

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

John S. Berber and Richard L. Rice

U. S. Department of the Interior, Bureau of Mines,
Morgantown Coal Research Center, Morgantown, West Virginia 26505

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 kg/cm^2 of compressive strength and 0.007 to 0.009 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 g/cc and an electrical resistivity of 0.045 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.

ACKNOWLEDGMENTS

Appreciation is expressed to: Dr. V. L. Bullough, Director, Applied Research, Reynolds Metals Company, and Mr. J. J. McGahan, Manager, Development Department, The Carborandum Company, for their advice and help in high-temperature calcination of our lignite coke; Dr. T. Henrie, Research Director, Reno Metallurgy Center, Dr. D. Schlain, Project Coordinator, and Mr. V. A. Cammarota, Jr., Project Leader, of the College Park Metallurgy Research Center, for their help in evaluating our electrodes.

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 ³	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 ³	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 ²	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 ¹	Unknown	0.088	0.0087	254	1.28

¹ 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	

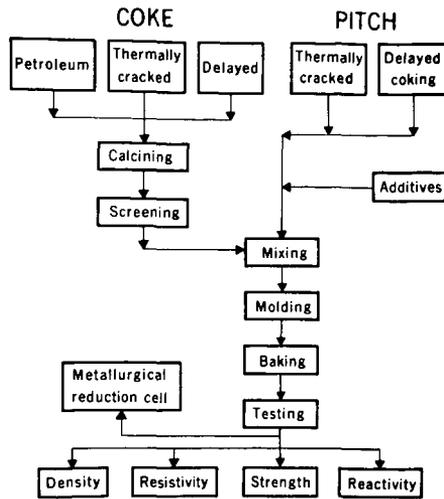


FIGURE 1. - Flowsheet for preparation of coke and pitch for carbon electrodes.

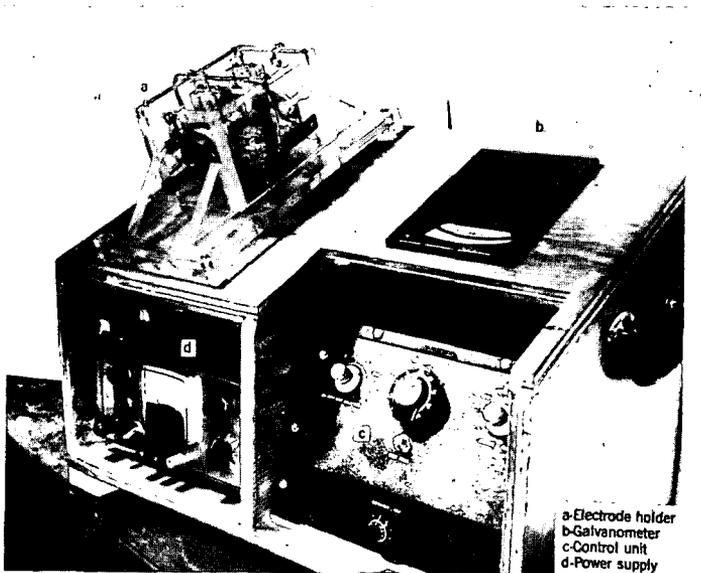


FIGURE 2. - Electrical resistivity apparatus.

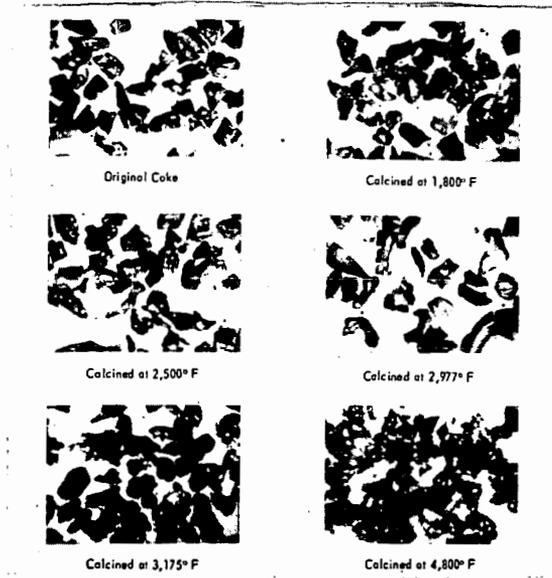


FIGURE 3. - Coke from low-temperature lignite pitch calcined at 1,800° to 4,800° F (X 50).

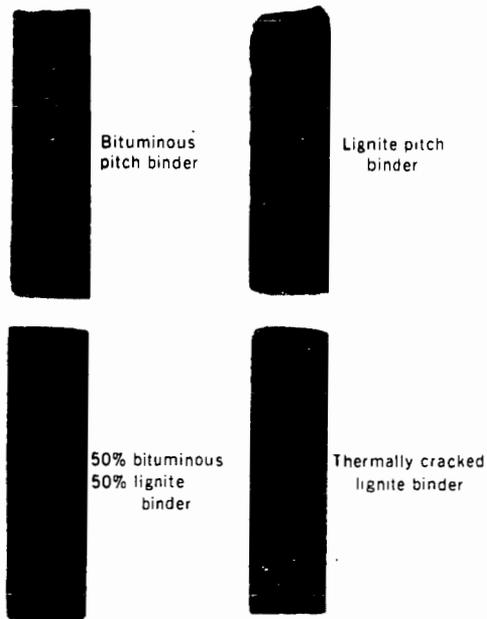


FIGURE 4. - Longitudinal cuts of electrodes from bituminous and lignite binders.

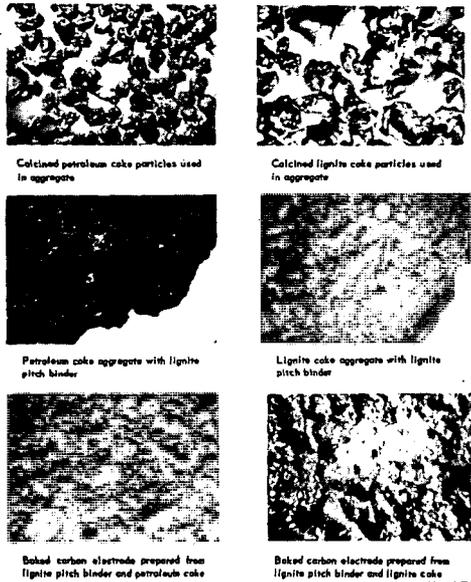
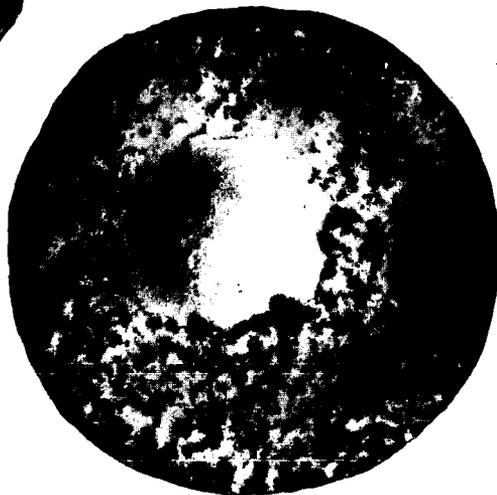


FIGURE 5. - Photomicrographs of carbon electrodes and their components (X 30).



Anode B-11-0 2.2x magnification.

1. Anode B-111 2.2x magnification.



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

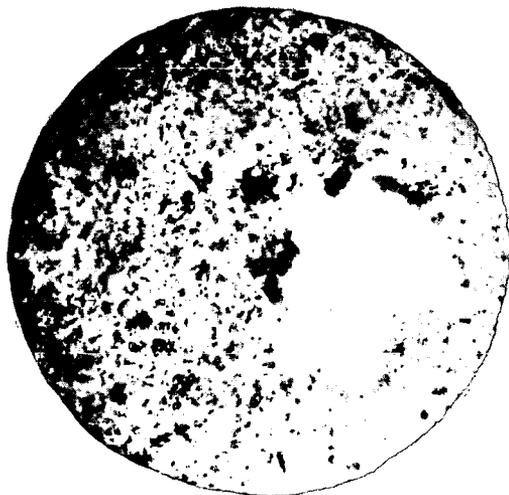


FIGURE 6. - Anodes, machined from electrodes prepared from low-temperature lignite coke and lignite pitch binder, after use in an alumina reduction cell.

THE EFFECT OF PITCH QUINOLINE INSOLUBLES
ON GRAPHITE PROPERTIES

James Jerauld Ferritto

Airco Speer
A Division of Air Reduction Co., Inc.
Electrode & Anode Development Dept.
Niagara Falls, New York 14302

Joseph Weiler

Allied Chemical Company
Plastics Division
Edgewater, New Jersey

INTRODUCTION

For several years Airco Speer has been working with raw materials suppliers in order to characterize or better define these raw materials, in terms of their effects on final graphite properties. In particular, Airco Speer's work with Allied Chemical Company, a major pitch supplier, was directed toward the development of a better electrode binder, through a clearer definition of their process parameters (such as column atmospheres, distillation temperatures, tar sources and other feed stream variables), as they affect pitch characteristics, hence, graphite properties.

Of the many pitch characteristics specified by the graphite electrode industry,^{1,2,3} the Q.I. content was chosen the subject of this investigation. The Q.I.'s consist primarily of solid particles^{4,5,6} ranging in size from colloidal to coarse⁷. The colloidal particles are mostly complex hydrocarbons of high molecular weight. They are derived from the decomposition of coal directly or may be derived indirectly from the condensation and dehydrogenation of small aromatic molecules coming from the coal. The coarse particles can be any insoluble "dirt", such as coal or coke dust. The function of the Q.I. is to provide sites for crystallite growth (nucleation) during carbonization or graphitization.⁸

Many investigators feel that the Q.I. of coal tar pitch is important in determining graphite quality.^{9,10} It is known, for example, that the higher the Q.I., the higher will be the graphite strength, density and conductivity. However, Q.I. levels of over 16 to 18% generally have no beneficial effect and, in fact, may be detrimental. Not as well known, but perhaps more important, is the type of Q.I., vis., the process parameters by which certain levels are attained, affect not only those levels, but also the nature of the Q.I., and, consequently, may affect the nature of the graphite.

EXPERIMENTAL

After managerial approval of both Companies, the basic plan was formulated. A 3 x 4 factorial-type experiment was proposed in which Allied would process one low (~5%) Q.I. tar by filtration, distillation, two heat treatments, addition of Thermax (a thermostatically decomposed "black") and blending. Four different pitches would initially be made. Each would be modified by the processes described,

to contain three levels of Q.I. --about 7, 14 and 21%. Twelve (12) pitches in all would result.

In the preparation of the raw materials and the blend components (Figure 1), the starting material was feed Tar "A", with a low (5%) Q.I. This tar was filtered to yield low (4%) Q.I. Pitch "Z". This, in turn, was used as the blending pitch for Processes I through IV. The residue from feed Tar "A" was used to make the high (12%) Q.I. Tar "B", which was used as the raw material in Processes I and II.

In the preparation of natural Q.I. pitches (Process I), the high Q.I. Tar "B" was distilled (Figure 2) to yield a high Q.I. Pitch "Y", raising the Q.I. from 12 to about 21%. This pitch was blended with low Q.I. Pitch "Z" to give Pitches "X" and "W", thus lowering the Q.I. to about 7 and 14%, respectively.

The pitches in Process II were produced from the high Q.I. Tar "B" in Process I (Figure 3). This pitch was distilled to yield Pitch "U", with a Q.I. of 21%. As in Process I, this pitch was blended with low Q.I. Pitch "Z" to give Pitches "T" and "S", again, lowering the Q.I. to 7 and 14%, respectively.

The high Q.I. tar from Experimental Process II was used in preparing the pitches in Process III (Figure 4). This tar was distilled to yield Pitch "P", with a Q.I. of about 21%. Pitch "P" was blended with Pitch "Z" to give Pitches "Q" and "N", with Q.I. 's of 7 and 14%, respectively.

Process IV pitches were prepared by starting with one of the original raw materials, low Q.I. Tar "C", which was feed Tar "A" with the insolubles removed by filtration. The low Q.I. Tar "C" then had Thermax dispersed in it, thus raising the Q.I. from 2 to about 12% (Figure 5), resulting in high Q.I. Tar "E". By distillation, the Q.I. was increased to about 21% and was now called Pitch "M". The Q.I. content of Pitch "M" was lowered to 7 and 14%, by blending with Pitch "Z" to yield Pitches "L" and "K", respectively.

The characteristics of all these pitches, as received by Airco Speer, is shown in Table 1. Since Allied used new or modified polymerization techniques, it proved difficult to make some of the pitches with specific Q.I. values. In particular, Pitch "P" was considerably lower in Q.I. than predicted. To be consistent with their process scheme, it would have been economically impractical or technically impossible for them to change their processing to raise the Q.I.

When Airco Speer received the pitches, they were extruded in an electrode formulation in the Pilot Plant, in five inch diameter rods. Concurrently, a control lot, using a standard binder pitch, was also extruded.

It was the intention to extrude all pitches at three binder levels, according to standard Pilot Plant operating procedures. However, Pitches "K", "M" and "P" were non-extrudable at the lower binder level. The as-formed rods were then baked to about 800 C in the Pilot Plant furnace, then graphitized to about 2800 C. All stock was tested by the Chemical and Physical Measurements Group of the Research Department.

RESULTS AND DISCUSSION

Table 2 summarizes all of the pertinent graphite data and also gives the relative

Table 1

CHARACTERISTICS OF 12 ALLIED EXPERIMENTAL PITCHES

Pitch Type	Softening	Q.I.	Q.I.	Q.I.	Carbon
	Point	(Predicted)	(Airco Speer)	(Allied)	Disulfide Insoluble
	C	%	%	%	%
Y	102	21.0	20.5	20.0	34.1
W	104	14.0	14.6	14.5	32.9
X	103	7.0	9.9	8.6	29.2
M	103	21.0	20.8	21.7	38.4
K	104	14.0	15.6	15.0	34.2
L	102	7.0	9.4	8.9	28.1
U	105	21.0	17.4	18.9	37.1
S	105	14.0	13.8	12.0	33.8
T	105	7.0	9.4	7.3	29.8
P	105	21.0	12.3	10.9	35.5
N	105	14.0	10.7	9.7	32.6
Q	105	7.0	7.7	7.2	28.5

binder levels at which the formulations were extruded. Since these were electrode formulations, it is reasonable to assume that the spread in binder levels, 2 pph, can result in significant differences in graphite properties. The actual binder levels and formulations are proprietary. It should also be noted that the graphite properties are coded. Though the actual values are not represented, they do show the true, relative differences in values, which correctly shows the change in effects due to the different pitches.

A portion of the data is graphically represented in Figures 6, 7 and 8. Only the optimum values for some of the most important properties were plotted. These values are: transverse coefficient of thermal expansion (T-CTE), flexural strength and apparent density. Thus, for the T-CTE's (Figure 6), only the binder levels that resulted in the lowest CTE, were considered. Those binder levels are not necessarily the same ones that resulted in optimum flexural strengths (Figure 7) or apparent densities (Figure 8), and vice versa. In determining the suitability of a particular pitch for further evaluation, a compromise is sometimes necessary in considering which binder levels merit most attention.

On this basis, the most important process, in terms of T-CTE, is Process III. In particular, Pitch "P", at its optimum value (Figure 6), had a T-CTE of about $0.54 \times 10^{-6}/C$, which was substantially lower than the standard. However, the flexural strengths (Figure 7) were also lower, but could be increased, if required, through impregnation. It is of further interest to note that all of the T-CTE's were either lower or equivalent to the standard, with no apparent degradation of structural integrity.

Pitch "Y", from Process I, is also important, not only because of its low graphite T-CTE, but also because the flexural strengths and apparent densities (Figure 8) were at least equivalent to the standard. From the same standpoint, but to a somewhat lesser degree, Pitches Q, N and W were also important because of their low T-CTE's. Graphite strengths were equivalent to the standard.

From the longitudinal electrical resistivity data (Table 2) it can be seen that all the values were higher than the standard, with the exception of graphites from Pitches "T", "U" and possibly "L" and "N", which were about equivalent. However, even those with equivalent resistivities were no better than the standard, in terms of apparent density, flexural strength or transverse CTE.

CONCLUSION

The most significant fact to arise out of our research is that graphite physical properties, such as CTE, flexural strength, apparent density and electrical resistivity, are apparently unrelated to pitch Q.I. levels, alone, but to the nature or type of Q.I. This, in turn, is directly related to the method of preparation, i. e., process route, by which specific Q.I. levels are attained.

