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By

P. L. Walker, Jr., J. F. Rakszawski and A. F. Amington



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Distinguishing Between Graphitic and Amorphous Carbon

By P. L. Walker, Jr., J. F. Rakaszawski, and A. F. Armington

THE ability to distinguish between amorphous carbon and graphitic carbon (pure graphite) is a practical necessity. For many applications, graphite is the premium product because of its higher electrical and heat conductivity, lubricating properties, lower reactivity to gases, greater thermal-shock resistance, and superior machinability.

Biscoe and Warren¹ and Franklin,² among others, have shown that both amorphous carbon and graphite are composed of essentially parallel layer planes, each layer plane being in turn composed of a number of condensed benzene rings. However, in amorphous carbons the stacked layer planes are found to be randomly oriented, whereas in graphite the layer planes have a fixed "three dimensional" order. The order affects the spacing between layer planes, which in turn is thought to account for the majority of the differences in properties between these two forms of carbon.

Amorphous carbon varieties are numerous and include all coals, cokes, pitches, and carbon blacks. Graphitic carbon is less plentiful and, at the moment, is taken as the carbon that has the smallest spacing between layer planes.² Ceylon natural graphite is an example. Carbons are also found that run the gamut between completely amorphous and completely graphitic material. These intermediate carbons

A comparison of estimations of graphitic carbon by X-ray diffraction and a recently suggested ASTM "float and sink" test.

show a degree of "three dimensional" ordering, usually produced by heating an amorphous carbon to temperatures above 2000 C.^{3,4} A mechanical mixture of an amorphous carbon and Ceylon natural graphite can also be considered an intermediate carbon insofar as its over-all properties and X-ray analysis are concerned.

Classically, the method used for the distinction between amorphous and graphitic carbon is based on the fact that graphite can be converted to graphitic acid by strong oxidizing agents whereas amorphous carbon is unaffected.⁵ However, this technique has been found by numerous workers,⁵ including the present authors, to be a time-consuming, tedious, and sometimes dangerous procedure, which is not practical as a routine test.

Recently ASTM Committee D-2 on Petroleum Products and Lubricants

published a suggested procedure for the determination of amorphous carbon.⁶ It is a "float and sink type of test that" uses ethylene bromide (specific gravity 2.18-2.19) as the separating fluid. It is based on the fact that graphite has a specific gravity of approximately 2.26, whereas amorphous carbons have a specific gravity of less than 2.18. However, the only type of separation that can be realized by this technique is that where the amorphous and graphitic carbon are in a mechanical mixture. If the amorphous and graphitic carbon are integrally mixed within the same crystallite (and, hence, particle), as is the case² for heat-treated carbons, these two types of carbon will not be separated by the above technique. It is from the above that the possibilities of using X-ray diffraction as the broad tool to determine graphitic carbon content are presented.

Results and Discussion

The flexibility of the X-ray technique can best be described by examining the shape of the (002) diffraction peak, Fig. 1, for sample No. 1, consisting of a mechanical mixture of 87 per cent amorphous carbon and 13 per cent graphitized carbon (itself not com-

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¹ J. Biscoe and B. E. Warren, "An X-Ray Study of Carbon Black," *Journal of Applied Physics*, Vol. 13, No. 6, pp. 364-371 (1942).

² Rosalind E. Franklin, "The Structure of Graphitic Carbons," *Acta Crystallographica*, Vol. 4, pp. 253-261 (1951).

³ W. D. Schaeffer, W. R. Smith, and M. H. Polley, "Structure and Properties of Carbon Black," *Industrial and Engineering Chemistry*, Vol. 45, No. 8, pp. 1721-1725 (1953).

⁴ A. E. Austin and W. A. Hedden, "Graphitization Processes in Cokes and Carbon Blacks," *Industrial and Engineering Chemistry*, Vol. 46, No. 7, pp. 1520-1524 (1954).

⁵ H. W. Abbott, "Encyclopedia on Chemical Technology," Vol. 3, p. 23, Interscience Encyclopedia, Inc., New York, N. Y. (1940).

⁶ ASTM Standards on Petroleum Products and Lubricants, Am. Soc. Testing Mats., p. 328 (1953).

P. L. WALKER, Head, Department of Fuel Technology, The Pennsylvania State University, State College, Pa., has had 20 publications in the general field of carbon.



J. F. RAKSZAWSKI, Graduate Assistant, Department of Fuel Technology, The Pennsylvania State University, State College, Pa.



