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Infrared Study on Pitches

INFRARED ABSORPTION AT TWO MICRONS AND COAL-TAR PITCH PROPERTIES

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The infrared absorption of nineteen coal-tar pitches, on which a considerable amount of processing and chemical data were available, was studied. In particular, the background absorption at 2μ was measured. More detailed studies on one of the pitches showed that this absorption originates exclusively in the quinoline insoluble (Q.I.) phase of the whole pitch. It is suggested that only a fraction of the Q.I. phase absorbs at 2μ, however, and that this fraction is not constant for different pitches. It is concluded that this fraction serves as sites for new coke formation from the quinoline soluble (Q.S.) phase during carbonization and that the extent of heterogeneity of the sites in this fraction determines the mode of crystallite growth of the Q.S. phase. In particular, it appears that the coarser carbonaceous particles in the Q.I., which are carried over from the coke ovens during coal carbonization, do not provide sites which promote good crystallite alignment upon coking of the Q.S. phase. It is shown that the nature of the Q.S. phase is also of importance in determining the extent of crystallite alignment during carbonization.

I. INTRODUCTION

In the manufacture of carbon and graphite bodies, it is desirable to be able to predict the properties of the end-product from the properties of the filler and binder raw materials entering into the fabrication process. The carbon industry has made excellent progress in this direction. Many of the physical properties of petroleum cokes (the material used almost exclusively as the filler), which are of importance in determining carbon and graphite properties, have been studied[1]. The chemical properties and constitution of coal tar pitch (the material used almost exclusively as the binder) have been studied extensively[2–4]. Recently, pitch properties like coking value, C/H, and quinoline insoluble (Q.I.) content have been correlated qualitatively with the subsequent strength and electrical resistivity of baked carbon bodies[5,6].

Montgomery and Goodspeed[7] conducted studies to determine whether the infrared spectra of pitches could be used to predict the binder quality of the pitch when used in the manufacture of carbon electrodes. They found that increased infrared absorptivities at 6.25 and 11.4μ and increased background absorption at 2μ could be correlated with increased electrode compressive strengths. They conclude from this correlation that the proportion of condensed aromatic nuclei in the pitch is the dominant factor governing pitch quality.

Workers[8,9] have recently shown that the

[1] P. L. Walker, Jr., F. Rusinko, Jr., J. F. Rakszawski, and L. M. Liggett, *Proc. Third Carbon Conf.*, Pergamon Press (1959), p. 643.

[2] H. G. Schafer, *Freiberger Forschungshefte* **A51**, 35 (1956).

[3] H. G. Franck, *Brennstoff-Chem.* **36**, 12 (1955).

[4] L. J. Wood and G. Phillips, *J. Appl. Chem. London*) **5**, 326 (1955).

[5] L. P. Charette and G. T. Bischofberger, *Ind. Eng. Chem.* **47**, 1412 (1955).

[6] J. A. Branscomb, V. L. Bullough, and H. A. Morrissey, Preprints of Papers presented before the Gas and Fuel Division, Amer. Chem. Soc. Sept. 1960.

[7] F. E. Goodspeed and D. S. Montgomery, Report No. FRL-213, Fuels Division, Dept. of Mines and Tech. Surveys, Ottawa, Canada, December 1956.

[8] M. S. Morgan, W. H. Schlag, and M. H. Wilt, *J. Chem. Eng. Data* **5**, 81 (1960).

[9] S. S. Pollack and L. E. Alexander, *J. Chem. Eng. Data* **5**, 88 (1960).

character of the Q.I. phase of pitches can play an important role in determining electrode quality. This is of interest, since in this work it will be shown that the extent of infrared absorption at 2μ is determined primarily by the character of the Q.I. phase of the pitch.

II. EXPERIMENTAL

A. *Infrared Absorption Studies*

Samples for infrared studies were prepared using the KBr technique[10]. The procedure was designed to provide a finely ground mixture of pitch in KBr, which would have negligible scattering in the infrared beam. After drying the KBr (infrared grade from Harshaw Co.) in an air oven for 12 hr at 105°C, it was mixed with pitch (finely ground in an agate mortar at 20°C) to make up a 5% mixture. This mixture was ground in a rapidly vibrating steel capsule containing steel balls for 10 min. At 2-min intervals during the grinding, the mixture was removed from the capsule with a spatula to prevent caking of the pitch along the periphery of the capsule. The 5% mixture was further diluted with dry KBr to 0.2%, followed by 5 min of grinding. A 300 mg portion of this 0.2% mixture was pressed into a pellet window at 2000 psi. The die used for pressing was similar to that described by Grendon and Lovell[11]. When the pressure was released, the die position was reversed and the pellet pressed at 4000 psi. This method produced a window of 0.092 ± 0.002 cm thickness, which was transparent to visible light.