GRAPHITE PROPERTIES OF 12 ALLIED EXPERIMENTAL PITCHES

Pitch Type	Pitch Process	AD	Long. Resist.	Trans. Resist.	Long. CTE	Trans. CTE	FS	Binder Level
		g/cc	$\times 10^{-5}$ ohm-in	$\times 10^{-5}$ ohm-in	$\times 10^{-6}/C$	$\times 10^{-6}/C$	psi	
K	IV	1.23	7.8	18.1	0.59	1.32	499	M
K	IV	1.15	9.5	10.9	0.57	1.14	211	H
L	IV	1.17	4.9	6.2	0.57	0.99	311	L
L	IV	1.15	7.6	10.9	0.61	1.18	344	M
L	IV	1.15	8.9	13.3	0.61	1.18	309	H
M	IV	1.21	10.3	29.2	0.68	1.04	307	M
M	IV	1.19	10.5	32.2	0.61	1.04	291	H
N	III	1.12	5.0	20.6	0.49	0.83	235	L
N	III	1.10	8.5	31.8	0.58	1.13	292	M
N	III	1.12	5.4	23.2	0.53	0.94	269	H
Q	III	1.13	10.1	31.2	0.49	0.99	189	L
Q	III	1.14	9.3	22.6	0.55	1.04	202	M
Q	III	1.13	7.7	29.6	0.55	0.91	222	H
P	III	1.01	14.8	32.2	0.65	0.67	28	M
P	III	1.08	9.0	31.9	0.61	1.11	201	H
S	II	1.18	8.4	11.6	0.58	1.18	232	L
S	II	1.19	6.8	13.8	0.57	1.52	430	M
S	II	1.12	8.8	14.5	0.54	1.33	227	H
T	II	1.17	2.9	16.3	0.48	0.96	306	L
T	II	1.15	4.2	18.9	0.51	0.99	281	M
T	II	1.13	6.8	25.0	0.49	1.00	239	H
U	II	1.14	8.8	24.7	0.58	0.99	295	L
U	II	1.17	4.0	26.1	0.69	1.13	332	M
U	II	1.12	7.4	29.9	0.65	1.00	263	H
W	I	1.18	7.9	9.6	0.60	0.90	323	M
W	I	1.15	9.2	9.8	0.59	0.92	334	H
X	I	1.18	9.4	11.9	0.56	1.20	290	L
X	I	1.16	9.2	30.9	0.57	1.17	366	M
X	I	1.17	8.6	15.8	0.45	1.13	412	H
Y	I	1.19	7.1	28.5	0.66	1.11	280	L
Y	I	1.19	7.6	24.4	0.57	0.91	347	M
Y	I	1.17	7.9	24.4	0.59	1.00	245	H
Standard		1.21	2.4	16.4	0.68	1.21	375	M

Note: Binder Level--H - high, M - medium, L - low. There is a difference of 2 pph of binder (based on the weight of filler) between each binder level; thus, there is a spread of 4 pph between the highest (H) and lowest (L) level.

REFERENCES

- 1 M. B. Dell, "Characterization of Pitches for Carbon Anodes", presented before the Division of Gas and Fuel Chemistry, American Chemical Society, Urbana, Illinois (May 15 & 16, 1958).
- 2 D. McNeil and L. J. Wood, "The Use of Coal Tar Pitch as an Electrode Binder", Coal Tar Research Association, Gomersal, Leeds, Industrial Carbon and Graphite, Society of Chemical Industry, paper read at the conference in London (September 24 - 26, 1957).
- 3 P. L. Walker, Jr., C. R. Kinney, D. O. Baumbach, and M. P. Thomas, "The Relationship of the Chemical and Physical Properties of Coal Tar Pitches to Their Carbonization and Graphitization Character", Fuel Technology Department, The Pennsylvania State University, University Park, Pennsylvania.
- 4 S. J. Green and S. G. Ward, "The Insolubles Matter of Coal Tar", Journal of the Society of the Chemical Industry (London), 67, 422 (1948).
- 5 J. O'Brochta, Koppers Company, Inc., "The Composition and Properties of Coal Tar Pitches", presented April 13, 1956, at Dallas, Texas, before the Gas and Fuel Division of the American Chemical Society.
- 6 A. J. Lindsay, et al, "Polycyclic Aromatic Hydrocarbons in Carbon Blacks", Chemical and Engineering (London), pp. 1365-66 (1958).
- 7 S. S. Pollack and L. E. Alexander, Journal of Chemical Engineering Data, 5, 88 (1960).
- 8 J. Taylor and H. Brown, "Carbon Obtained from Thermal and Catalytic Cracking of Tars", Japan Carbon Conference (1964).
- 9 M. S. Morgan, W. H. Schlag, and M. H. Wilt, "Surface Properties of Quinoline Insolubles Fraction of Coal Tar Pitch", Journal of Chemical Engineering Data, 5, No. 1, pp. 81 - 84 (1960).
- 10 S. W. Martin and H. W. Nelson, Industrial Engineering Chemical, 50, 33 (1958).

FIGURE 1
 PREPARATION OF RAW MATERIAL
 AND BLEND COMPONENTS

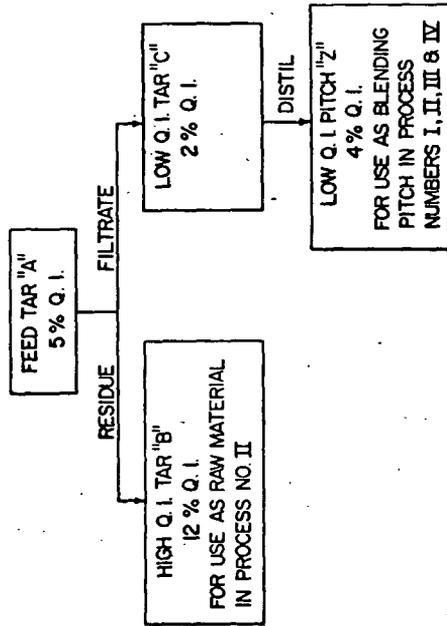


FIGURE 2
 PROCESS NO. I
 PREPARATION OF NATURAL Q. I. PITCH

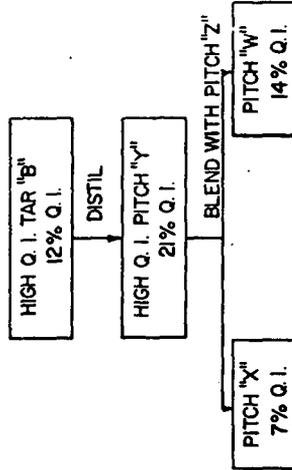


FIGURE 3
PROCESS NO. II
PREPARATION OF PITCH USING
EXPERIMENTAL PROCESS TYPE I

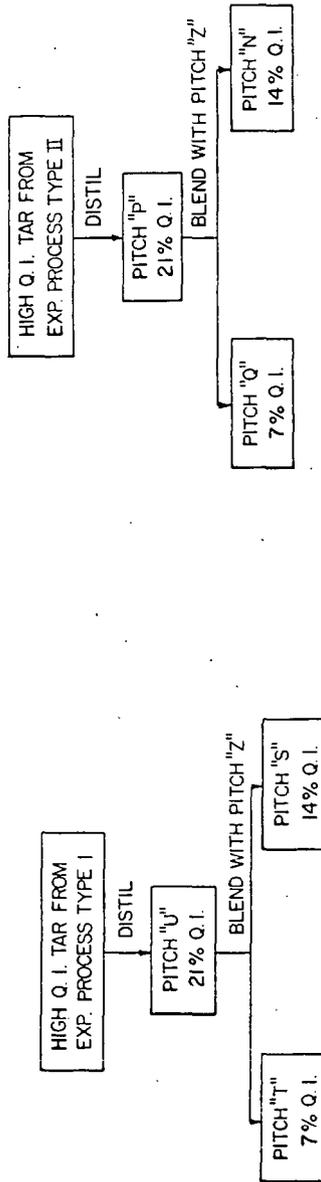
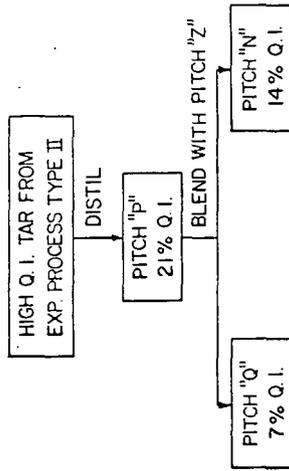


FIGURE 4
PREPARATION OF PITCH USING
EXPERIMENTAL PROCESS TYPE II



ACTUAL Q.I. LEVELS vs T-C.T.E. LEVELS

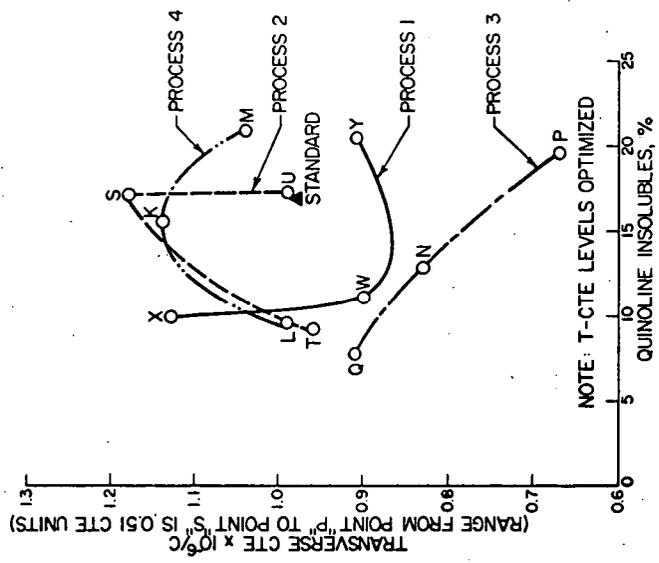
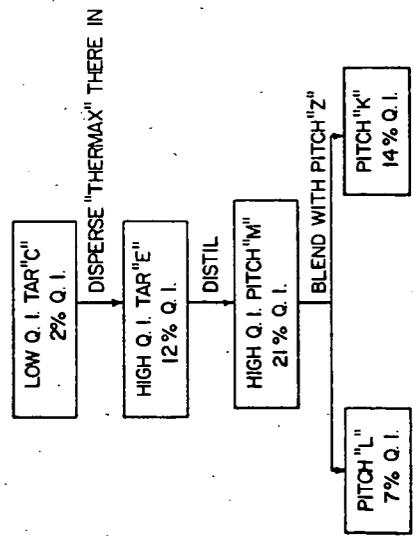


FIGURE 6

FIGURE 5
PREPARATION OF "THERMAX"-
MODIFIED Q. I. PITCH



ACTUAL Q. I. LEVELS vs FLEXURAL STRENGTH LEVELS

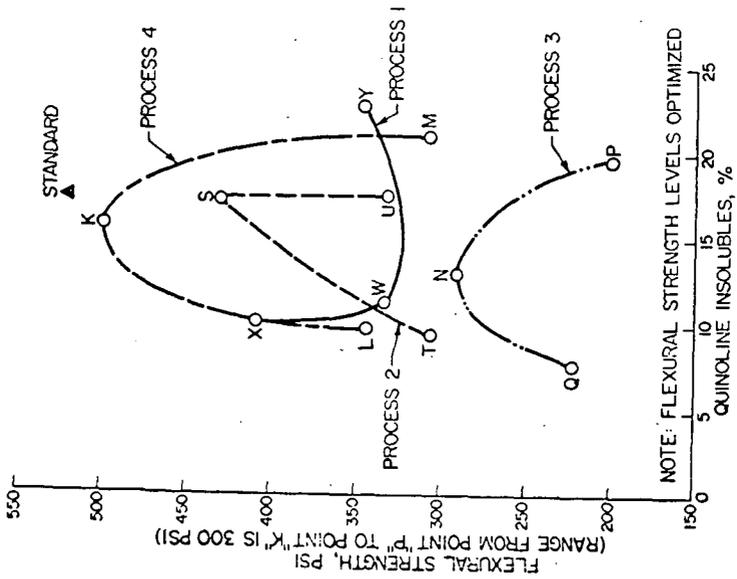
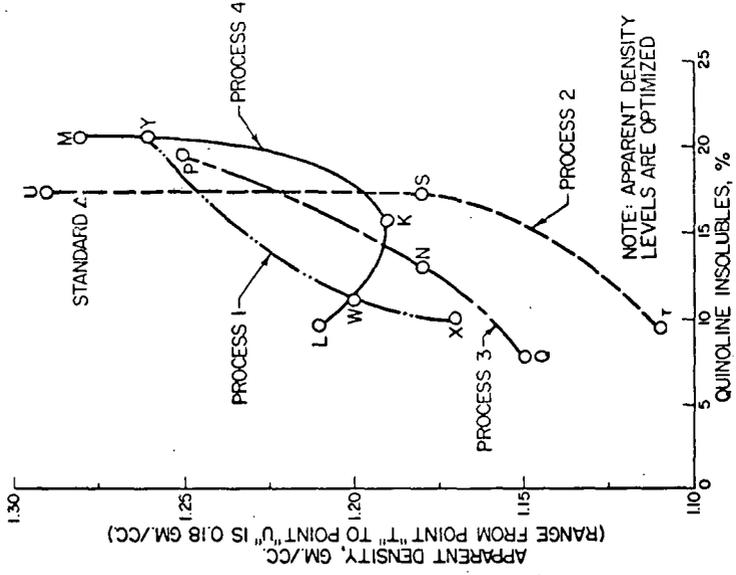


FIGURE 7

ACTUAL Q. I. LEVELS vs APPARENT DENSITY LEVELS



NOTE: APPARENT DENSITY LEVELS ARE OPTIMIZED

FIGURE 8

ELECTRODE TESTS OF PURIFIED COKE FROM
COAL IN ALUMINUM MANUFACTURE

V. L. Bullough, L. O. Daley, W. R. Johnson and C. J. McMinn

Reduction Research Laboratory, Reynolds Metals Company, Sheffield, Alabama

During the electrowinning of aluminum from aluminum oxide by the Hall process nearly 0.5 pounds of high grade carbon is consumed for each pound of aluminum produced. The raw materials making up this carbon must, of necessity, be of high purity because many metallic impurities in the carbon are transferred to the aluminum produced, and affect the metallurgical properties of the aluminum. For this reason raw materials used in anode manufacture for the aluminum industry have stringent purity specifications.

In addition to the specifications of purity, coke used in the manufacture of electrodes for aluminum production must be heat treated to temperatures of about 1300°C to insure the high temperature dimensional stability of the electrode. It must also contain about 25 percent of particles larger than 1/4 inch to allow for a graduated aggregate in electrode manufacture that is needed to prevent the propagation of stress cracks in large carbon masses.

Because petroleum coke represents a large volume source of relatively pure carbon, it is used almost exclusively for anode manufacture by the aluminum industry in the United States. Some coal tar pitch coke is used in Europe to supplement the supply of petroleum coke.

Coke derived from coal is not used in alumina reduction cell anodes because of the high ash content. Several investigators¹⁻⁶ have studied methods of removing the mineral matter from coal for the purpose of making purified coke for electrode use, and coke from purified coal has been used in Europe on a commercial scale in at least two cases.^{7,8} These were wartime uses, however, and were not competitive when adequate supplies of high grade petroleum coke were available.

Possible future shortages of electrode grade petroleum coke have encouraged the continued investigation of methods of producing high purity coke from coal as a substitute and competitive material for use in electrodes. This report will be concerned primarily with a performance test of electrodes made from a purified coke from coal in pilot plant and commercial alumina reduction cells.

Process Description

Figure 1 is a diagram of the major steps of a process for manufacturing high grade coke from coal. In a pilot plant operated by Reynolds Metals Company for the production of coke, a mixture of high volatile bituminous coal and a solvent oil was digested in a continuous pressure digester to a temperature slightly above the temperature of maximum solubility of the coal.⁹ The coal solution from the pressure digester was charged to centrifuges where the

suspended mineral matter and fusain were separated from the coal solution. This solution from the centrifuge was charged to a continuous distillation still where the solvent was separated and returned to the mixing cycle. The still bottoms which contained the purified coal were charged directly to a coke oven where a purified coal was converted to coke and heat treated to a temperature that would assure dimensional stability at the operating temperature of an alumina reduction cell.

Coal from two sources was run in the pilot plant — the Black Creek seam in North Alabama and the No. 9 seam in Western Kentucky. Typical analyses of these coals are shown in Table I. Typical properties of cokes made from these coals compared with an electrode grade petroleum coke are shown in Table II. Electrical resistivity was determined by the Great Lakes Carbon Company Method, C-12, and the Hardgrove grindability index was determined by ASTM Method No. D409-51. The coke prepared from these coals had a grey metallic luster and was more resistant to grinding than regular petroleum coke. The iron content was the only property of this coke that was inferior to electrode grade petroleum coke and did not meet specifications imposed by aluminum producers. Since the iron content of the coke produced in the pilot plant was about three times higher than coke produced from the same coals in laboratory scale equipment, it is believed that this difference represents iron pickup from the pilot plant processing equipment and is not an inherent limitation of the process.

Two types of carbon anodes are used in the aluminum process. In the prebaked anode type cell, electrode blocks are fabricated from a graded carbon aggregate and coal tar pitch. This mixture is pressed into blocks by large hydraulic presses, and the resulting blocks are heated in furnaces to about 1200°C. The baked block is suspended in the molten salt electrolyte by the electrical connection which is usually made with a steel pin held in a specially molded well in the carbon block by cast iron. In the other type of anode system, which is known as the continuous electrode or Soderberg system, heat from the electrolytic process is used to bake a carbonaceous paste prepared from a graded coke aggregate and coal tar pitch. This paste is added to the top of the anode casing as carbon is consumed by the process from the bottom of the anode. Electrical connections are made through steel pins embedded in the carbon.

Approximately 6000 pounds of coke from purified coal were processed into electrode blocks at the carbon plant of a commercial aluminum plant for tests in a 10,000 ampere scale alumina reduction cell. These blocks were 20 x 16 x 13 inches and each weighed about 200 pounds.

There are two major sources of anode carbon consumption in an alumina reduction cell. These are electrolytic reaction with oxygen released from the aluminum oxide at the working face of the anode and reaction with oxygen from the air on the sides and top of the anode in the area not wet by the molten salt electrolyte. To determine the amount of carbon lost to oxygen from each of these sources, a number of the anodes were capped with an alumina cap prepared from a tabular alumina castable refractory. The rest of the blocks were run without a cap to protect against air burning which is the normal practice in an alumina reduction plant. To provide experimental control and comparison against regular electrode materials, half of the anodes in the cell at any time were prepared from petroleum coke.