A. F. ARMINGTON, Graduate Assistant, Department of Fuel Technology, The Pennsylvania State University, State College, Pa.



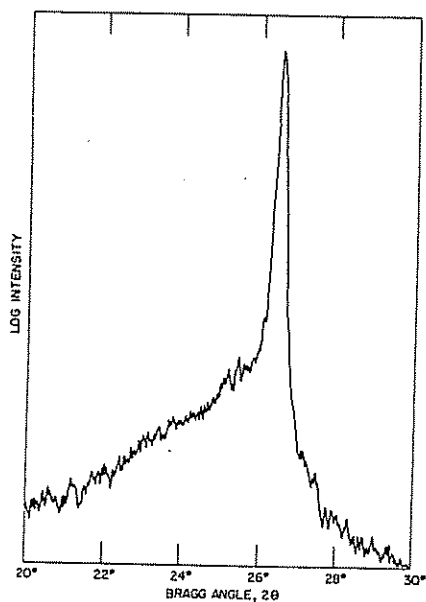


Fig. 1—X-ray Diffraction Pattern of the (002) Region for a Mechanical Mixture of Amorphous Carbon and Graphitized Carbon (Sample 1)—Cu Radiation.

pletely graphitic). The experimental X-ray diffraction techniques and discussion of the significance of the different carbon diffraction peaks are completely discussed elsewhere.⁷ The (002) region consists of the superposition of the broad and weak (mechanically mixed) amorphous carbon peak, particularly on the low angle side, onto the sharp and strong peak of the graphitized carbon. From the angular location of the stronger peak, the interlayer spacing of the graphitized carbon is calculated to be 3.3600 Å at 15 C (again see the earlier paper⁸ for techniques used to determine accurate interlayer spacings). Using the Franklin² and Bacon⁸ correlation relating interlayer spacing to graphitic carbon content (reproduced in Fig. 2), the graphitized carbon is estimated to contain 80 per cent graphitic carbon.

⁷ P. L. Walker, Jr., H. A. McKinstry, and J. V. Pustinger, "X-Ray Diffraction Studies on Carbon Gasification," *Industrial and Engineering Chemistry*, Vol. 46, No. 8, pp. 1651-1653 (1954).

⁸ G. E. Bacon, "The Interlayer Spacing of Graphite," *Acta Crystallographica*, Vol. 4, pp. 558-561 (1951).

⁹ P. L. Walker, Jr., and F. Rusinko, Jr., "X-Ray Diffraction Studies on Carbon Gasification," *Fuel*, Vol. 34, pp. S22-S23 (1955).

¹⁰ H. T. Pinnick, "X-Ray Diffraction of Heat-Treated Carbon Blacks," *Journal of Chemical Physics*, Vol. 20, No. 4, pp. 756-757 (1952).

Determination of the interlayer spacing of the carbon producing the weaker peak, seen in Fig. 1, is complicated by the difficulty of selecting the position of maximum peak intensity. However, if the main information desired is whether the weaker peak originates from amorphous carbon or semi-graphitic carbon, an approximation of its peak width at half peak intensity should be made. If this width is greater than 0.5 deg, using copper radiation (that is, the carbon has an average crystallite size of less than 150 Å),⁹ the carbon can be considered as amorphous.¹⁰ If the width is less than 0.5 deg, an estimation of the angle at maximum peak intensity must be made to determine the graphitic carbon content. In sample No. 1, the width of the weak peak at half intensity approximates 4 deg, bearing out the amorphous character of this carbon.

In summary, the following information about the above carbon is obtained from Fig. 1:

1. The superposition of two (002) peaks indicates that the sample is a mechanical mixture of two carbons.

2. One of the carbons is amorphous; the other is 80 per cent graphitic.

3. The over-all sample, therefore, contains 90 per cent amorphous carbon, 87 per cent as discrete amorphous particles, and 3 per cent as amorphous carbon intimately mixed on a microscopic scale² with the 10 per cent graphitic carbon.

X-ray diffraction does not enable a determination of the percentage of mechanically mixed amorphous carbon in the above sample unless prior calibration runs have been made relating intensity of the peaks to different known amounts of the particular amorphous carbon in the particular graphitized carbon.

It should also be pointed out that the above information on a carbon, from preparation of an X-ray slide to interpretation of the data, can be obtained within 1 hr.