A Perkin-Elmer Double Beam "21" Recording Infrared Spectrophotometer was used to obtain the absorption results. The instrument was adjusted to zero and 100% transmittancy with blank KBr windows in the sample and reference beams. The I_0 at 2μ was $100 \pm 1\%$.

B. *X-Ray Diffraction Studies*

Approximately 1 g of 40 × 60 mesh coke (produced from the pitches) was ground for 30 sec in a rapidly vibrating steel capsule and then screened to obtain a 200 × 325 mesh fraction. This fraction was dried in a vacuum oven for 24 hr at 110°C and then cooled in a dessicator purged with helium. Twenty milligrams of sample were dispersed in a collodion-amyl acetate solution on a glass slide over an area of $\frac{3}{8}$ in^2.

A 164° (2θ) General Electric X-ray diffraction unit, XRD-3, emitting a non-filtered copper radiation was used to determine the (002) peak intensities. A 1° beam slit and 0.1° receiving slit were employed. A proportional counter mounted on a goniometer scanned the spectra from 15° to 37° (2θ) at a speed of 2°/min. A time constant of 2 sec and a chart range of 100 c/s were used. After an analysis, the slide was reversed and a second scan was made of the (002) peak. A second sample of each coke was analyzed in a similar manner. Using a base-line method, the peak intensities were averaged to give an I(002) value for each coke.

C. *Coking of the Pitches*

The pitches were coked at 1000°C. The complete procedure used for the coking has been given elsewhere[12,13]. In addition the electrical resistivities and gas reactivities of the cokes and graphitized carbons produced from these pitches have been reported on[12,13].

III. RESULTS

A. *Description of the Pitches*

Nineteen pitches, derived from high-temperature coke-oven tars, have been studied. Table I summarizes some pertinent data on the tars and gives information relative

[10] M. M. Stimson and J. O'Donnel, *J. Amer. Chem. Soc.* **74**, 1805 (1952).

[11] H. T. Grendon and H. L. Lovell, *Anal. Chem.* **32**, 300 (1960).

[12] D. O. Baumbach, M.S. Thesis, The Pennsylvania State University (1959).

[13] P. L. Walker, Jr., C. R. Kinney, and D. O Baumbach, *J. Chim. Phys.* **58**, 86 (1961).

to the processing and conversion of the tars to pitches.

TABLE I

Information on the Tars and Their Processing to Pitches

Pitch BD-PSU	Coal[a] tar	Quinoline[b] insoluble of tar, %	Distn. pressure
1	A	7	Atm
2	B	3[c]	Reduced (R)[f]
3	B	3[d]	R[f]
4	B	3[e]	R[f]
5	Lignite	4	R[f]
6	C	7.5	Atm
7	C	7.5	Atm
8	C	7.5	R
9	C	7.5	R
10	C	3.0	Atm
11	C	3.0	Atm
12	C	3.0	R
13	C	3.0	R
14	D	10.0	R
15	D	10.0	R
16	D	3.0	R
17	D	3.0	R
18	D	3.0	Atm
19	D	3.0	Atm

(a) A, B, C, D are coke oven tars from bituminous coal. The tars are from different coke plants; the actual coals may or may not be different.

(b) Before additions of substitute materials as in pitches 2, 3, and 4.

(c) Bituminous coal, digested in heavy anthracene oil, added to increase Q.I.

(d) Natural Q.I. (sludge from filtering same tar) added to increase Q.I. above normal content.

(e) Thermax added to bring Q.I. content of tar to 7%.

(f) Batch distn. in laboratory stills—all others are continuous distillation in commercial equipment.

Table II presents data on the chemical analyses of the whole pitches. The analysis for sample 5 is markedly different from the remaining samples, since it is a lignite pitch. Table III presents semi-quantitative data on the concentration of metallic impurities in some of the selected pitches.

Table IV presents miscellaneous data on the pitches. The coking values were determined using the Barrett Method B-8[14], which consists of rapidly heating the pitch to 900°C and holding the temperature for 7 min. As pointed out by Martin and Nelson[15], this test gives a coking value considerably below that found commercially upon the baking of green electrodes. The test, however, does give a relative indication of the coking value of the binder pitch. The softening point of the pitches was determined by the cube-in-air method[14].

B. *Infrared Absorption at Two Microns*

Figure 1 presents results for the variation in log (I_0/I_b) with the wt % Q.I. in the KBr

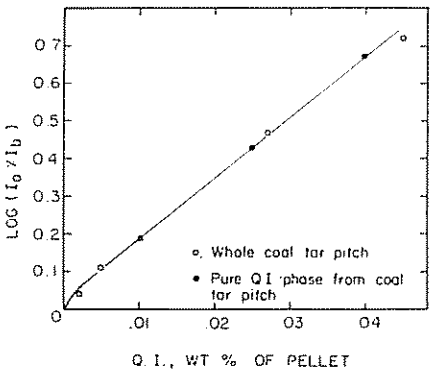

FIG. 1. A comparison of the absorption at 2μ for the Q.I. fraction and whole coal-tar pitch 14.

pellet for pitch 14. I_b is the intensity of the background (as % transmission) at 2μ. To make up the pellet, either whole pitch 14 or pure Q.I., which had been previously extracted from pitch 14, was added to the KBr. At low concentrations of Q.I., Beer's law is obeyed. Further, only the Q.I. phase of the pitch produces measurable absorption at 2μ.