Each anode was weighed before being placed in the test cell. After seven days of electrolysis the unburned portion was removed from the cell and weighed. The difference between the initial and the final weights was taken to be equal to the carbon consumed during the test period. The anodes that were capped with an alumina refractory were weighed before capping and after test the remaining cap was broken from the block before the stub was weighed. Each individual anode position on the test cell was equipped with electrical shunts and the current passing through the block during the test period was recorded with integrating ammeters. Results of the test are summarized in Table III. Approximately 30 anode blocks made from the coke from purified coal were tested as were a like number of control blocks made from petroleum coke. This number of blocks was established by statistical treatment of data from previous experiments as being the number required to distinguish a carbon consumption difference of 0.5 gms. /amp. hr. in this type of test cell.

The anode stubs from the coke from coal blocks removed from the test cell were hard and dense and showed no tendency for coke particles to dust from the electrode surface.

In a second test, more than 20,000 pounds of coke made from purified coal were made into a carbon paste and tested in a 45,000 ampere Soderberg type reduction cell. Mechanical properties of electrode specimens prepared from samples of the carbon paste that were baked to about 1,000°C in a laboratory furnace are shown in Table IV with the mechanical properties of specimens from comparable paste made from electrode grade petroleum coke. One notable characteristic of the paste prepared from coke from purified coal was that about two percent less pitch was required than was normally used to prepare paste of comparable viscosity from petroleum coke.

Midway through the test the anode was raised from the electrolyte and inspected. The working face of the anode was flat and smooth and the anode was free of large cracks indicating that the coke from the pilot plant was thermally stable for use at the anode operating temperatures. Cell operation was smooth and efficient and the anode generally could not be distinguished from anodes made from petroleum coke.

Discussion

Examination of the test results summarized in Table III indicate that the consumption of carbon blocks was nearly the same for the coke from coal anodes as it was for the petroleum coke anodes. The difference in consumption between capped and uncapped anodes shows that 20 percent of the carbon in the petroleum coke anodes was lost to air burning compared to 16 percent for the anodes made with coke from coal. This is an indication that the coke from coal electrodes were less susceptible to attack by oxygen in the air. This indication is supported by observations made while determining the ash content that the cokes made from coal required considerably longer time to burn away than did petroleum cokes.

The performance testing of electrodes made from coke from purified coal in both prebaked and Soderberg type anodes indicated that the coke was satisfactory and could meet the specifications for anode grade coke for the aluminum industry.

ACKNOWLEDGMENT

The permission of Reynolds Metals Company to publish the results of this investigation is gratefully acknowledged.

LITERATURE CITED

1. Selvig, W. A., W. H. Ode, and F. H. Gibson, "Coke From Low-Ash Appalachian Coals for Carbon Electrodes in Aluminum Industry," Bureau of Mines Report of Investigations 3731, 1943, 188 pp.
2. Graham, H. G., and L. D. Schmidt, "Methods of Producing Ultra-Clean Coal for Electrode Carbon in Germany," Bureau of Mines Information Circular 7481, 1948, 13 pp.
3. Campbell, R. J., Jr., R. I. Hilton, and C. L. Boyd, "Coal As a Source of Electrode Carbon in Aluminum Production," Bureau of Mines, Report of Investigations 5191, 1956, 53 pp.
4. Klemgard, E. N., "Electrode Carbon From Washington State Coal," Bulletin No. 218, Washington State Institute of Technology, Pullman, Washington, 1953, 37 pp.
5. Bloomer, W. I., and F. L. Shea, "Coal Deashing and High-Purity Coke," American Chemical Society, Division of Fuel Chemistry, Preprints, 11 No. 2, 378-392 (April 1967).
6. Kloepper, Dean L., Thomas F. Rogers, Charles H. Wright, and Willard C. Bull, "Solvent Processing of Coal to Produce a De-ashed Product," Research and Development Report No. 9, Office of Coal Research.
7. Nelson, H., "The Selective Separation of Super Low Ash Coal by Flotation, Gas World," Vol. 127, 1947, pp 125-130-132.
8. Lowry, H. H., and H. J. Rose, "Pott-Broche Coal Extraction Process and Plant of Ruhrol G. M. B. H., Bottrop-Wilhelm, Germany," Bureau of Mines Information Circular 7420, 12 pp.
9. U. S. Patent 3,240,566.

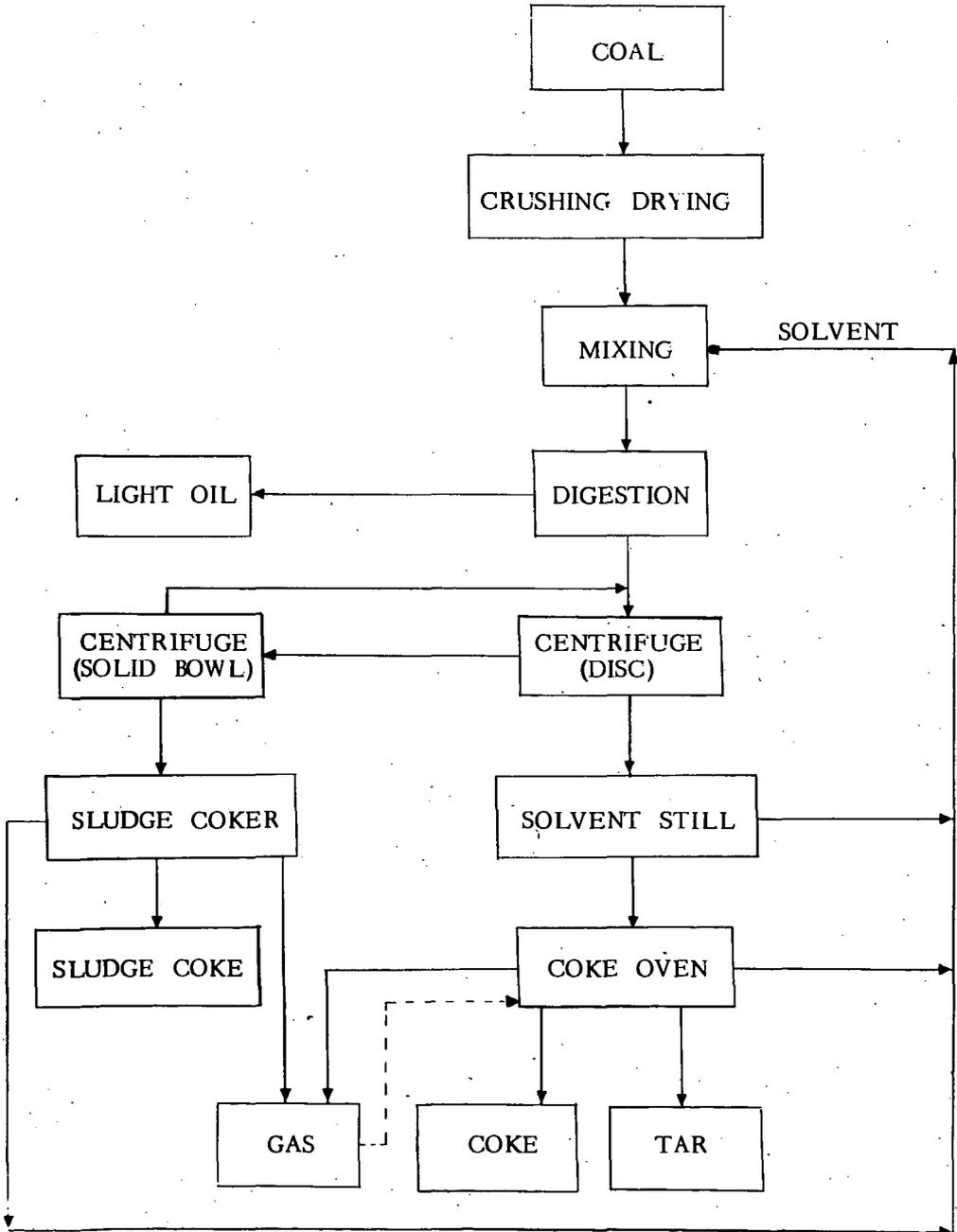


FIGURE 1. DIAGRAM OF A COKE-FROM-COAL PROCESS

TABLE I
ANALYSES OF COALS USED IN INVESTIGATION
OF ELECTRODE COKE FROM COAL.

	Black Creek Coal Seam		Kentucky No. 9 Coal Seam	
	As Received %	Dry Ash-free %	As Received %	Dry Ash-free %
Moisture	2.7	----	----	----
V. M.	35.4	37.4	40.5	45.0
Ash	2.8	----	9.9	----
H ₂	5.4	5.7	5.1	5.6
C	79.8	84.4	72.5	80.5
N ₂	1.7	1.8	1.5	1.7
O ₂	9.5	7.6	7.9	8.8
S	.8	.8	3.1	3.4

TABLE II

PROPERTIES OF COKES FROM KENTUCKY COAL AND
ALABAMA COAL AFTER CALCINING TO 1340°C

	Alabama Coke	Kentucky Coke	Typical Petroleum Coke
Specific Gravity	2.02	2.01	2.03
Electrical Resistivity, ohm-in.	0.029	0.034	0.034
Hardgrove Grindability Index	22	22.5	37
Sulfur, Percent	0.46	0.67	0.8 - 1.65
Silicon, Percent	0.04	0.09	0.03
Iron, Percent	0.07	0.08	0.05
Aluminum, Percent	0.09	0.09	0.02
Ash, Percent	0.58	0.76	0.34

TABLE III
 CONSUMPTION OF CARBON IN A 10,000
 AMPERE PREBAKE ALUMINUM CELL

	Electrode Consumption, gms. /amp. hr.			
	Coal Coke		Petroleum Coke	
	Result	σ	Result	σ
Capped Carbons	0.121	± 0.002	0.118	± 0.003
Uncapped Carbons	0.144	± 0.004	0.147	± 0.004

TABLE IV
 PHYSICAL PROPERTIES TEST RESULTS OF
 SODERBERG ELECTRODE SPECIMENS WITH
 COKE-FROM-COAL AGGREGATE

	Aggregate			
	Coke-From-Coal		Petroleum Coke	
	Result*	σ	Result*	σ
Apparent Density, gms. /cm. ³	1.58	$\pm .03$	1.56	$\pm .02$
Electrical Resistivity, ohms/m/mm ²	53	± 2.2	60	± 1.6
Compression Strength, Kg. /cm. ²	601	± 56	436	± 35

* Average of eight determinations.

THE IRREVERSIBLE EXPANSION OF CARBON
BODIES DURING GRAPHITIZATION

M. P. Whittaker and L. I. Grindstaff

Great Lakes Research Corporation
Elizabethton, TennesseeINTRODUCTION

The formation of synthetic graphite from amorphous carbon should theoretically be accompanied by a continuous shrinkage of material. However, in many instances an irreversible volume expansion, commonly referred to as puffing, is actually observed to occur at some point in the transformation. The addition of certain metals, particularly iron and calcium or their compounds, is known to inhibit or eliminate this expansion. Although "puffing" has generally been associated with the sulfur content of the petroleum coke, very little information has actually been published concerning this phenomenon. Based largely upon analogies found in the puffing behavior of sulfur-containing petroleum cokes and of carbon-bromine lamellar residue compounds, H. C. Volk¹ advanced the theory that puffing resulted from the decomposition of carbon-sulfur lamellar residue compounds. The formation of a thermally stable carbon-sulfur-metal ternary lamellar compound was proposed as an explanation for the inhibition mechanism. However, the existence of these compounds has not been convincingly established and our results are certainly difficult to reconcile with lamellar compound formation.

EXPERIMENTAL

The carbon bodies were made from a standard mixture of calcined petroleum coke, particle sizes ranging from -35 mesh to -100 mesh, and a coal tar pitch binder by hot pressing in an electrically heated mold at 12,500 psig for thirty seconds at 100°C. The cylindrical plugs were baked to a temperature of 850°C.

The extent of irreversible expansion exhibited by the baked carbon bodies as a function of heat treatment was measured with a graphite dilatometer. The dilatometer holding the carbon plugs was heated in a graphite tube furnace to temperatures as high as 2900°C at a rate of 14°C/min. A nitrogen atmosphere was maintained throughout the heating period.

A 15,000 psi mercury porosimeter was used to obtain micropore volume distribution in the heated carbon plugs. The plugs were crushed to -35/48 mesh and pore volume determinations made on 0.400 g. samples of this material.

X-ray diffraction examinations were made with a recording diffractometer using monochromatic Cu K α radiation at room temperature.

The sulfur in the carbon samples was determined by igniting the sample in an oxygen atmosphere at 1400°C. The SO₂ formed was titrated continuously by iodometry in the presence of starch indicator. Good agreement was found between this method and the method using the Parr-peroxide bomb combustion technique.

RESULTSCause of the Deformation

The petroleum cokes studied which were subject to deformation could be separated roughly into two broad groups according to their puffing characteristics. Typical dynamic elongation curves of the two groups are compared in Figure 1 and Figure 2. It can be seen that there exists a difference of 300°C between the two groups of carbons with respect to the temperature at which the deformation begins. The cokes which deform at the lower temperature do not respond well to puffing inhibitors and generally have a higher concentration of sulfur, oxygen and nitrogen.

The loss of the volatile constituents of a large number of carbons as a function of heat treatment was determined. In all cases oxygen and nitrogen were lost at temperatures below 1000°C. The sulfurous gases, however, were evolved over precisely the same temperature range as that at which the deformation occurred. The sulfur evolution from the samples was followed by heating the bodies at the same rate, 14°C/min., as was used in the dynamic puffing test to various temperatures before the desired analyses were made. The composition of the samples was compared and correlated with the dynamic puffing characteristics. An example of such a correlation is presented in Figure 3. The rate of sulfur evolution in the carbon samples in which the initial decomposition and corresponding deformation occurred at the lower temperature, 1400°C, was ten to twenty times greater than the rate observed in samples with the more thermally stable sulfur.

The escaping gas from several carbons was carefully trapped and analyzed. The gas was found to be essentially hydrogen sulfide. Unfortunately, all of the carbons studied with a high enough sulfur content to permit meaningful gas analysis puffed in the low temperature range.

If a sample is heated to the temperature at which the sulfur first begins to evolve and is held at that temperature until the desulfurization is essentially complete, deformation of the sample occurs only at this temperature, see Figure 4. There is little doubt that puffing results from internal pressures generated by the sudden expulsion of H₂S.

By carefully measuring the crystallite dimensions during the course of the deformation by means of x-ray diffraction, it becomes apparent that the puffing is an inter-crystalline phenomenon. However, in one experiment in which a sample made from a coke having an unusually high sulfur content was pushed directly into a furnace at 1400°C, an anomalous x-ray pattern was obtained from the sample. The 00 ℓ diffraction peaks were split, one portion of the peak being located at the expected 2 θ angle and the other occurring at a slightly higher angle, see Figure 5. Upon further heat treatment a coalescence into a single peak occurs, the lower angle portion of the peak overtaking the other. One possible explanation is that the high internal pressure generated within the sample has actually forced part of the sample to a more graphitic state. It is certainly well known that externally applied pressure facilitates graphitization.²

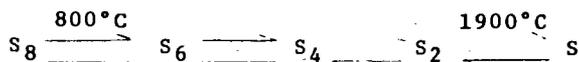
The pore structure of the samples during puffing was evaluated by means of mercury porosimetry. Typical pore size distribution curves are presented in Figure 6. Puffing is characterized by an increase in

pores having diameters in the 0.1-.015 μ range. The total deformation of the sample can be accounted for by the creation of this additional porosity resulting from the hot expanding gas channeling its way to the sample surface.

The magnitude of the deformation does not depend entirely upon the sulfur content of the coke. The microstructure of the coke is also important. As would be expected, hard carbons characterized by a high degree of cross-linking between crystallites are much more resistant to deformation than the more graphitic "softer" type carbons. For this reason there are several cokes which do not puff although they have a sulfur content comparable to that of a puffing softer type coke and the sulfur is evolved over the same temperature range at the same rate. This microstructural dependence was further illustrated by producing a softer type carbon from a feedstock which ordinarily forms a relatively hard carbon by making certain changes in processing and comparing the puffing characteristics of the two cokes. The sulfur content of the more graphitizable carbon exhibiting a linear CTE of $5.0 \times 10^{-7}/^{\circ}\text{C}$ was exactly the same as the less graphitizable carbon having a CTE of $23.0 \times 10^{-7}/^{\circ}\text{C}$. The softer carbon, however, puffed while the other coke exhibited no measurable deformation.

Mechanism of Puffing Inhibition

As illustrated in Figure 7 for the case of iron oxide, certain materials when added to the carbon sample eliminate or at least diminish in magnitude the puffing effect. The temperature required to initiate the volatilization of sulfur is higher and the rate of the subsequent gaseous evolution is lower in the samples containing an inhibitor, see Figure 8. An analysis of the effluent gas reveals that the sulfur is principally in the form of elemental sulfur rather than H_2S . The composition of the sulfur vapor at these temperatures is governed by the following equilibria:



Even above 1900°C the sulfur vapor is 55% associated.³ An increase in association of the sulfur atoms would, of course, result in a decrease in gas volume. By following the composition of the inhibitor as a function of temperature by means of x-ray diffraction, the mechanism of inhibition becomes apparent. This type of analysis for iron oxide is given in Figure 9. The inhibitor reacts with the sulfur to form a sulfide which subsequently decomposes at a higher temperature liberating sulfur in its elemental form and at a reduced rate. The effectiveness of the metal in preventing puffing is a function of the stability of its sulfide. Sodium, for example, forms a sulfide which is expelled rapidly at a relatively low temperature resulting in distortion of the sample, see Figure 10.