X-ray diffraction has been further used to clarify the proposed ASTM "float and sink" technique. A sample of the above carbon was ground to pass a No. 325 sieve, separated by centrifuging in ethylene bromide (directions of the ASTM test being carefully followed) and patterns taken of the top and bottom material, as shown in Fig. 3. As would be expected, the relative intensity of the amorphous carbon peak of the top material and that of graphitic carbon in the bottom material are found to be increased. However, it is noted that the top

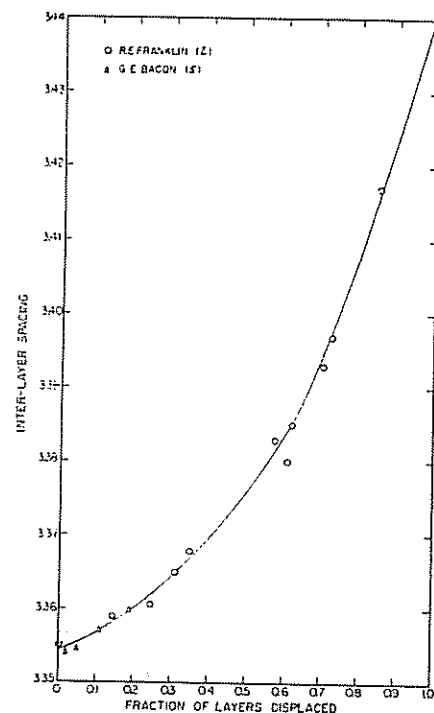


Fig. 2.—Variation of Mean Interlayer Spacing with Proportion, p , of Graphite Layers.

material still contains some graphitic carbon and the bottom material some amorphous carbon. From its X-ray parameters, the graphitic carbon is calculated to have a true density of 2.25. If the number of blind pores in the sample is small, the specific gravity will also approximate this figure, and all of the graphitic carbon should have settled to the bottom of the ethylene bromide. A substantial number of blind pores in the carbon particles would explain the floating of graphitic carbon as would also a preponderance of amorphous carbon in the individual particle.

Table I presents comparable data on the graphitic carbon content of a series of carbons as determined by the techniques just discussed. An indication of the effect of particle size on the graphitic carbon content, as determined by the ASTM procedure, was determined on sample No. 1. It is seen that a decrease in particle size of the carbon resulted in a decrease in the amount of material floating on the ethylene bromide (called amorphous carbon by definition). This result could also be attributed to a decrease in the number of blind pores per particle upon finer grinding. Furthermore, the graphitic content of these samples, as determined by the ASTM procedure,⁶

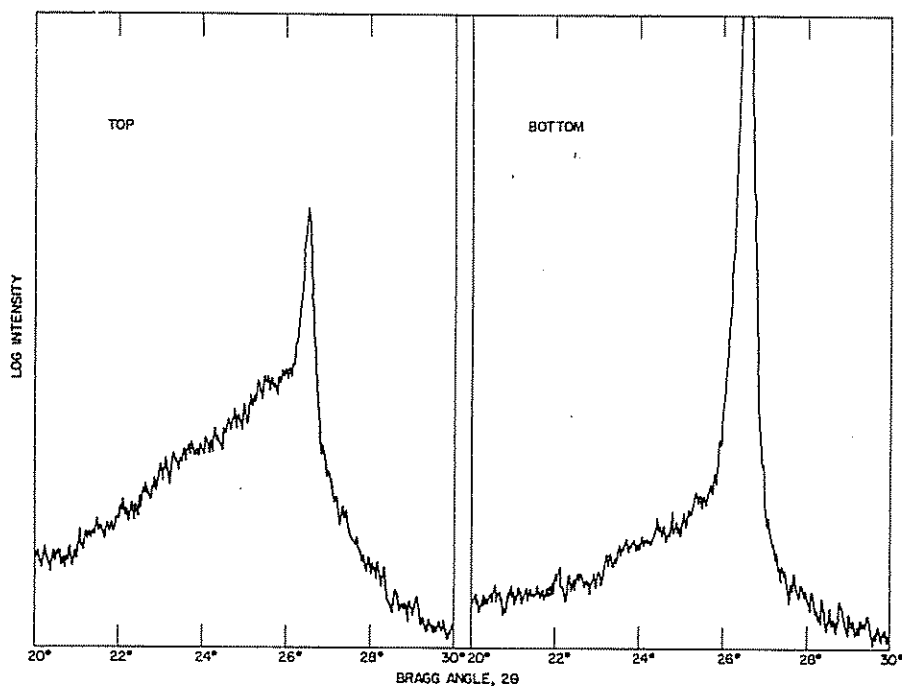


Fig. 3.—X-ray Diffraction Pattern of the (002) Region of Top and Bottom Material after Separation by ASTM Float and Sink Test (Sample 1)—Cu Radiation.

is higher than that reported by X-ray diffraction. Since only 13 per cent graphitic carbon was added to this carbon, it is obvious that some of the amorphous carbon sank to the bottom of the ethylene bromide. This is confirmed in Fig. 3. It may be assumed that it was carried down by graphitic carbon.

