, G. G., and K. P. Bonstedt. Factors Influencing the Performance of Pitch Binders in the Baking of Small Carbon Electrodes. *Carbon*, v. 1, No. 2, February 1964, pp. 165-169.
8. Martin, S. W., and H. W. Nelson. Carbon Materials Required in Electrolytic Reduction of Alumina. *J. Metals*, v. 7, No. 4, April 1955, pp. 540-543.
9. Morgan, M. S., W. H. Schlag, and M. H. Wilt. Surface Properties of the Quinoline-Insoluble Fraction of Coal-Tar Pitch. *J. Chem. Eng. Data*, v. 5, No. 1, January 1960, pp. 81-84.
10. Stepanenko, M. A., N. I. Matusyak, A. T. Movchan, and P. L. Saltan. Electrode Pitch Manufacture by Thermal Treatment. *Coke Chem. (USSR) (English Transl.)*, No. 12, 1965, pp. 20-23.
11. Thomas, B. E. A. Electrode Pitch. *Gas World*, v. 151, No. 3946, Coking Suppl., v. 56, No. 564, April 2, 1960, pp. 51-64, 66.

TABLE 1. - Electrical resistivity and density of coke at different calcination temperatures

Calcination temp., °F	Resistivity, ohm/in <sup>3</sup>	Density, g/cc
1,850	0.0940	1.83
2,200	0.0640	1.95
2,500	0.0450	1.96
3,000	0.0081	1.97
3,175	0.0075	1.97
4,800	0.0053	2.00

TABLE 2. - Analytical differences between green and leached coke

	Green	Leached
Percent:		
Ash	1.15	0.75
Iron	0.11	0.03
Sulfur	0.82	0.83
Resistivity, ohm/in <sup>3</sup>	0.051	0.035
Calcination temperature, °F	2,500	2,500

TABLE 3. - Properties of electrodes from coke produced by delayed coking and thermal cracking

Batch No.	Coke			Electrodes		
	Method	Calcining temp., °F	Resistivity, ohm-cm	Resistivity, ohm-cm	Strength, kg/cm <sup>2</sup>	Density, g/cc
87	Delayed	2,000	0.163	0.013	284	1.31
89	do.	2,500	0.122	0.010	363	1.32
105	do.	2,500	0.122	0.011	258	1.36
106	do.	2,500	0.122	0.0088	315	1.43
90	Cracked	2,500	0.089	0.012	274	1.23
92	do.	2,500	0.089	0.011	321	1.37
93	do.	2,500	0.089	0.012	208	1.25
95	do.	2,500	0.089	0.013	205	1.22
100	do.	2,500	0.089	0.012	225	1.27
111	do.	2,500	0.089	0.0080	393	1.45
113	do.	2,500	0.089	0.0070	413	1.46
101	do.	3,175	0.038	0.0052	237	1.47
94	Petroleum <sup>1</sup>	Unknown	0.088	0.0087	254	1.28

<sup>1</sup> Coke obtained from a commercial supplier. Lignite pitch used as binder.

TABLE 4. - Characteristics of pitch binder from lignite

Batch No. EB	Processing conditions			Characteristics of binder						
	Coking method	Binder, pct	Softening point, °C	Carbon, wt pct	Hydrogen, wt pct	C-H ratio	Coking value	Benzene insolubles, pct	Quinoline insolubles, pct	
106	Delayed	26.3	106	88.16	5.20	1.41	60.5	27.9	20.1	
105	do.	27.6	106	88.16	5.20	1.41	60.5	27.9	20.1	
113	Cracked	25.5	105	89.17	4.89	1.51	58.0	36.7	25.1	
111	do.	26.0	105	89.17	4.89	1.51	58.0	36.7	25.1	
89	do.	28.0	110	88.25	4.72	1.56	61.5	39.9	23.7	
90	do.	28.0	118	89.09	4.94	1.50	61.4	51.4	16.8	
102	do.	28.0	110	88.73	5.14	1.44	70.1	29.9	15.6	
95	do.	29.0	106	86.90	5.98	1.21	49.8	38.2	10.7	
87	do.	30.0	110	82.25	4.72	1.56	61.5	39.9	23.7	
93	do.	30.0	106	86.90	5.98	1.21	49.8	38.2	10.7	
94	do.	30.0	106	86.90	5.98	1.21	49.8	38.2	10.7	
101	do.	30.0	112	90.89	5.04	1.50	67.3	34.0	25.2	