A secondary deformation of reduced magnitude was observed to occur at around 2500°C in the most graphitic or needle type carbons studied upon inhibition with iron oxide, see Figure 11. A gaseous evolution resulting from the decomposition of the iron sulfide is occurring at this temperature, however, the rate of volatilization at 2500°C is not substantially different from that at temperatures immediately below this delayed puffing range. This indicates that structural changes must be occurring in the carbon body which

effectively reduce its resistance to puffing. It is well known that the mechanical strength of graphite increases with temperature to about 2500°C and then decreases sharply with temperature above 2500°C.⁴ A substantial amount of creep occurs in graphite at 2500°C and higher. This sudden decrease in strength of the body coupled with the internal pressure generated by the decomposition of the metal sulfide provides a logical explanation for the observed delayed puffing.

Lamellar Residue Compounds

Lamellar and lamellar residue compounds are known to have a pronounced effect on the resistivity of the carbon. Dilute residue compounds with a composition $C_{100}X$ (X = intercalated species) are reported to decrease the resistivity of graphite to between 1/2 to 1/10 of its original value, both for n- and p-type compounds.¹ The resistivity of a sample heated to a temperature at which puffing is initiated should increase with time as the residue compound decomposes. We have not found this to be the case. In some carbons, in fact, the resistivity as illustrated in Figure 12 in which the weight percent sulfur loss and resistivity are plotted against holding time actually bears a direct relationship to sulfur evolution. In these materials a decrease in d-spacing and rapid crystallite growth accompanied the decrease in resistivity, see Figure 13. This is additional evidence that premature graphitization is induced by the high internal pressure of the sulfurous gases.

The presence of sulfur per se does not affect the d-spacing in carbon. Therefore, the proposed carbon sulfur lamellar residue compounds cannot be located between the layer planes since a difference in d-spacing would be observable due to their presence. However, residue compounds located at imperfections in the graphite structure would be unlikely to cause a change in the c axis of the graphite if the imperfections are randomly distributed. The diffraction pattern would either not be changed or else only a slight line broadening would occur due to the enlargement or creation of new random imperfections. The existence of the parent lamellar compounds would be expected to be detectable by means of x-ray diffraction except for the fact that the x-ray pattern of carbon heated only to the low temperatures, below 1200°C, at which they are thought to exist is quite diffuse.

Similarly, the resistivity of an inhibited sample is not adversely affected by the removal of the sulfur and inhibitor by heat treatment. Volk noted that the resistivity of the sample was apparently independent of the inhibitor concentration. For this reason, he postulated that the carbon-sulfur-iron compounds were ternary lamellar compounds in which iron functions as a spacer and is therefore not ionized. However, a lamellar compound such as this should be easily detectable by x-ray diffraction analysis. The x-ray spectra of an inhibited carbon is essentially the same before elimination of inhibitor by means of heat treatment alone or with the aid of a purifying gas as after removal. In addition, the diffraction pattern of an inhibited puffing carbon is not significantly different from that of a non-puffing carbon with the same metal concentration. The existence of a ternary lamellar compound is, therefore, certainly doubtful.

CONCLUSIONS

Puffing of carbon bodies results from internal pressure generated by the sudden formation of sulfurous gases, primarily hydrogen sulfide. This pressure is sufficient, in some cases, to cause premature graphitization. The increased volume of the body is in the form of small micropores 0.1 to .015 μ in diameter. Various metals act as inhibitors by reacting with sulfur to form sulfides which subsequently decompose at a temperature and with a rate which is dependent upon the stability of the sulfide. The magnitude of the deformation is also a function of the coke structure. The hard, cross-linked carbons are much more resistant to deformation than the softer, more graphitic carbons. No evidence was found for the existence of lamellar or lamellar residue compounds involving sulfur or the inhibitor.

REFERENCES

1. H. C. Volk, "Lamellar Compounds of Non-Graphitized Petroleum Coke", WADD Tech. Report 61-72, Vol. XXV, (August, 1963).
2. T. Noda, "Graphitization of Carbon under High Pressure", Paper presented at Eight Biennial Conference on Carbon, June 19-23, 1967, Buffalo, N. Y.
3. R. C. Brasted (ed.), Comprehensive Inorganic Chemistry, Vol. 8, D. Van Nostrand Co., Inc., Princeton, N. J., 1961, p-29.
4. S. Mrozowski, "Mechanical Strength, Thermal Expansion and Structure of Cokes and Carbon", Proceedings of the First and Second Conferences on Carbon, Univ. of Buffalo (1956) p-31.

Figure 1.

**DYNAMIC ELONGATION OF A
PETROLEUM COKE (RATE 14°C/min)**

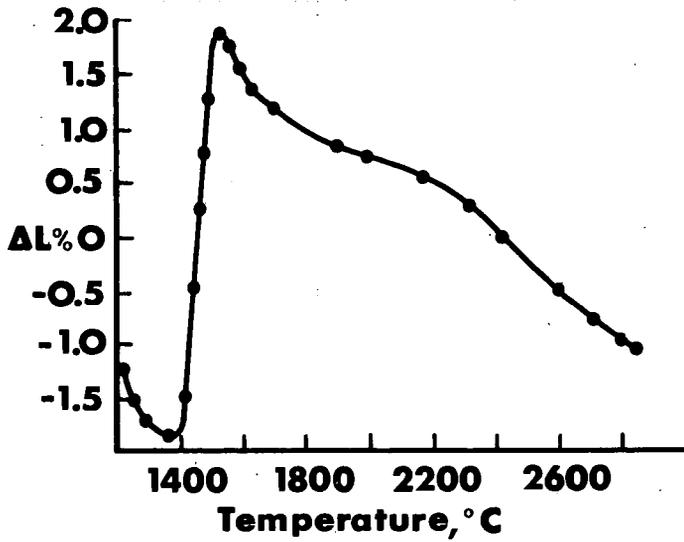


Figure 2.

**DYNAMIC ELONGATION OF A
PETROLEUM COKE (RATE 14°C/min)**

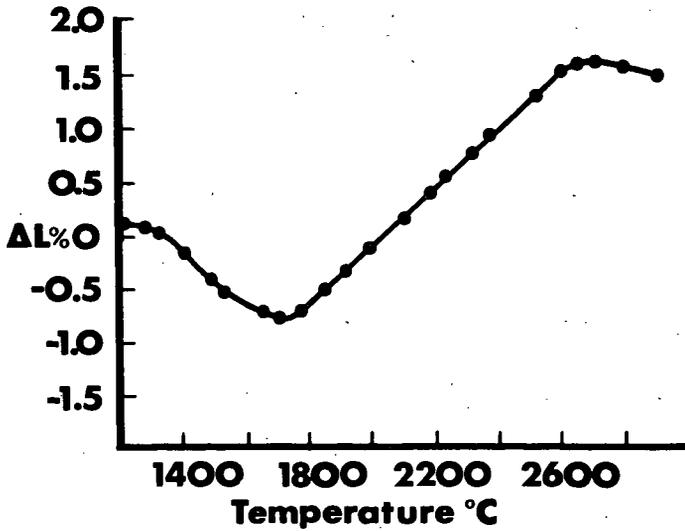


Figure 3.

**EVOLUTION OF SULFUR AND DYNAMIC
ELONGATION OF PETROLEUM
COKE VS. TEMPERATURE**

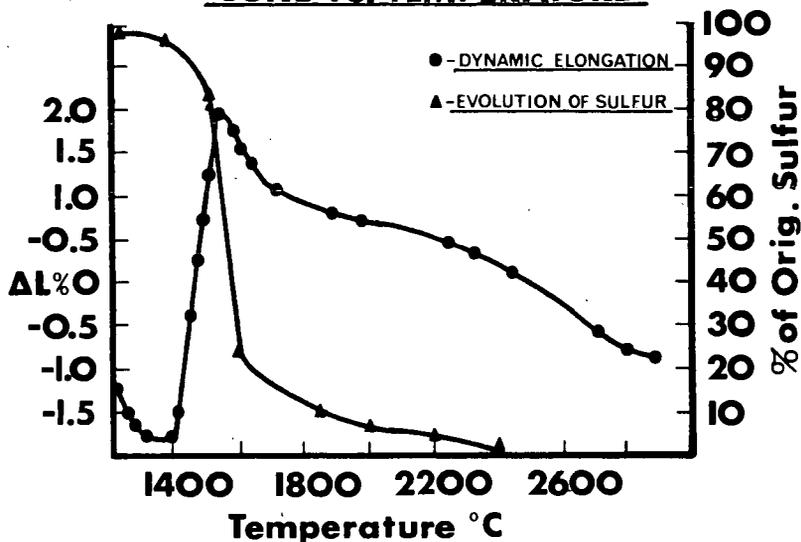


Figure 4.

**DYNAMIC ELONGATION OF PETROLEUM
COKE AT CONSTANT TEMP.**

(Held at 1400°C 3.5 hrs, then to 2900°C @ 14%/m)

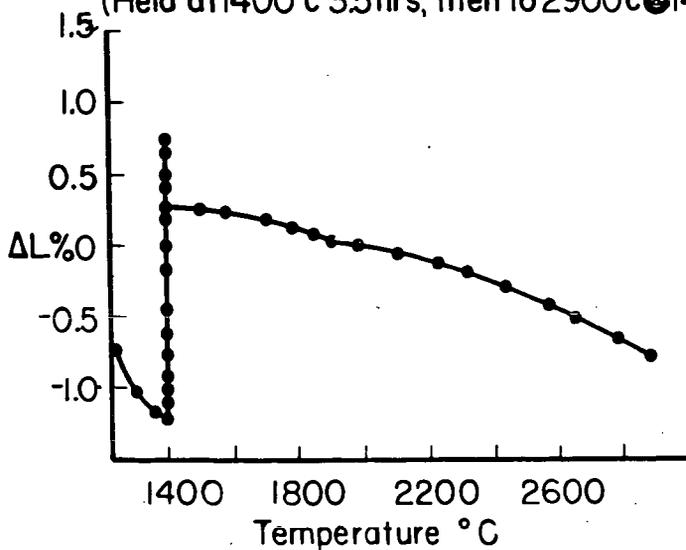


Figure 5. .002 X-RAY DIFFRACTION PEAK

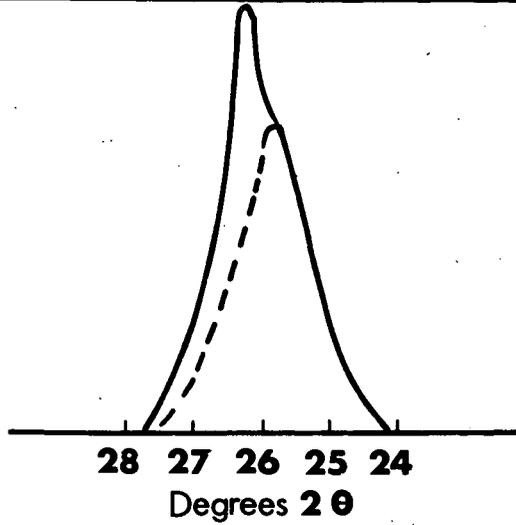


Figure 6. PORE SIZE DISTRIBUTION IN PETROLEUM COKE HEATED TO VARIOUS TEMPERATURE

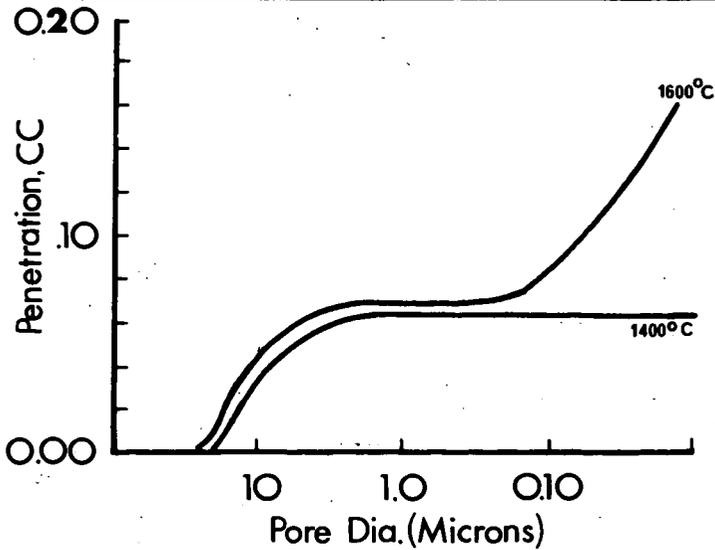


Figure 7. DYNAMIC ELONGATION OF A PETROLEUM COKE CONTAINING Fe_2O_3

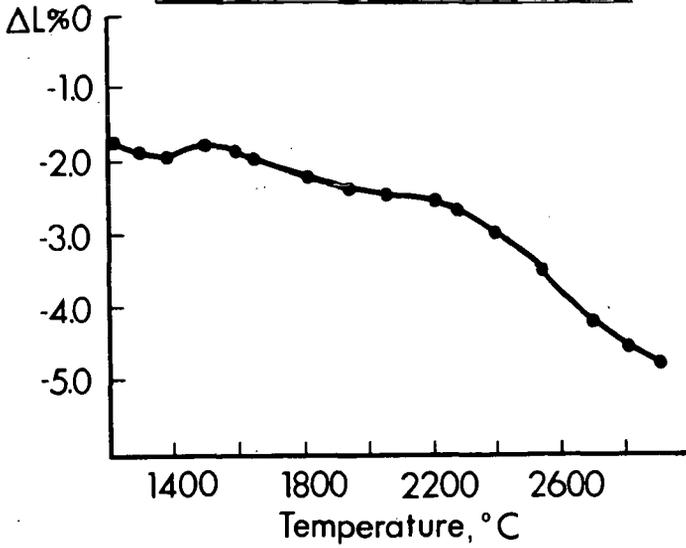


Figure 8. EFFECT OF ADDED Fe_2O_3 ON THE THERMAL STABILITY OF SULFUR IN PETROLEUM COKE

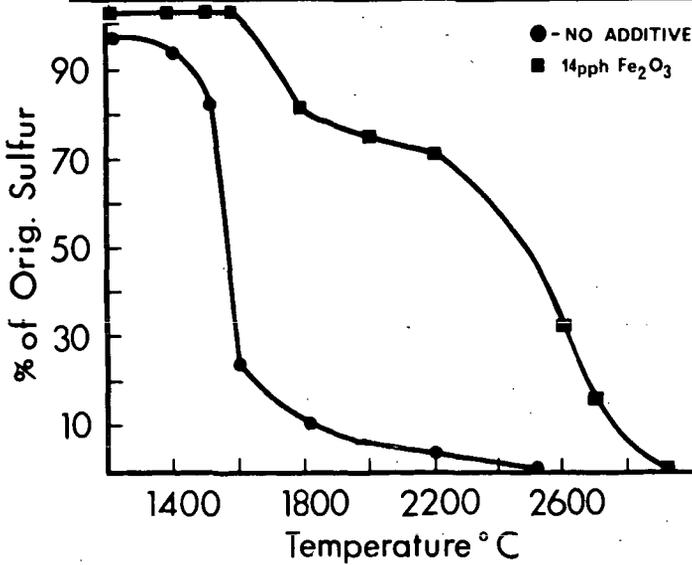


Figure 9.

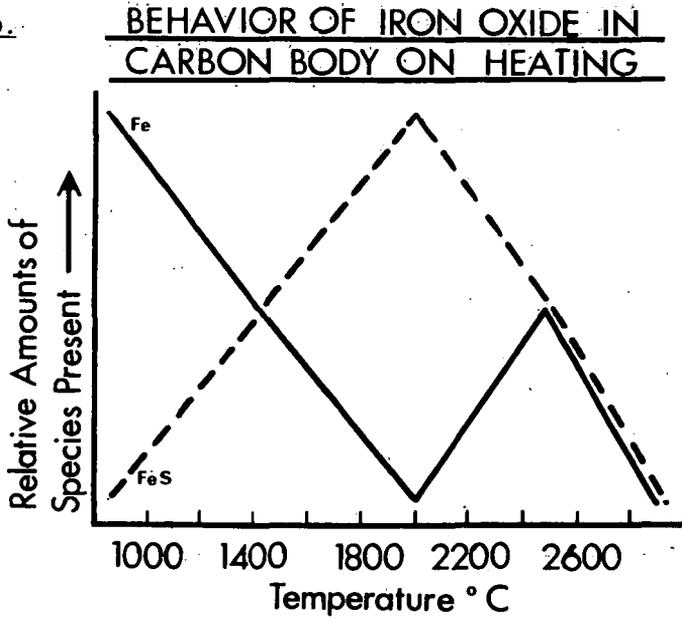


Figure 10.