Figure 2 presents results for the variation in log (I_0/I_b) with the Q.I. content of the 19 pitches studied. In all cases, 0.2%, by weight, of the whole pitch was added to the KBr. The results do not fall on a smooth line. It is of interest to note, however, that the samples which fall considerably off the line (arbitrarily

[14] *Methods of Treating Coal-Tar Products*, The Barrett Division, Allied Chemical Corp. (1950).

[15] S. W. Martin and H. W. Nelson, *Ind. Eng. Chem.* **50**, 33 (1958).

TABLE II

Chemical Analyses of the Pitches

Pitch BD-PSU	%C	%H	%N	%S	% Other*	% Ash	Atomic C-H ratio
1	93.35	4.32	1.08	0.27	0.98	0.17	1.81
2	91.70	4.55	1.31	0.53	1.91	0.63	1.69
3	92.77	4.32	1.21	0.58	1.12	0.07	1.80
4	93.34	4.10	1.10	0.49	0.97	0.05	1.91
5	81.67	7.31	1.16	0.77	9.09	2.55	0.94
6	93.34	4.38	1.01	0.30	0.97	0.12	1.79
7	93.36	4.44	1.00	0.31	0.89	0.14	1.77
8	93.26	4.40	1.01	0.24	1.09	0.11	1.78
9	93.18	4.46	1.00	0.32	1.04	0.10	1.76
10	93.47	4.44	0.98	0.25	0.86	0.05	1.77
11	93.25	4.49	0.99	0.31	0.96	0.05	1.74
12	93.31	4.46	1.01	0.31	0.91	0.04	1.76
13	93.17	4.57	1.00	0.30	0.96	0.03	1.71
14	93.00	4.20	1.06	0.41	1.33	0.25	1.86
15	93.08	4.29	1.06	0.47	1.10	0.22	1.82
16	92.24	4.53	1.11	0.39	1.03	0.06	1.72
17	92.78	4.65	1.10	0.37	1.10	0.06	1.68
18	93.13	4.42	1.08	0.37	1.00	0.08	1.77
19	93.13	4.49	1.11	0.37	0.90	0.08	1.74

* Includes % ash.

TABLE III

Concentration of Metallic Impurities in Selected Pitches in PPM

Pitch BD-PSU	Al	B	Ca	Cu	Fe	Mg	Mn	Na	Ni	Pb	Si	Ti
2	310	0.88	110	5.0	360	23	11	—	21	11	510	25
4	12	0.14	6.4	1.3	58	2.0	1.2	—	2.8	8.5	120	1.4
5	2400	67	160	15	1200	180	160	—	33	72	3100	260
6	100	0.14	46	1.6	96	6.4	7.4	46	4.5	34	130	7.4
9	97	0.085	23	0.92	79	6.7	4.4	28	3.0	58	120	9.4
11	28	0.019	13	0.63	43	1.6	1.7	37	1.8	26	27	2.3
12	27	0.020	17	0.90	40	2.8	4.6	42	3.5	35	60	6.0
13	59	0.031	52	1.1	90	3.9	9.8	90	6.1	59	57	6.2
14	170	0.12	75	2.9	180	16	13	57	4.2	68	360	16
16	24	0.0062	23	0.48	86	3.4	5.8	39	1.8	56	22	1.0
18	28	0.016	13	0.62	98	3.4	5.2	32	2.0	41	43	1.9
19	62	0.028	120	0.80	150	7.0	8.5	50	2.9	60	100	4.3

drawn through pitch 14) are those which, in most cases, have seen differences in processing in going from tar to pitch. Pitches 6, 7, 10, 11, 18, and 19, which fall below the line, have been produced by distillation of tar at atmospheric pressure. Pitches 2, 3, and 4 have undergone unusual treatment in their processing. Pitch 5 has been produced from a lignite tar.