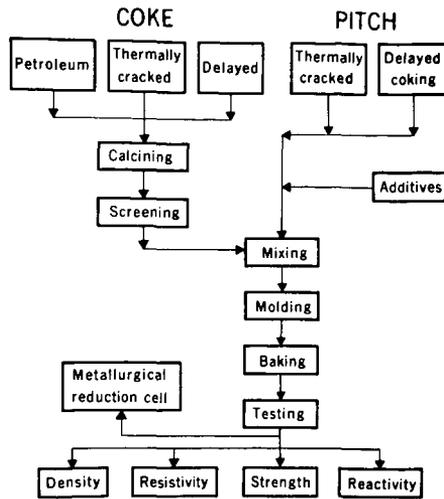


FIGURE 1. - Flowsheet for preparation of coke and pitch for carbon electrodes.

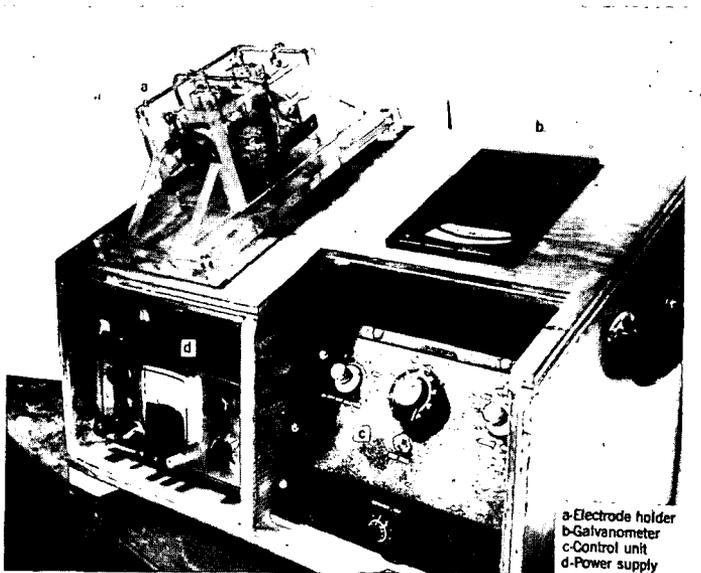


FIGURE 2. - Electrical resistivity apparatus.

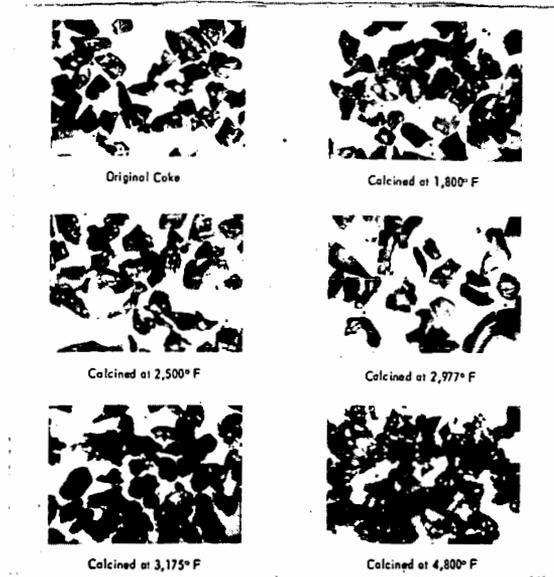


FIGURE 3. - Coke from low-temperature lignite pitch calcined at 1,800° to 4,800° F (X 50).