DYNAMIC ELONGATION OF A PETROLEUM
COKE CONTAINING Na_2CO_3

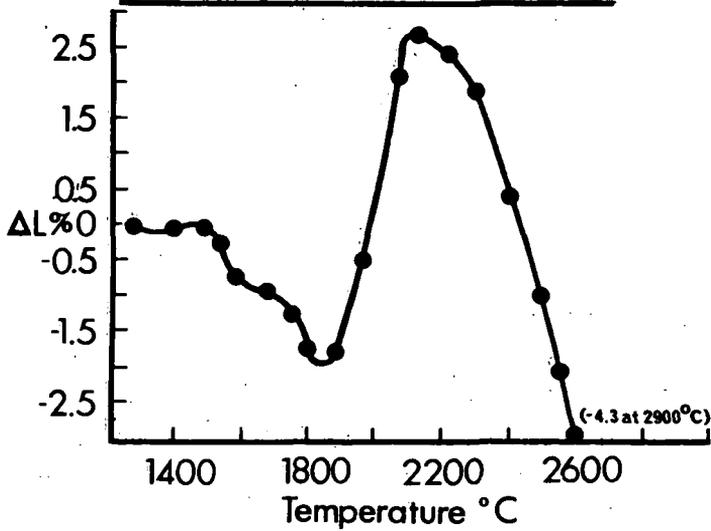


Figure 11. DYNAMIC ELONGATION OF A PETROLEUM COKE CONTAINING Fe_2O_3

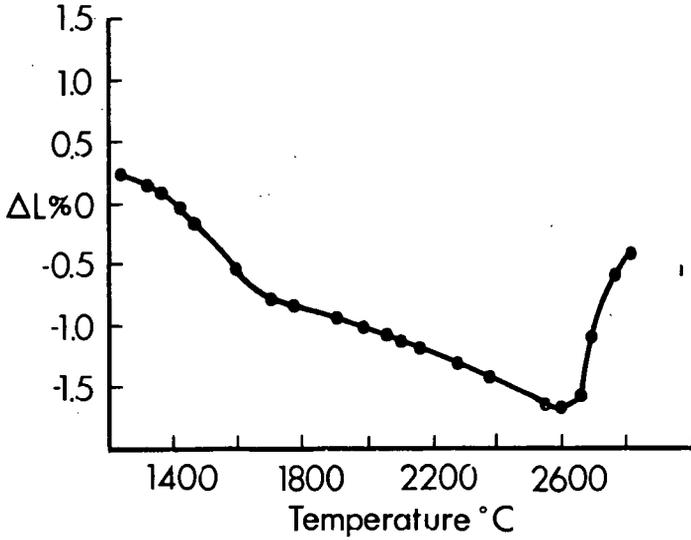


Figure 12. EFFECTS OF HEATING A PETROLEUM COKE AT 1400°C

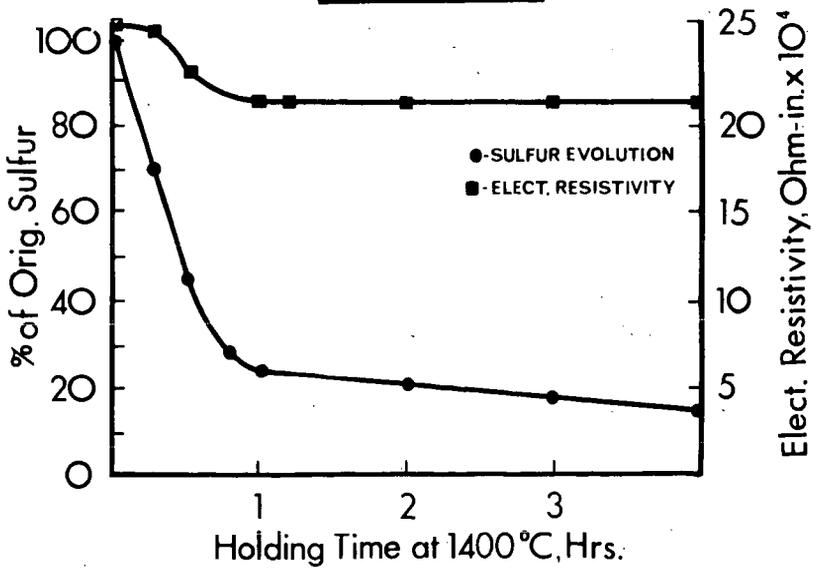
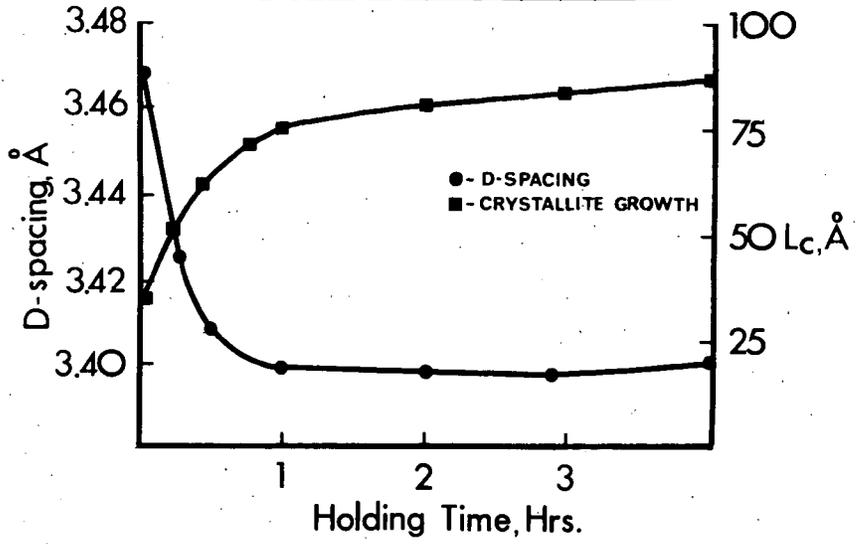


Figure 13.

D-SPACING AND CRYSTALLITE GROWTH
IN COKE HEATED AT 1400°C



"GRAFOIL" GRAPHITE TAPE - ITS MANUFACTURE, PROPERTIES AND USES

Joseph F. Revilock

Union Carbide Corporation, Carbon Products Division, New York, N. Y.

SUMMARY

This paper will describe a new form of graphite - GRAFOIL graphite tape, paper-like in structure and having unusual properties including a high degree of flexibility and compressibility. The paper will discuss briefly the manufacture of GRAFOIL tape products, their properties and their uses in research and development and in chemical and other industrial applications.

MANUFACTURE

GRAFOIL is Union Carbide's trade mark for graphite tape which is made up of interlocking and self-adhering graphite particles. The tape contains no bonding agents such as adhesives, resins or rubber compounds. The particles and the layers which give the tape a laminar structure through its thickness are held together by Van der Waal forces. GRAFOIL graphite tape is manufactured by a patented process in which graphite particles are rolled into sheets .005 or .010 inches in thickness. These 5 and 10 mil thick tapes are flexible as can be seen by the spiral in Figure 1. The normal density of the tape is 70-75 pounds per cubic foot, and by varying the rolling pressure, the density of the tape can be controlled down to 12 pounds per cubic foot.

From these basic graphite tape forms, GRAFOIL laminates (Figure I) are made by cementing layers of tape together with a resin cement which is then carbonized while the laminate is held under pressure. As the thickness of these laminates increase, the flexibility characteristic of the GRAFOIL tape decreases. However, they are still flexible compared to solid graphite and they are still compressible.

Two other forms of GRAFOIL tape illustrated in Figure I are foam and molded forms, made by compressing graphite particles in a mold under pressure. Again the bond is strictly a particle surface phenomenon, no bonding agents being used. Foam materials are light, having a density in the range of 3 to 6 pounds per cubic foot, whereas the molded materials have densities in the range of 70 to 100 pounds per cubic foot, depending on their configuration and end use.

PROPERTIES

The physical properties of GRAFOIL tape are shown in Table I. As can be seen from the data, GRAFOIL tape has a relatively high tensile strength for graphite material. Compressive strength is more than adequate for most applications. The low permeability of GRAFOIL tape is shown by its helium admittance of 2×10^{-4} sq. cm./sec., which is comparable to that of cast brass. (Conventional extruded graphites have admittances of 10^2 to 10^3 sq. cm./sec., while premium graphites have helium admittances in the range of 10^{-2} sq. cm./sec.)

TABLE I
PROPERTIES OF "GRAFOIL" TAPE

<u>Property</u>	<u>Approximate Value</u>
Bulk Density (lb./cu.ft.)	60-80
Ash Content (Weight %)	0.1
Melting Point	Does not melt; sublimes at 6600°F.
Tensile strength (surface plane or "a" direction) (lb./sq.in.)	1500-2500
Elastic Modulus, Tensile (10^6 lb./sq.in.)	0.2
Ultimate Compressive Strength (lb./sq.in.)	15,000
Helium Admittance: 0.005 in. thick foil (sq. cm./sec.) laminated bodies (sq. cm./sec.)	2×10^{-4} 5×10^{-5}
Coefficient of Friction (against stainless steel @ 8 lb/sq.in.)	0.05

The material is very anisotropic and this is shown by the directional nature of the electrical resistances, which are given in Table II. In this respect, GRAFOIL material is similar to pyrolytic graphite.

Table II.

ELECTRICAL RESISTANCE OF "GRAFOIL" TAPE

<u>Form</u>	<u>Surface Plane or "a" Direction</u>	<u>Across Surface Plane or "c" Direction</u>	<u>Ratio "c" to "a" Direction</u>
Tape	.00046 ohm-cm	70 ohm-cm	150,000
Laminate	.0008 "	0.4 "	500

The thermal conductivity of GRAFOIL graphite tape in the surface plane or "a" direction is similar to that of most graphite materials in that it decreases with increasing temperature. Table III shows thermal conductivities at various temperatures for a GRAFOIL graphite tape laminate with a density of 70 lbs/cu.ft.

TABLE III
THERMAL CONDUCTIVITY OF "GRAFOIL" LAMINATE

<u>Temperature</u>	<u>Surface Plane or "a" Direction</u>	<u>Across Surface Plane or "c" Direction</u>
70°F	100 BTU/hr./sq.ft./°F/ft.	3.0 BTU/hr./sq.ft./°F/ft.
900°F	50 "	1.8 "
1800°F	25 "	1.7 "
4000°F	11 "	2.0 "
4500°F	11 "	"

Table IV shows data on compressive load deflection characteristics of GRAFOIL laminates as a function of starting density. The data were taken at a load of 250 lbs./sq.in. With a density of 43 pounds/cu.ft., a load of 250 lbs./sq.in. produced a 22.8% deflection of which 13.6% was permanent set. The resiliency was 7.4% and there was no hysteresis. At densities of 73 and 90 pounds per cubic foot, deflections were 5.5% and the resiliencies were 2.6%. The permanent sets were 2.7% and 2.2%, respectively. These data show the ability of the GRAFOIL material to be cold worked to a higher density at relatively low loads. The material retains resiliency at the higher densities. With the range of densities available, material can be fabricated to a specified low deflection characteristic over a wide range. In one instance, GRAFOIL laminates were made to a specification of 67% deflection at 11 psi load.

TABLE IV
COMPRESSIVE LOAD DEFLECTION OF "GRAFOIL" LAMINATE

<u>Starting Density - lbs/cu.ft.</u>	<u>Deflection-% of Original Thickness</u>	<u>Permanent Set-% of Original Thickness</u>	<u>Resilience-% of Final Thickness</u>
44	22.8	13.6	7.4
73	5.5	2.7	2.6
90	5.5	2.2	2.6

As GRAFOIL graphite tape is all graphite without any binders, its corrosion and temperature resistance are those of graphite. It can be used at temperatures from those of cryogenic liquids, such as liquid oxygen, to those of molten metals, such as molten aluminum and steel. It can be used in any chemical environments other than those of a highly oxidizing nature, such as air above 740°F, hot concentrated nitric acid and hot wet chlorine. In neutral and reducing atmospheres, the material has been used at temperatures up to 3000°C. Table V is a brief list of corrosives to which GRAFOIL materials are resistant. The corrosion resistance at higher temperatures is illustrated by the references to molten caustic, high pressure steam and molten aluminum.

TABLE V
CORROSION RESISTANCE OF "GRAFOIL" MATERIAL

	<u>Conc.</u>	<u>Temp.</u>
Hydrochloric Acid	All	All
Sulfuric Acid	To 95%	300°F
Phosphoric Acid	All	All
Hydrofluoric Acid	All	All
Nitric Acid	To 60%	70°F
Caustic Soda	All	750°F
Aluminum	-	1350°F
Steam	-	1000°F
Chlorinated Organics	All	All
Organic Alcohols	All	All
Organic Esters	All	All
Benzene	All	All
Air	-	740°F

APPLICATIONS

Corrosion and temperature resistance combined with their resilience and compressibility make GRAFOIL materials outstanding as gaskets for flange joints and as packings for seals in rotating and reciprocating equipment. Typical gaskets and packings are shown in Figure II. GRAFOIL tape's sealing characteristics are similar to those of rubber-like materials. Neither cold flow nor creep are experienced with the material and no special flange face conditions are required. Table VI shows applications in which GRAFOIL gaskets give excellent service.

TABLE VI

"GRAFOIL" GASKET APPLICATIONS

<u>Chemical Environment</u>	<u>Temperature-°F</u>	<u>Pressure-Lbs/Sq.In.</u>
Molten Aluminum	1350	5000
Molten Polyester Resins	600	6000
Dowtherm	660	80
Anhydrous Hydrogen Fluoride	660	50
Molten Caustic	650	25
Anhydrous Hydrogen Chloride	1000	Atmospheric
Steam	490	600
Hydrogen Chloride;Chlorine;Organics	100	25
Chlorine plus Organics	650	10
Titanium Tetrachloride	1800	10
Chlorinated Hydrocarbons	212	200

Of even greater importance to the Chemical Process Industries is the use of GRAFOIL packings in pumps, valves, mixers, etc. To take advantage of the material's directional thermal conductivity, the packing is fabricated with the high 'a' direction thermal conductivity perpendicular to the shaft so that frictional heat developed in the stuffing box is transmitted rapidly away from the shaft, preventing overheating and possible impairment of the strength and corrosion resistance of the shaft. Conversely if the stuffing box must be heated, GRAFOIL packing will rapidly conduct the heat throughout the box. As there are no binders or additives in GRAFOIL packing, thermal breakdown, chemical attack, leaching or squeezing out of additives commonly used in other types of packings can not degrade performance. GRAFOIL packing is self-lubricating, has a low coefficient of friction and prevents shaft, stem or plunger scoring.

Figure III illustrates equipment in which GRAFOIL packing is giving extended packing life without shaft damage in a wide variety of corrosive environments. Table VII lists some of the results obtained in commercial installations of GRAFOIL packing.

TABLE VII

"GRAFOIL" PACKING APPLICATIONS

<u>Equipment</u>	<u>Corrosive</u>	<u>Temp.-°F</u>	<u>Pressure-lb/sq.in.</u>	<u>Comments</u>
Plunger Pump	Acid Water	200	1,500	Life up 50 times. No scoring.
Plunger Pump	Organics	70	2,500	Life up 10 times. No lubrication required.
Centrifugal Pump	Organics	100	80	Out-performed mechanical seal; leak- free operation
Centrifugal Pump	Pitch	340	50	Life up 12 times. No scoring.

TABLE VII (Continued)

"GRAFOIL" PACKING APPLICATIONS

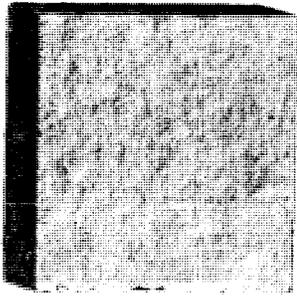
<u>Equipment</u>	<u>Corrosive</u>	<u>Temp.-°F</u>	<u>Pressure-lb/sq.in.</u>	<u>Comments</u>
Centrifugal Pump	Mobiltherm-600	400	50	No leakage after 6 months.
Control Valve	Chlorinated Organics	350	100	Life up 9 times. No scoring.
Control Valve	Dowtherm	660	80	Life up 4 times.
Pressure Control Valve	Steam	490	600	Life up 3 times.

Other uses of GRAFOIL tape take advantage of its flexibility together with its electrical conductivity, its chemical inertness and its low thermal conductivity in the "c" direction at extremely high temperatures. Thin film batteries designed for high power outputs use GRAFOIL tape as internal conductors and anodes. GRAFOIL is an excellent separator in multiple hot pressing of refractory metal compounds and ceramic items since its laminar construction allows easy separation of adjacent pressed parts.

The low "c" direction thermal conductivity and dimensional stability at extremely high temperatures of GRAFOIL materials are being put to use in insulating barriers used in missiles, nuclear reactors, and high temperature vacuum furnaces. GRAFOIL tapes cut into narrow strips are used as electric resistance heating elements. Research and development laboratories throughout the country stock GRAFOIL tape for use in high temperature experimental work.

In conclusion, GRAFOIL tape is a unique form of graphite. Properties such as directional thermal and electrical conductivities, excellent corrosion resistance, low permeability and temperature stability are available in a thin, flexible, compressible, easily fabricated form for a wide range of demanding chemical, metallurgical, nuclear and aerospace uses.