Ceylon natural graphite was found to be 100 per cent graphitic by both techniques.

Again, for the spectroscopic, graphitized carbons, samples Nos. 3 and 4, and the graphitized carbon, sample No. 5, the ASTM procedure indicates a higher graphitic carbon content than does X-ray diffraction. If the amorphous material was microscopically dispersed among the graphitic material, as is supposedly the case, the "float and sink" procedure should have indicated 100 per cent graphite in all three cases. That this is not so for two of the samples perhaps indicates that the specific gravity of a portion of the particles was less than that of the ethylene bromide. Again blind pores within the particles, even after grinding to pass a No. 325 sieve, could be responsible.

For the petroleum coke sample No. 6, which was gas baked at only 1000 C and should be completely amorphous after this mild heat treatment, as confirmed by X-ray diffraction, the ASTM test indicates over 4 per cent graphitized carbon. It is barely possible that the 0.24 per cent ash in the sample was so distributed

between particles that the resulting specific gravity of a fraction of the particles was greater than that of ethylene bromide (2.18).

On samples Nos. 5 and 6 the graphitic carbon content has also been determined by the graphitic acid test. It is seen that in both cases it gives a value intermediate between the X-ray diffraction and the "float and sink" test.

A further revealing comparison of the two techniques is found in testing the carbons produced from carbon monoxide decomposition. Carbon 7 is an intermediate carbon, 53 per cent gra-

phitic, as indicated by X-ray diffraction. However, all of the carbon sank to the bottom of the ethylene bromide, indicating by this test 100 per cent graphitic carbon. On the other hand, another sample, which X-ray diffraction indicates possesses 15 per cent graphitic material, floated to the top of the ethylene bromide. These results clearly confirm the fact that the ASTM procedure is not able to distinguish between amorphous carbon and graphite when these two materials are present within the same crystallite or particle.

According to Seeley,¹¹ one of the things that prompted the writing of the ASTM "float and sink" test for graphitic carbon was the desirability of detecting the presence of carbon additions to natural graphite. The above test probably would be successful in detecting the presence of amorphous carbon if complete dispersion were achieved in the ethylene bromide. However, if carbon produced from carbon monoxide were substituted for a portion of the natural graphite, it would not be detected by the "float and sink" test. On the other hand, X-ray diffraction would show a doublet (002) peak and thereby indicate dilution of the graphite with a carbon of intermediate character.

Acknowledgment:

The authors wish to express their thanks to S. B. Seeley for his interest and advice regarding the presentation of this work.

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¹¹ S. B. Seeley, Private communication, September, 1954.

TABLE I.—GRAPHITIC CONTENT OF DIFFERENT CARBONS.

Sample	Description	Passing Sieve	Interlayer Spacing at 15 C. Å	Graphitic Carbon Content, per cent		
				X-ray Diffraction ²	ASTM "Float and Sink" Test ³	Graphitic Acid Test ⁴
No. 1a...	Mixture of 87 per cent petroleum coke and 13 per cent graphitized petroleum coke	No. 48	3.456—87% 3.3600—13%	10	24.4	...
No. 1b...	Repeat of 1a	10	28.9	...
No. 1c...	No. 325	10	36.5	...
No. 1d...	Repeat of 1c	10	37.6	...
No. 2...	Ceylon natural graphite	No. 325	3.3546	100	100	...
No. 3...	Spectroscopic graphitized petroleum coke powder	No. 325	3.3572	89	92.5	...
No. 4...	Spectroscopic graphitized petroleum coke, coal tar pitch rod	No. 325	3.3572	89	100	..
No. 5...	Graphitized petroleum coke, coal tar pitch rod	No. 325	3.3600	80	98.6	91.3
No. 6...	Petroleum coke, coal tar pitch rod	No. 325	3.456	0	4.3	0.30 0.54
No. 7a...	Carbon from CO decomposition	No. 200	3.374	53	100	...
No. 7b...	No. 325	3.374	53	100	...
No. 8...	Carbon from CO decomposition	No. 325	3.416	15	0	...