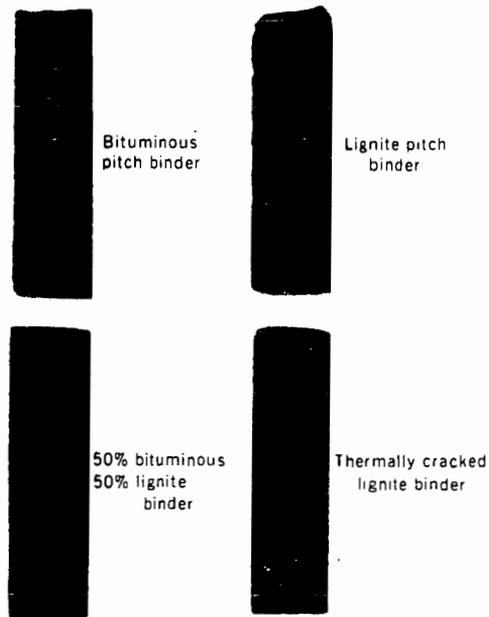


FIGURE 4. - Longitudinal cuts of electrodes from bituminous and lignite binders.

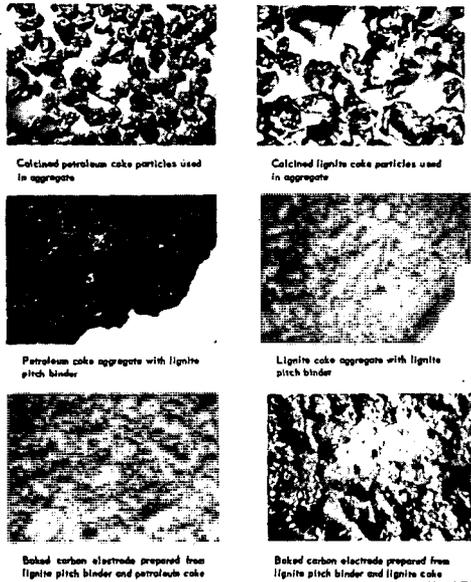
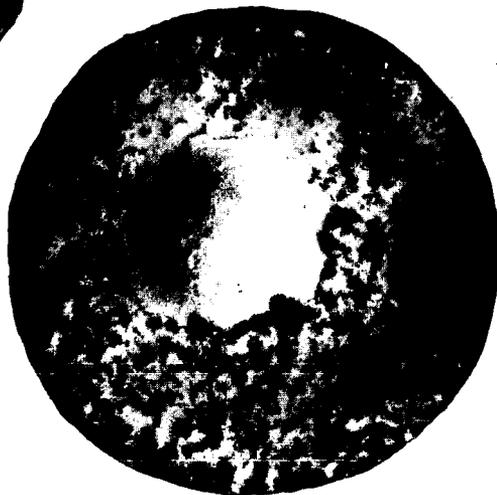


FIGURE 5. - Photomicrographs of carbon electrodes and their components (X 30).



Anode B-11-0 2.2x magnification.

1. Anode B-111 2.2x magnification.



3. Anode B-113-0 2.2x magnification.

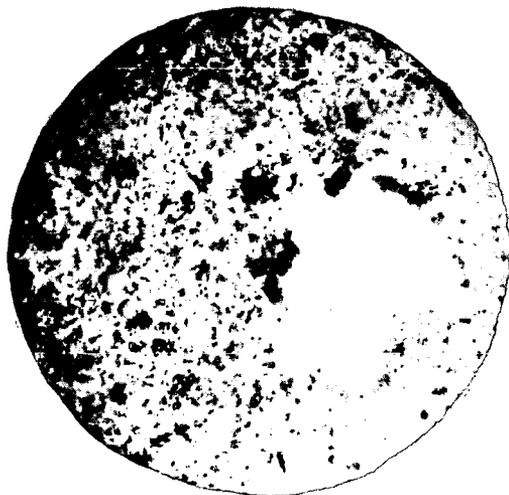


FIGURE 6. - Anodes, machined from electrodes prepared from low-temperature lignite coke and lignite pitch binder, after use in an alumina reduction cell.