FIGURE I

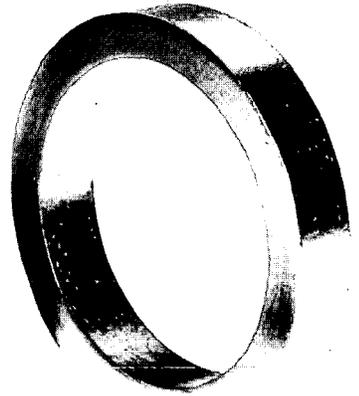


LAMINATE



FOAM

TAPE



MOLDED RING

FIGURE II

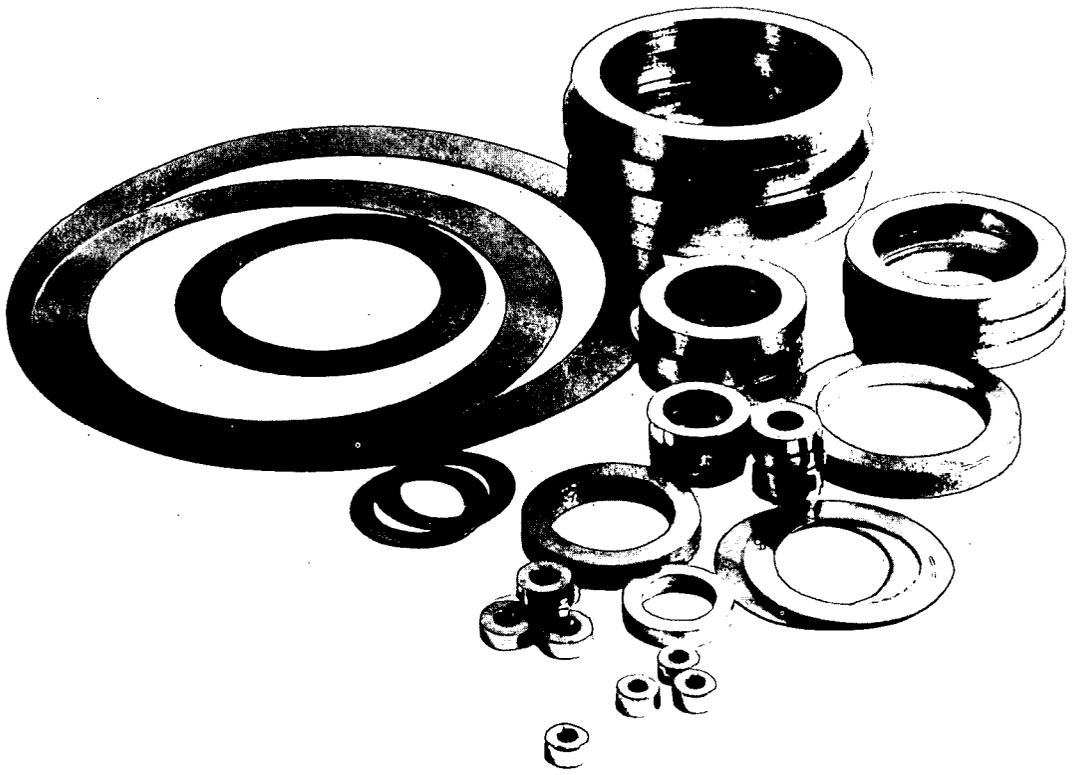
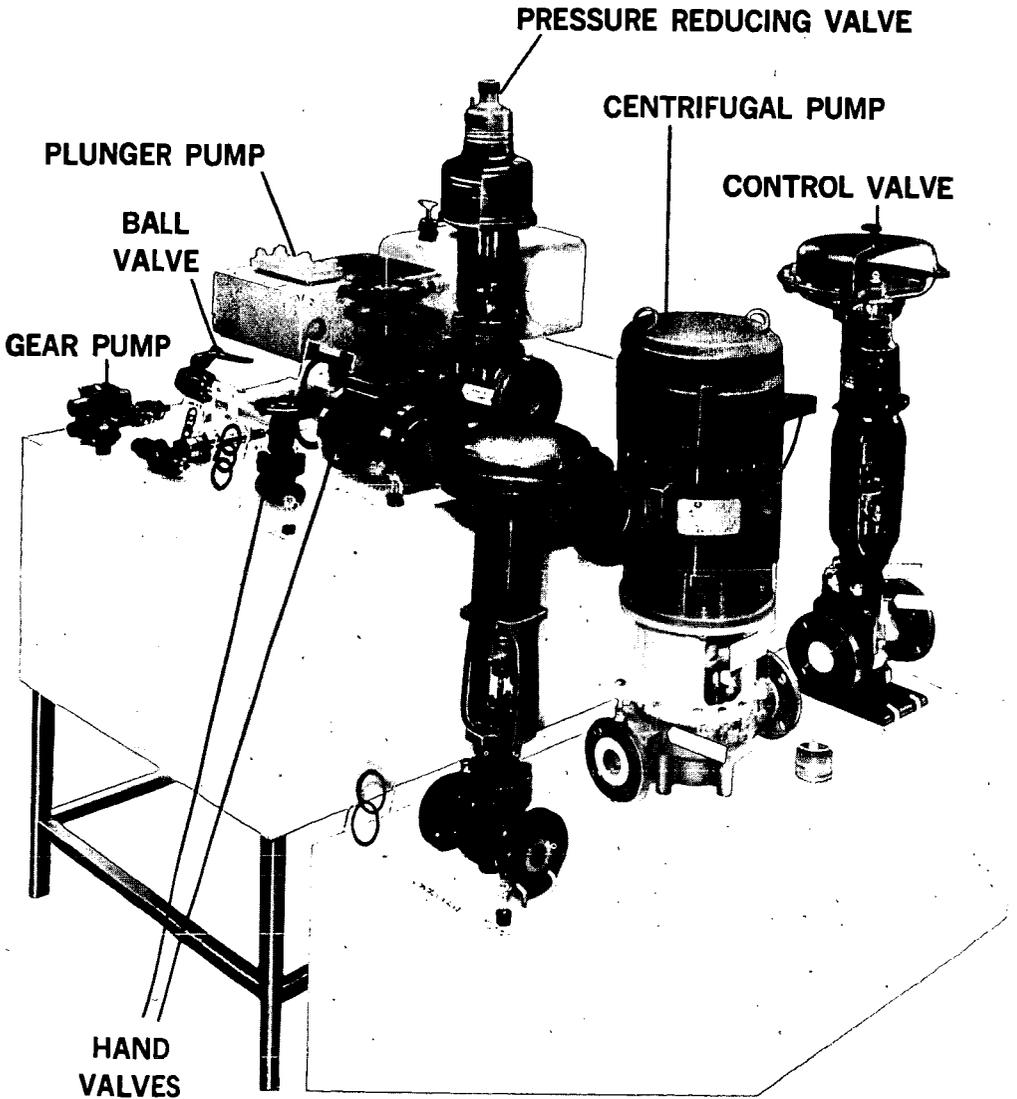


FIGURE III



CARBON FOAM - ITS PREPARATION AND PROPERTIES

R. A. Mercuri, T. R. Wessendorf, and J. M. Criscione

Union Carbide Corporation
Carbon Products Division
Parma Technical Center
Parma, Ohio 44130

I. INTRODUCTION

Light weight cellular carbons are widely used in many industrial and aerospace applications as high temperature thermal insulators and as structural support materials. The Carbon Products Division of Union Carbide Corporation has for many years been engaged in the research and development of carbon foams made by means of the pyrolysis of thermo-setting organic foam precursors. This paper describes the preparation and properties of two types of carbon foams, one based on a phenolic foam and the other on a polyurethane foam precursor. By varying the conditions of preparing the precursor foams and also the rate of pyrolysis, a very broad range of product properties can be obtained.

II. PREPARATION OF CARBON FOAMS

Many factors determine the density and suitability of an organic foam as a carbon precursor; the density of the resins, the temperature and resin balance of the formulation, the molding procedures, and various post curing operations are important examples. A typical foam formulation contains four components: the resin; a surfactant to maintain cell integrity during the foaming process; a foaming aid to obtain a smooth even foaming action starting at low temperatures; and, finally, a catalyst, which is used to initiate the resin polymerization reaction.

The organic foam is converted to cellular carbon by heating in a controlled environment. The heating rate depends on both the precursor thickness and formulation. If the foam is heated improperly, the structure may melt, rupture, or even explode.

A. PYROLYSIS OF PHENOLIC FOAM

The pyrolysis of the phenolic foam is accomplished in a nonoxidizing environment which may be provided by the product gases. Heating rates from 1° to 200°C/hour have been employed in the pyrolysis of phenolic foams. The rate depends on sample size, density, and the strength requirements of the products carbon. For example, samples of low density (0.05 g/cc) phenolic foam with dimensions of 16" x 16" x 2" may be heated at a rate of 100°C/hour to 1000°C to effect the conversion to carbon.

The preferred pyrolysis schedule for any starting foam represents a compromise between product yield and properties. When 0.25 g/cc carbon foams were prepared from phenolic foam at a heating rate which gave a 90 percent yield of crack-free pieces, the compressive strength ranged from 500 to 820 psi. When the heating rate was extended over twice that period of time, the yield of crack-free pieces was increased only slightly but the compressive strength was nearly doubled, to 1000 - 1480 psi. On the other hand, when the original heating rate was doubled, the yield was less than 50 percent acceptable pieces.

The weight and volume changes which occur during pyrolysis vary with the density of the precursor foam. The high density phenolic foams lose 60 percent of their weight and 70 percent of their volume when heated to 2600°C. The shrinkage is anisotropic to the extent that the change in length is usually 3 or 4 percent greater than the change in diameter. Table I shows the changes in weight and density for high density phenolic foam (0.25 g/cc) at various temperatures from 100° to 2600°C. The cyclic behavior of the density indicates that the major weight and volume losses do not occur at the same temperatures. Most of the work was done with semi-cylindrical phenolic foam samples approximately 19" diameter and 7" long; but the trends have been verified with samples as long as 24". The results at 2000°C and higher are averages of at least 30 semi-cylindrical samples 19" diameter and 7" long. The lower temperature studies involved no fewer than four samples.

TABLE I
Heat Treatment of 0.25 g/cc Phenolic Foam

Temperature °C	Weight Loss, %	Density Change, %
100	2.7	- 1.4
200	5.6	+ .6
300	14.1	- 4.7
400	26.8	- 2.9
500	44.2	-12.8
600	50.0	- 8.2
700	54.9	- 4.2
800	54.4	- 1.2
900	56.0	- 0.9
1000	56.1	0.1
2000	60	- 3.0
2200	61	- 1
2400	61	+18
2600	61	+26

The data in Table I are characteristic of phenolic foam over the entire range of densities; however, low density foam tends to shrink slightly more at treatment temperatures above 700°C.

B. PYROLYSIS OF URETHANE FOAM

The heat treatment of the urethane foams involves a two-step oxidation prior to pyrolysis in an inert atmosphere. The specific temperature and dwell time used in the polymerization-oxidation step varies with the size and density of the urethane precursor. Typically, the foam is held at 150°C and again at 250°C for 24 hours to prevent fusion during pyrolysis. The weight and volume changes which occur during pyrolysis to 1000°C are about 55 and 60 percent respectively. There is a density increase of about 10 percent for the low density, and 20 percent for the high density carbonized urethane foam.

Union Carbide has patents (2) granted and pending which describe in detail the preparation of organic precursor carbon foam.

III. PROPERTIES OF CARBON FOAM

The physical properties of the product carbon foams are dependent on the type, quality, and treatment of the precursor. The major apparent difference among the types of organic precursor is the average cell size of the product carbon (see Table II). The cell size of the carbonized urethane foam is 8 to 32 mils for the 0.05 g/cc density and approximately 8 to 16 mils for the 0.25 g/cc density; the phenolic precursor carbon has a 2 to 6 mil cell size in the low density foam and approximately 1 to 3 mils in the high density material.

TABLE II
Cell Size of Carbon Foam

Foam Precursor	Density	Cell Diameter
Urethane	0.05 g/cc	8-32 mils
	0.25 g/cc	8-16 mils
Phenolic	0.05 g/cc	2-6 mils
	0.25 g/cc	1-3 mils

The cell structures of these carbon foams are shown in Figure 1. The cells are football shaped with the major axes parallel to the foaming directions. The pyrolyzed foams are pseudomorphs of the parent foam.

The compressive strengths, defined as the point at which a change in slope of the stress-strain curve occurs; of properly prepared 1000°C carbon foam from phenolic and urethane precursors are given in Figure 2, for foams in the density range of 0.15 to 0.35 g/cc. The strength of the phenolic precursor carbon varies from 500 to 1900 psi over the density range; the strength of urethane precursor carbon is about one-half these values.

The ultimate compressive strength of the 0.35 g/cc phenolic precursor carbon foam is usually above 3000 psi. The strength of low density foam exhibits a greater degree of anisotropy than high density foam. The strengths of 0.05 g/cc carbon perpendicular and parallel to the foaming direction are 30 and 50 psi, respectively. Subsequent heat treatment of carbon foam to 2800°C results in no change in strength for the phenolic precursor carbon but does result in as much as a 70% reduction in strength for urethane precursor.

The thermal conductivity of the foam, determined by the Fitch method, is quite low, approximately 0.1 and 0.2 BTU/ft-F°-hr for 0.05 and 0.25 g/cc carbon, respectively. The high temperature thermal conductivity was determined by the cyclic phase shift⁽¹⁾ technique for a sample of 0.27 g/cc density phenolic precursor carbon foam. The data are shown in Table III. The thermal conductivity parallel to foaming is 10 to 25 percent higher than the conductivity perpendicular to foaming. In the direction of high thermal conductivity, the range is 0.5 to 0.8 BTU/ft-F°-hr in the temperature range of 1400° to 2100°C. Other properties of material from the same sample are shown in Table III.

TABLE III

Properties of 0.27 g/cc Phenolic Precursor Carbon Foam

Property	Direction Perpendicular	Direction Parallel
Density, lb/ft ³	0.27 g/cc	0.27 g/cc
Compressive Strength, psi	1,350	2,150
Shear Strength, psi	725	570
Thermal Conductivity, BTU/ft-F°-hr		
RT →100°C	0.18	0.20
1400°C	0.47	0.53
1800°C	0.45	0.57
2100°C	0.60	0.75

Of particular interest is the high shear strength which demonstrates that when the material is used as an insulator, it can be firmly bonded to the surface to be insulated.

The permeabilities of various carbon foams are shown in Table IV along with the permeabilities of graphite and PC-45 a high density porous carbon. The best commercial grades of graphite with densities in the range of 1.6 to 1.73 g/cc have permeabilities in the range of 0.5 to 0.02 Darcy's. The permeability of phenolic carbon foam is in the range of 1.9 to 0.36 Darcy's, roughly an order of magnitude greater than that of graphite; the permeability of the urethane precursor carbon foam is in the range of 22.6 to 71.5 Darcy's, two orders of magnitude greater than that of graphite. Porous carbon, PC-45, has a porosity almost identical with that of the high density urethane precursor carbon, approximately 22 Darcy's.

TABLE IV

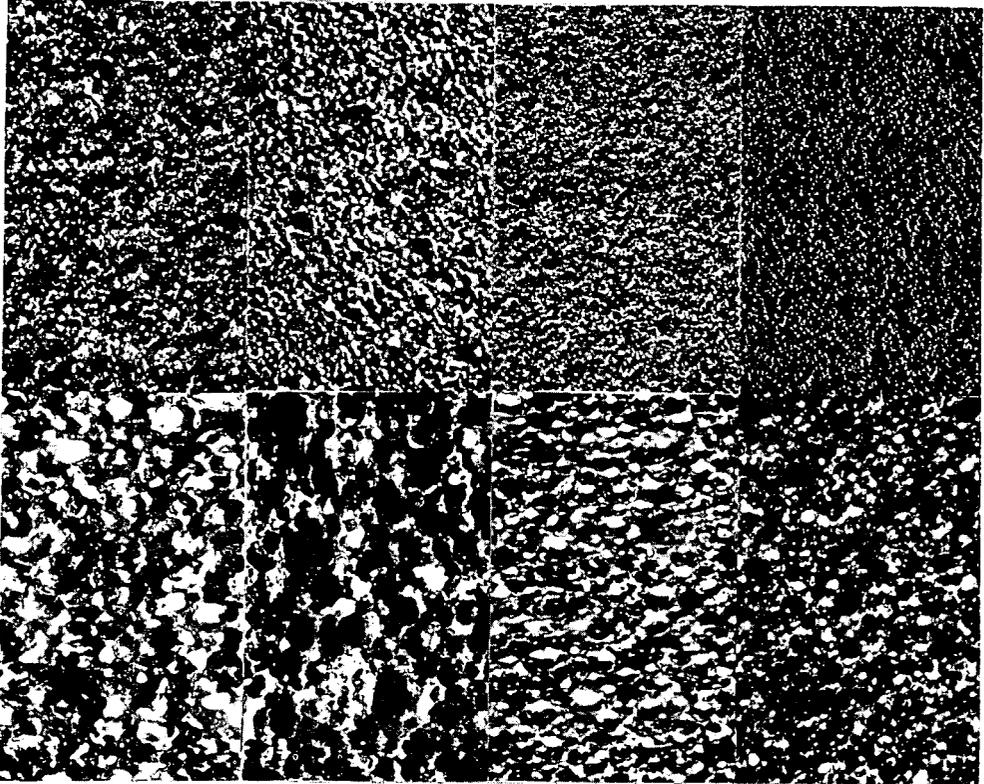
Permeability of Carbon Foam

Precursor Material 1000°C Treat	Density, g/cc	Permeability in Darcy's	
		Parallel to Foam	Perpendicular to Foam
Urethane	0.05	71.5	31.0
Urethane	0.30	24.3	22.6
Phenolic	0.08	1.9	1.1
Phenolic	0.30	0.95	0.36
PC-45	1.04	20	20
ATL Graphite	1.78	0.068	0.064

In summary, carbon foam is a light weight, high strength material which is stable above 2800°C. It may be used as an insulator, filter, or structural support material and is presently available in sizes as large as 14" diameter by 18" long.

Figure 1

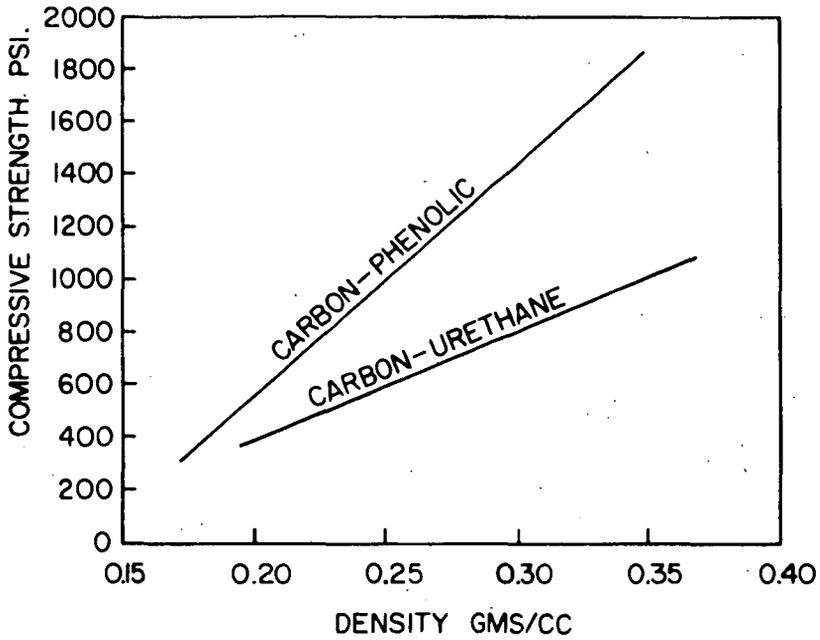
CARBON FOAM 1000°C HEAT-TREAT



The upper row is phenolic precursor carbons in both directions of 0.05 and 0.25 g/cc density. The lower row is corresponding urethane precursor carbons.

Figure 2

COMPRESSIVE STRENGTH VS. DENSITY
FOR CARBON FOAM



References

- (1) "Measurements of Thermal Diffusivity and Thermal Conductivity of Graphite with Carbon Arc Image Furnace," M. R. Null and W. W. Lozier, 5th Thermal Conductivity Conference, Denver, Colorado, October 20, 1965.
- (2) U. S. Patent 3, 121, 050; U. S. Patent 3, 302, 999; U. S. Patent 3, 387, 940.

Some Experimental Techniques Used in Carbon Reaction Studies

L. Kurylko, Stackpole Fellow
Combustion Laboratory, The Pennsylvania State University
University Park, Pennsylvania

R. W. Froberg, Research Scientist
Stackpole Carbon Company, St. Marys, Pennsylvania

R. H. Essenhigh, Associate Professor
Combustion Laboratory, The Pennsylvania State University
University Park, Pennsylvania

1. INTRODUCTION

Although research on carbon has proliferated unbelievably in the last decade, there are indications of a growing dichotomy between two somewhat disparate points of view regarding the objectives of the research. On the one hand, university-oriented work has tended to be of the so-called "pure" or "fundamental" variety, often concentrating on small, very specialized points and utilizing many highly-elaborate techniques of an impressive level of sophistication. Industrial research on the other hand has, of necessity, to be of an applied nature, and often contains a high component of empiricism. These latter are sometimes referred to as engineering studies. The two respective points of view can be summed up in the phrases "Know Why" and "Know How."

It is a truism to say that the Know Why ought to illuminate the Know How, but recently there has been increasing skepticism of the part of some investigators that this is possible, and in this lies the source of the dichotomy. The problem is best seen by way of an example. In the measurement of activation energies, for instance, it seemed possible at one time that if the energies could be measured for different carbons under known conditions then the value, or range of values for the different carbons, was likely, to imply a particular mechanism. However, recent work [1] on the adsorption isotherms at low temperatures have shown the evident existence of a range of possible and overlapping alternate steps in the reaction each with its own individual energy. Therefore, it would seem that any activation energy not determined by these very precise methods must be only an average with an evident ambiguity of interpretation. The problem is then compounded when we consider that, when the detailed mechanisms were elucidated, this was by using ultrapure, highly specialized "research" carbons, such as Spheron 6, whereas industrial carbons have the additional complexities of different degrees of graphitization, accessibility, and reactivity, of binder and filler, together with modifying factors due to ash, permeability, porosity, isotropism or lack of it, etc. It is, therefore, a very real question whether the "pure" and so-called "engineering" studies really have sufficient in common to make attempts at cross-correlations and interpretations worthwhile.

As we have ourselves been concerned primarily with more "engineering" studies, we have therefore been somewhat exercised by this very question. Whilst not finding the description sufficiently important to quarrel about, it does nevertheless seem to us that our studies do in fact lie more or less between the two (what might therefore legitimately be called technological studies if one looks for a name). Our conclusions are that cross-correlations between studies of different levels of fundamentality are in fact possible, if applied with caution; and also that the unfortunate dichotomy that has started to develop will have to be closed.

The first consideration to be examined was whether the lack of interpretation in terms of fundamental mechanisms actually mattered. After all, the carbon industry has existed quite successfully for decades (centuries if one includes charcoal burning) without access to the information now being developed. However, the last 10 or 20 years has been an increasing sophistication in carbon manufacture, paralleled by much more varied and extreme uses, which has been itself largely the stimulus for the increased research; and it is clear that we now require a matching sophistication in knowledge of reaction behavior of actual carbons as manufactured for industrial processes.

Now, when we consider the behavior of industrial carbons with the attendant complexity of reaction in real situations, it seems to us that, so long as we can unravel the complexity due to the real situation, the only factor likely to disturb any mechanistic interpretation is the parameter modification due to the presence of two or more components (such as filler, binder, ash, etc.). Here it is true that kinetic parameters such as frequency factors, activation energies and so on will be averages of some sort; but this does not seem to be an insuperable objection since all it means is that behind the average we measure is some (unknown) statistical distribution of the parameter values. Any such statistical distribution must itself be determined by composition and other material properties; and the use of an average value does not seem to be any less relevant than the use, for example, of average properties of gasses such as velocity, or energy, or temperature. In the case of carbon studies, the more fundamental work may in time determine the statistical distributions of the relevant parameters due to variable material compositions and properties, and this will be of immense assistance in filling out any interpretation. In the meantime, lacking such information, we may legitimately assume (till proved otherwise) that the background distributions are rather narrow, so that any kinetic constants obtained by experiment are presumed to be close to unique--and therefore mechanistically interpretable--values.

To us, the more important problem at this stage is the unambiguous experimental determination of these (statistical) property parameters, and this is primarily a matter of experimental design. The problem is that many of the more applied (engineering) methods of experimentation lack definition so that there can be considerable uncertainty what property a measured value is really related to--even before one starts to consider the problem of the statistical average. The activation energy, for example: it is true that the value measured is the weighted statistical average of all possible adsorption energies; or could it be the average of all possible desorption energies? This is typical of the type of ambiguity that can arise.

To eliminate such ambiguities requires good experimental design, and this is jointly a matter of technique and of instrumentation. Recently we described a technique, with some brief outline of the instrumentation that we were able to show did eliminate much ambiguity [2]. In this paper our purpose is to re-summarize the technique (for completeness) and to amplify the information on the instrumentation in the belief that this may be of value to those concerned with the more precise, unambiguous "engineering" values of kinetic constants, but still measured on such a basis that there is some hope of applying a valid mechanistic interpretation. This is not to say that we think this is the only technique able to develop kinetic information on the basis required, but we believe it to be the most fully developed so far. The point we are making is that the time has come to start closing the gap between the "fundamental" and "engineering" studies on carbon reactions, so that the latter are as valid as the former for obtaining kinetic data and mechanistic interpretations of behavior.

2. ESSENTIALS OF THE EXPERIMENTAL METHOD

2.1. General - In the studies of heterogeneous reactions it is of great importance that experimental data are obtained which define both the state of the reacting surface and the state of the fluid that influences the course of the reaction. This also requires a precisely known solid geometry. The need for meaningful data in research on carbon-oxygen reactions is especially acute; the reason being that within a temperature span of several hundred degrees and a pressure span of one atmosphere, many of the elementary steps of reaction change from dominant to nondominant, e.g., adsorption of reactants, desorption of products, diffusion of reactants to the surface, diffusion of reactants through the carbon, etc. Coupled with the problems of heat exchange and continuous changes in the diffusion rates and surface area that occur due to consumption of carbon, an experimenter is faced with a formidable task of analyzing the kinetics of the reaction [3]. An experimental system is thus required capable of generating data whose interpretation would be unambiguous.

To determine process kinetics of carbon reactions information is needed about the sample weight, rate of weight change, temperature of carbon and gas, sample geometry, gas composition, and the surface area and permeability of the carbon. To obtain such data we have developed a technique in which a carbon sample is suspended in a vertical furnace, continuous records of sample weight, sample geometry, and sample and gas temperatures are obtained (Fig. 1). In addition gas composition inside and around the sphere can be measured at regular time intervals. Other data which are obtainable on samples that were partially reacted then quenched at the desired level of burnout are an independent check of porosity profiles and the BET surface area.

In the experimental technique which was developed a carbon sphere is used because of its well defined geometry and symmetry during burnout. The reactant flow velocity is kept low so that the heat and mass transfer conditions are well defined. From continuous measurement of weight and diameter the average density change can be established. When temperature measurements are included, the Arrhenius plot of reaction rate can be developed, together with information about the heat release rates inside and outside the carbon sample.

2.2 Temperature Measuring System - The temperature of the carbon sphere was measured by imbedded thermocouples. A small hole about 0.3 mm. in diameter was drilled in the carbon sphere. One lead of a Pt-Pt-13% Rh Thermocouple was threaded through the hole and a butt weld was made to the other lead. Then the hot junction was pulled back to the desired location in the sphere. To insulate the thermocouple leads from the sphere, they were shielded by quartz capillary tubing or flame plated with silica prior to insertion into the sphere. As many as three thermocouples were used to record the inside temperatures at one time.

The thermocouple leads above the sphere were threaded through an eight-inch long ceramic support rod. Alternatively, a section of a metal-shielded thermocouple was stripped of its metal cladding and ceramic insulation to expose thermocouple leads ready for insertion. An ice bath was used for the cold junction.

The gas temperature was measured using shielded thermocouple assemblies with bare hot junctions. Micromanipulators were used to position the beads at precise locations around the carbon sphere.

The temperature recording system consisted of millivolt suppression circuits and amplifiers for adjustment of the recording scale, a 24 channel recording oscillograph, and a precision potentiometer for independent spot checks of thermocouple outputs.

2.3. The Weighing System - The weighing of the carbon sphere was made using a conventional analytical balance with an automatic recording attachment. A continuous record of the sample weight was obtained either on a potentiometric recorder or using one of the channels in the recording oscillograph. Typical reduced records of weight loss and temperature measurements are shown in Figure 2.

In the base of the balance a hole was drilled to receive a ceramic rod that was connected to one of the balance pans. At the other end of the ceramic rod was a small platinum wire loop to which the ceramic rod with the thermocouples and the carbon sphere was connected. The carbon sphere was thus suspended from the balance on two ceramic rods connected by hooks and loops. This arrangement permitted easy disconnection of the thermocouple assembly from the balance and allowed the furnace to be moved for insertion of a new test sample.

Prior to each run the test samples were weighed on an analytical balance to determine the exact original weight. Also with the cold sample suspended from the balance, a calibration run was made to simulate weight changes that would occur during sample burnout by adding weights to the proper pan.

2.4. The Sample Size Measuring System - The diameter of the carbon sphere was measured with a micrometer prior to placing of thermocouples in the sphere. After the insertion of the sphere in the furnace and its suspension from the balance, the size changes would be measured optically. To do this a telescope-projector was constructed through which one could measure the sphere visually or obtain a photograph at desired time intervals. Figure 1 shows the schematic of the size measuring system. Above the top of the furnace we have a 45° mirror which sends a projected light source through a transparent watch glass (with a hole to allow the ceramic rod to connect to the rod from the balance). The light passes vertically through the furnace tube exiting through a quartz window at the bottom of the furnace. A second 45° mirror connected to a movable telescope deflects the light through an iris diaphragm and focusing eye piece to a ground glass screen. After focusing, the ground glass screen was normally removed and a camera inserted in its place.

When the temperature of the carbon was less than about 800°C , a 1500 joule flash was used to project the shadow of the sphere onto the film. At higher temperatures the radiation intensity from the carbon sphere was sufficient for self-recording of the sphere image on ASA 125 film. An electric sequential timing switch was used to trigger the flash gun, camera, and a timing mark on the oscillograph. During a normal run the sphere was photographed about sixty times at X8 magnification.

2.5. The Furnace and Gas Feeding System - The electrical furnace contained a vertical tube which was two (2) inches in diameter by eighteen (18) inches long. The hot zone of nearly uniform temperature was about twelve (12) inches long located in the center of the furnace. On the bottom of the furnace was a water cooled brass cap containing various gas inlet ports and a quartz window in the center. One thermocouple extended through the brass cap to measure gas temperatures below the suspended carbon sphere. The furnace temperature-control thermocouple was located behind the heating elements. A proportional band controller was used to keep the furnace temperature constant. The top of the furnace was covered by a loose-fitting transparent glass lid. A hole was drilled in the lid to allow thermocouples as well as the carbon support rod to pass through.

The gasses were normally passed through molecular sieves and Drierite columns before being metered through rotameters and passed to the furnace. The pressure of gas entering the rotameters was also monitored.

3.6. Gas Sampling - A gas sampling system was developed in which a 0.1 mm. I.D. capillary steel tube was attached to the thermocouple assembly and suspended from the balance together with the carbon ball.

Gas was withdrawn both from the center of carbon sphere and from the vicinity of the sphere and analyzed using a Fisher gas chromatograph. By taking samples at regular intervals, changes in the gas composition inside the furnace could be established.

3. AMBIGUITIES AND FAILURES OF METHODS

3.1. Thermocouples - A thermocouple inserted in a carbon sphere or in a gas stream will under many circumstances indicate a temperature that is different from the true temperature of the solid or fluid at the hot junction. First, a large thermocouple will represent a large heat sink and, therefore, changes in the temperature of the material being measured will not be accurately reflected in changes in the thermocouple's readings. The goal therefore is to use as small a thermocouple as possible. Radiation exchange between the thermocouple and the surroundings is another source of error. A thermocouple exposed to walls which are at different temperature than the surrounding gas will indicate an intermediate temperature. Here it is also desirable to have a thermocouple as small as possible--the smaller the diameter of the hot junction the smaller will be the error. When the thermocouple leads are less than about 0.25 mm. and unsupported in the length of several centimeters, a serious error may develop due to vibration and movement of thermocouple leads. The vibrating thermocouple will indicate temperature fluctuations when in reality there are none. A good reference on thermometry in flames is "Flame Structure" by Fristrom and Westenberg [4], although they do not include discussion of the suction pyrometer (or HVT).

In measuring the internal temperature of an electrical conductor (like carbon) the thermocouple leads, except for the hot junction, have to be insulated from the conductor because the thermocouple will otherwise indicate some averaged temperature of the conductor rather than the temperature of the hot junction.

Another source of error in the measurement of temperature with very fine thermocouples are stray and induced currents due to furnace heating circuitry, on-off controller switching, starting and stopping of miscellaneous electrical equipment, etc. Here the recommendation is use grounded and shielded extension and thermocouple leads, amplifiers with high frequency noise filtering devices and constant voltage supply transformers. In our experience we had to use all these devices.

3.2 Gas Sampling - To obtain an accurate concentration profile while a gaseous chemical reaction is taking place, is quite difficult. First, the flow pattern of the gas around the sampling probe should not be significantly affected. Second, the chemical reaction must be quenched; otherwise, the composition of the gas as given by subsequent analysis will not be the same as that which enters the probe.

We found that during sampling of the gas from inside the carbon sphere, the hole through which the probe was inserted became enlarged. This indicated, of course, that, during sampling, a disturbance of the gas concentration profile occurred. Further information on gas sample probes is given in reference (4.).

3.3. Flow Pattern Inside the Furnace - The design of the gas feed system, the size of the furnace, and the gas throughput rate significantly influence the concentration and flow pattern of gases inside the furnace. Because the furnace, feed lines, tees, filters, etc., act as reservoirs, the change in gas concentration at the carbon sample surface normally does not follow a discontinuous change as one switches from inert to reacting gas or vice versa. After opening a valve, it is, therefore, most desirable to know when the concentration of the reacting gas reaches 95 or 98 percent of the desired value. Indeed, at low flow rates and with large holdup vessels it may take half an hour or longer to achieve a desired gas concentration around the sample.

To determine whether the flow pattern inside the furnace meets the desired characteristics, a plot of logarithm of concentration at the desired location versus time will indicate either the degree of back mixing, or the extent to which the reactor approaches plug flow conditions. The steeper the negative slope on the plot described, the closer the reactor approaches plug flow conditions (Fig. 3). If the concentration of the gas to be displaced, (nitrogen), approaches an asymptotic condition, then there exists the possibility of dead-end hold-up storage zones in the feed system, or of leakage of undesirable gas into the system.

4. SOME RECENT RESULTS

During the five years that the experimental technique has been in operation, and in process of gradual improvement, several significant experimental findings about carbon-oxygen reactions have been obtained.

First, the simultaneous measurement of both sample size and weight provided a direct method by which the data could be separated into the three zones of reaction. Thus, it was possible to construct an Arrhenius plot of the rate data in which the three major zones could be identified. The Arrhenius plot was constructed using the true sample temperature (not the furnace or gas temperature) which was measured by thermocouples within the carbon sphere. No meaningful analysis of the effect of oxygen concentration on the apparent reaction rate could be made without the sample temperature measurements. It was found that the apparent rate increased with increasing oxygen concentration but so did the sample temperature. The net result was that, regardless of the oxygen concentration, all data described a single rate curve at low temperatures (Zone I). It was concluded, therefore, that the chemical reaction was zero order.

In the further analysis of the data a definite conflict was apparent. If the reaction order was truly zero in the chemically dominant regime, why did the temperature of the carbon sphere reacting in oxygen exceed its temperature when reacting in air? This conflict was resolved only after temperature profile measurements were made of the sphere and of the surrounding gas. From these, heat exchange balances were made between the reacting sphere and the surrounding environment using a digital computer. These calculations revealed that in Zone I the heat release for the carbon-oxygen reaction amounted to that required to convert all carbon to CO_2 within the carbon sphere. But, for the case when oxygen concentration was low, such complete burn-up of the primary reaction product, CO, did not occur within the carbon boundaries; thus the temperature of the carbon reacting in air did not rise to as high a value as it did in pure oxygen.

In Zones II and III, the burn-up of carbon monoxide occurred outside the carbon sphere, as substantiated by gas sampling and temperature profile measurements and confirmed by heat balance calculations. It was also found that within a certain carbon porosity range a region of combustion instability existed between Zone II and Zone III during which the temperature of carbon oscillated by as much as 70 degrees and with a period of up to 100 seconds (Fig. 4).

5. CONCLUSIONS

Temperature, weight and size measurements of reacting carbon spheres can be made simultaneously in an electrically heated furnace. Combining these measurements with gas sampling, surface area, and density profile determinations, the progress and process of heterogeneous solid-gas and of subsequent gas phase reactions can be established. Measurements of atmospheric conditions gave results revealing the true

order of chemical reaction of carbon with oxygen, allowed the determination of the depth of penetration of the reaction zone into carbon, established the presence of an oscillatory combustion phenomena, etc. Problem areas to be encountered by the experimenter with the above techniques are pointed out.

These results show the importance and value of adequate experimental techniques designed to deliver results whose interpretation will be unambiguous.

REFERENCES

1. Bansal, R. C., F. J. Vastola, and P. L. Walker, Paper C130, Eighth Carbon Conference, State University of New York at Buffalo, June 19-23, 1967.
2. Essenhigh, R. H., and R. W. Froberg, Papers C111 and C112, Eighth Carbon Conference, State University of New York at Buffalo, June 19-23, 1967.
3. Wicke, E., Fifth Symposium on Combustion, New York: Reinhold, p. 245, 1955.
4. Fristrom, R. M. and A. A. Westenberg, Flame Structure, McGraw-Hill, New York, 1965.

ACKNOWLEDGMENTS

This work was carried out in the Combustion Laboratory of the Department of Fuel Science, The Pennsylvania State University, for the Office of Naval Research under Contract NONR 656-29 whose support is acknowledged. We also have pleasure in acknowledging joint support for the project from the Stackpole Carbon Company, St. Marys, Pennsylvania, by provision of Research Fellowships to the first two authors.

ON THE USE OF PHOSPHATES TO INHIBIT OXIDATION OF INDUSTRIAL CARBONS

Robert W. Froberg

Stackpole Carbon Company, St. Marys, Pennsylvania 15857

I. INTRODUCTION

The use of additives to inhibit the oxidation of carbon-graphites has been well-known in the industry for many years. Among the earliest to report on the use of phosphorus-containing additives was Wicke [1]. He studied the effect of phosphoryl chloride which was added to the gas phase during oxidation. Others who have examined the effects of oxidation-inhibiting additives include Arthur [2,3], Hadman et al [4], Day [5], and Hedden [6].

The exact mechanism by which phosphates, in particular, inhibit the oxidation of carbon is still a moot question. However, it is generally agreed that both chemical and physical processes are involved. That is, the phosphate covers potentially active sites on the carbon surface both by a strongly chemisorbed layer [7] and/or a physical barrier of either a glassy or crystalline nature as in the case of some oxides [8]. The latter would appear to be the case in the work reported by Paxton [9].

Factors which determine the effectiveness of a given phosphate treatment include the chemical composition of the impregnant, the molar concentration of the starting solution, the amount of material finally deposited within the pore system of the carbon, the distribution of the treatment within the carbon, and the reactivity of the original carbon-graphite [10-13]. Of importance also is the permeability of the original carbon to the solution or liquid used for the impregnation.

The oxidation of untreated carbon at some temperature is usually expressed as the Specific Reaction Rate [14, 15]. That is, weight loss per unit time per unit area [15]. The area used to calculate the rate may be the geometric or apparent surface area of the sample [14], the B.E.T. or nitrogen adsorption area, or some fraction of the total surface area [16]. There are certain advantages and shortcomings involved in the use of all of these [1, 17]. The rate of reaction is known to be dependent upon both chemical and diffusional mechanisms [18]. In addition, the rate of oxidation of an untreated carbon at temperature below 1800°F may be strongly affected by the nature of the carbon itself. Such variables as heat treatment history, impurity content, crystallinity, porosity, and permeability are all inherent properties of the sample material which can, in fact, influence the rate of oxidation [14, 17, 19].

In the case of a treated material, an additional set of variables (mentioned earlier) are introduced which are concerned with impregnant and its interaction with the base material. These new variables are then added to the list given above to produce the entire collection of factors which may be changed so as to affect the resulting reaction rate of treated carbon with oxygen. It is obvious that the system must be simplified greatly by making many of these quantities a constant before meaningful data may be obtained on the reaction.

The work described in this paper concerns the evaluation of phosphate impregnants for improving the oxidation resistance of commercial carbon-graphites. Impregnation of the carbon may be done by a variety of methods including molten

salts, water-or acid-based solutions, and vapor deposition. The technique used to treat the materials described was a solution impregnation via a vacuum-pressure cycle. The objective herein is to examine the experimental results and discuss some of the factors which make these phosphate treatments effective inhibitors of the oxidation of carbon.

II. EXPERIMENTAL

The TGA equipment used in this work is shown in Fig. 1. It is simply an electrobalance (Cahn RH) mounted above a vertical tube furnace. The sample is suspended within the furnace, from the balance, on a Mullite rod and the sample weight is continuously recorded as the material is burned off. The furnace control is such that the temperature may be varied with a preselected program or held constant. For the purpose of this work, the furnace temperature was held constant at 1200°F for all the runs in order to minimize the variables described earlier.

The samples were preheated in nitrogen before the oxidizing gas was admitted into the tube furnace. For this work, only air was used to burn the samples. The equipment, however, includes the necessary metering system to feed various oxygen-nitrogen mixtures into the furnace, if required.

The test data are reported as the time required for ten percent burnoff of the sample under test. With certain qualifications, the longer it takes the material to lose ten percent of its original weight, the more effective is its oxidation resistance (OR).

All samples used were in the form of 3/4-inch cubes. With a few exceptions, the same base material was used for all tests in order to minimize the variation of the data due to the reactivity of the carbon.

III. RESULTS

Table I is a compilation of the primary experimental data to be discussed in this paper. Some additional data will be presented later to clarify particular points. The base grades and treatments are given letter names because the nature of these materials is not vital to following the discussion.

TABLE I
EXPERIMENTAL RESULTS FOR 1200°F IN AIR

<u>Base Grade</u>	<u>Treatment³</u>	<u>% Treatment</u>	<u>Hours to 10% Burnoff*</u>
G ¹	None	-	0.08
G	A	10.4	54
L ²	None	-	3.4
L	A	7.5	54
L	B	4.65	103
L	C	8.2	106
L	D	9.0	134
L	E	12.6	36
Glassy Carbon	None	-	10.5

1 = graphitized material, pitch-bonded natural graphite

2 = graphitized material, pitch-bonded lampblack

3 = all treatments are metallic phosphates

*Average values

IV. DISCUSSION

The data given in Table I represent average values for a number of samples of each material. This is a point worth emphasizing since the spread in experimental data is usually about 20 percent. Therefore, a reliance upon only a few data points may be very misleading when one draws conclusions concerning the OR effectiveness of a given treatment and/or material.

A. Uniformity of Treatment:

It is usually not sufficient to know only how much of a given treatment is deposited in the carbon (percent pickup), but one should also have some information concerning the distribution of the impregnant within the carbon. To exemplify this point, data are presented in Fig. 2, which resulted from successive weighing and grinding of a number of treated cubes. It is clear from the curves in Fig. 2 that the local concentration of impregnant decreases toward the center of the cubes. Several reasons for this uneven distribution may be suggested: first, the degree to which the impregnant penetrates the sample is determined by the permeability of the carbon and the viscosity of the solution; and, second, the uniformity of the treatment may be adversely affected if the impregnant is a suspension and not a true solution. If the suspension is coarse enough, the solid particles may be filtered out and only the clear liquid may, in fact, reach the center of the sample. It is noted, however, that treatments used in this work were true solutions. Another reason suggested for this concentration gradient within the treated carbon is that when the treated material is being dried, the impregnant may migrate toward the surface of the sample. Whatever the reason, it is clear that, for the data shown in Fig. 2, there is a concentration gradient. The effect that this has on OR is obvious if the treatment is in the form of a shell and if the oxygen penetrates the pore system beyond the treated shell. Therefore, a large amount of treatment does not necessarily insure a high OR. An exception to this occurs when the pores are physically blocked as seems to be the case for the molten salt treatments described by Paxton [9].

B. Hygroscopic Behavior:

A characteristic of many phosphate treated carbons, which is undesirable from the viewpoint of product use, is the tendency to absorb moisture and ultimately exude droplets of sticky liquid from the pore mouths. It is this behavior that rules out the use of a number of treatments which are, in fact, quite effective in inhibiting the oxidation reaction. For example, the material called "Treatment D" (line 5, Table I) is quite reasonable as an OR treatment. However, the treated carbon becomes tacky and moist after several days in room air.

An improvement can be made with coatings, cure cycles, and storage conditions in that some delay can be realized in moisture pickup. These measures, however, usually do not eliminate the problem. The solution is, of course, to find a phosphate treatment which is not hygroscopic while, at the same time, it possesses excellent OR properties.

While certain phosphate compounds such as those of tungsten and molybdenum are apparently hygroscopic, it also is possible that some other treatments exhibit this behavior because of excess phosphoric acid within the finished piece. Therefore, in evaluating the moisture pickup behavior of phosphate treatments, it is advisable to consider the excess acid present, if any.

C. Glassy and Crystalline Phosphates:

Another property of the phosphate treatments which increase the OR of carbon is the structure of the material deposited on the surface of the carbon. Many treatments examined in this work were obviously glassy or crystalline (grainy) when examined visually, after cure. In general, it was found that glassy deposits offered more protection to the carbon than did those which appeared grainy and discontinuous. This fact would tend to support the view that the oxidation is inhibited by means of a physical barrier of phosphate glass between the carbon surface and the oxidizing gas. This is shown in Table I, as line 7 (glassy deposit) and line 8 (grainy deposit) with 134 and 36 hours to 10 percent, respectively.

D. Stability of the Treatment:

One of the more obvious points which can be made in this discussion is that the particular phosphate used as an impregnant must be stable at the test temperature. To prove that the interaction between the carbon surface and the phosphate material does not change the stability of the treatment, several compounds known to be unstable at 1200°F were run and the OR, measured as time to 10 percent weight loss, was very poor (less than 24 hours).

E. Reactivity of the Carbon:

The results from this work indicate that with treatment levels used in the samples tested for OR, the impregnant does not completely mask the reactivity of the basic carbon material. In the case of the untreated natural graphite grade G, the reactivity was so high that it ignited at 1200°F in air. On the other hand, the untreated lampblack material L did not, in fact, ignite, although the sample temperature rose about 40°F above the furnace temperature. These results are given in Table I in lines 1 and 3, respectively. The meaning of these results is that the natural graphite-based material was of such a reactivity that the heat-release rate greatly exceeded the heat-loss rate. Thus the sample temperature rose to the ignition temperature and from there to the maximum obtainable temperature which, in this case, would be in the bulk-diffusion combustion region, or Zone III. The lampblack-base material was less reactive and showed none of the behavior described above. For a detailed explanation of the significance of this behavior, the reader is referred to an excellent text by Vulis [20].

The same treatment was given each of these base grades and the treated pieces were then tested for OR. As expected, the treated grade G reacted faster than the treated grade L (lines 2 and 4, Table I), even though the former contained almost twice the amount of treatment as the latter.

When industrial carbons are oxidized, it is generally agreed that there is usually a preferential attack on the binder [21]. In the oxidation of phosphate treated carbons, similar results have been noticed. Here again, at the treatment levels used in this work, the phosphate failed to completely mask off the basic reactivity of the materials.

For the purpose of completeness, glassy carbon material was also oxidized (line 9, Table I). This impervious material ran 10.5 hours to 10 percent weight loss. It would seem that from the viewpoint of OR, phosphate-coated glassy carbon would be quite acceptable. In a practical sense, however, application and fabrication problems would make this an unlikely choice.

V. CONCLUSIONS

When evaluating phosphate treatments for oxidation resistance, one should have information not only on the total amount of treatment within the carbon but the distribution of that treatment as well. Such information could help to explain results which otherwise would appear quite contradictory.

The factors which determine the effectiveness of a particular OR treatment, other than percent pickup and distribution, include the glassy properties of the treatment, the thermal stability of the compounds formed at the test temperature (1200°F in this work) and, in some cases, the reactivity of the base grade.

Properties other than OR may disqualify an impregnation from being considered for commercial use. In the case of phosphates, the tendency to exude a sticky solution is usually the most troublesome behavior.

VI. REFERENCES

- [1] Wicke, E., "Fifth Symposium on Combustion," New York: Reinhold, p. 245, 1955.
- [2] Arthur, J.R., Trans. Faraday Soc., 47, 164, 1951.
- [3] Arthur, J.R., J. R. Bowering, J. Chim. Phys., 47, 540, 1950.
- [4] Hadman, G., H. W. Thompson, and C. N. Hinshelwood, Proc. of Royal Soc., (London), A137, 87, 1932.
- [5] Day, R.J., Ph.D. Thesis, The Pennsylvania State University, 1949.
- [6] Hedden, W.L., G. J. Dienes, Advances in Catalysis, 9, 398, 1957.
- [7] Pallmer, P.G., Carbon, New York: Pergamon Press Ltd., 4, p. 145, 1966.
- [8] Schultz, D.A., P.H. Higgs, and J.D. Cannon, authors, "Oxidation-Resistant Coatings for Graphite," WADD TR61-72, Vol. XXXIV, Union Carbide Corp., June, 1964.
- [9] Paxton, R.R. and G.I. Beyer, U.S. Patent 3,342,627, 1967.
- [10] Woodburn, J., and R.F. Lynch, U.S. Patent 2,685,539, 1954.
- [11] Woodburn, J., and R.F. Lynch, U. S. Patent 2,685,540, 1954.
- [12] Woodburn, J., and R. F. Lynch, U.S. Patent 2,685,541, 1954.
- [13] Woodburn, J., and R.F. Lynch, U.S. Patent 2,685,542, 1954.
- [14] Walker, P.L., F. Rusinko, and L.G. Austin, Advances in Catalysis, XI, 134, 1959.
- [15] Khitrin, L.N., "Sixth Symposium (International) on Combustion," New York: Reinhold, 1951.
- [16] Lain, N.R., F. J. Vastola, and P.L. Walker, J. Phys. Chem., 67, p. 2030, 1963.
- [17] Austin, L.G., Ph.D. Thesis, The Pennsylvania State University, 1961.
- [18] Essenhigh, R.H., R. Froberg, J.B. Howard, Ind. Eng. Chem., 57, p. 33, 1965.
- [19] Gregg, S.J., and R.F.S. Tyson, Carbon, New York: Pergamon Press Ltd., 3, p. 39, 1965.
- [20] Vulis, L.A., Thermal Regimes of Combustion, New York: McGraw-Hill, 1961.
- [21] Froberg, R.W., Ph.D. Thesis, The Pennsylvania State University, 1967.

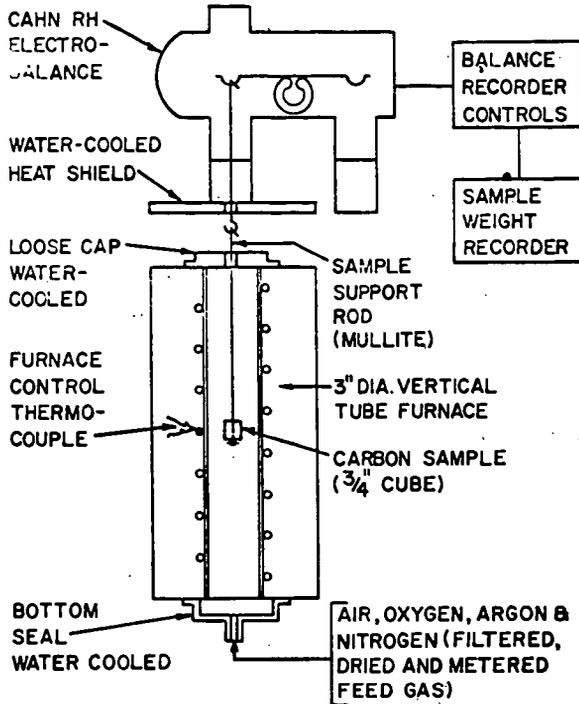


FIG. 1 OXIDATION RESISTANCE TEST SYSTEM

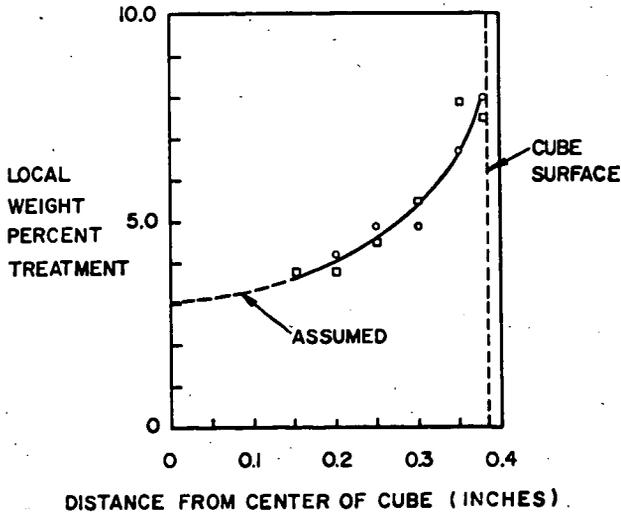


FIG. 2 LOCAL DISTRIBUTION OF PHOSPHATE TREATMENT WITHIN CUBE OF GRADE L (LAMPBLACK BASE)