The extent of absorption of radiation at 2μ by the pitches can be correlated with important parameters. Figure 3 shows a relationship between log (I_a/I_0) for the pitches (where I_a/I_0 is the fraction of radiation absorbed) and the maximum intensity of the (002) X-ray diffraction peak for the corresponding cokes. The intensity of the (002) X-ray diffraction peaks for the cokes are given in Table V. As

TABLE IV

Miscellaneous Properties of the Pitches

Pitch BD-PSU	Coking Value	Sp. gr. 25°C	Soft. pt., °C	% Insoluble in	
				Quinoline	Benzene
1	42.8	1.318	98.8	15.8	32.5
2	35.7	1.298	109.7	5.7	25.5
3	40.0	1.318	102.5	13.3	27.1
4	41.7	1.340	110.0	13.4	27.8
5	24.8	1.174	110.7	8.6	18.9
6	41.5	1.313	99.5	13.0	29.4
7	39.8	1.306	93.0	12.2	28.4
8	37.5	1.307	97.0	10.2	22.5
9	36.2	1.300	95.2	9.9	20.2
10	40.5	1.308	101.0	11.6	28.3
11	37.1	1.297	91.0	8.8	23.7
12	36.1	1.299	97.0	7.6	19.6
13	33.3	1.292	95.2	6.0	17.9
14	42.3	1.328	100.0	18.1	28.6
15	40.2	1.314	93.6	17.2	27.2
16	34.7	1.294	99.0	5.2	17.5
17	32.3	1.286	90.0	5.1	16.3
18	40.1	1.306	108.5	10.4	26.9
19	36.1	1.296	92.5	8.3	24.2

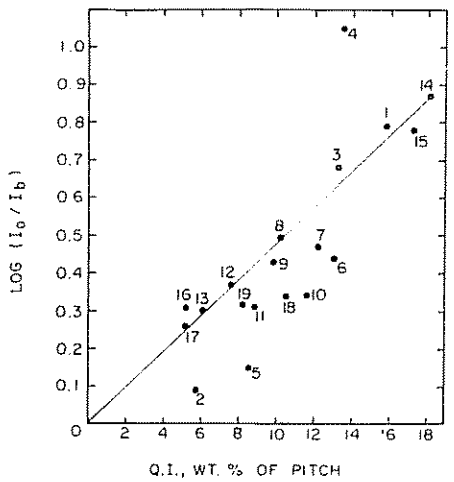

FIG. 2. A relation between the absorption at 2μ and the Q.I. content of coal-tar pitches.

was discussed previously in studies on petroleum cokes[1], the intensity of the (002) diffraction peak can be taken as a measure of the relative degree of orientation of crystallites. Crystallite orientation is important in determining the graphitizability[16] of carbons

[16] R. E. Franklin, *Nature* **177**, 239 (1956).

TABLE V

Intensity of the (002) X-ray Diffraction Peaks for Cokes from Coal Tar Pitches

Pitch BD-PSU	(002) Peak Intensity, c/s
1	34.0 ± 1.7
2	79.0 ± 0.0
3	34.5 ± 2.0
4	52.3 ± 3.6
5	25.3 ± 0.9
6	41.1 ± 0.7
7	39.3 ± 2.4
8	41.7 ± 0.4
9	45.1 ± 4.2
10	53.1 ± 1.5
11	48.2 ± 1.6
12	51.3 ± 0.4
13	49.4 ± 3.1
14	34.6 ± 2.2
15	34.8 ± 0.7
16	45.2 ± 1.6
17	51.0 ± 1.2
18	46.8 ± 1.0
19	45.5 ± 0.7

and resultant properties of carbon bodies such as electrical resistivity[1], coefficient of thermal expansion[1], oxidation resistance[1], and stability to radiation damage[17]. Pitches 4 and 5 are obvious exceptions to the correlation shown in Fig. 3. Also the unusually low absorptance of pitch 2, accompanied by the relatively high I(002) for its coke, is of interest.

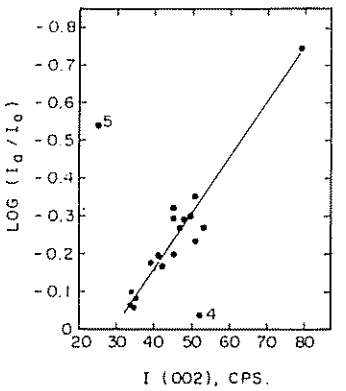

FIG. 3. A relation between the energy absorbed at 2μ for the pitches and the X-ray intensity of the (002) diffraction peak for the resulting cokes.

Charette and Bischofberger[5] obtained a linear correlation between the product of the coking value and the atomic C/H of coal tar pitches and the compressive strength of test electrodes made from the pitches. As the product increased, the compressive strength increased. It is, therefore, of interest to show the relationship between log (I_a/I_0) and (coking value × C/H) for the different pitches. The correlation is shown in Fig. 4. These results predict that as the absorptance of the pitch at 2μ increases, the strength of carbon bodies produced from the pitch will increase. Goodspeed and Montgomery[7] came to the same conclusion from their studies of coal tar and petroleum pitches. A notable exception to the correlation shown in Fig. 4 is pitch 2. Pitch 5 is not shown in Fig. 4, because of its very low coking value and C/H.

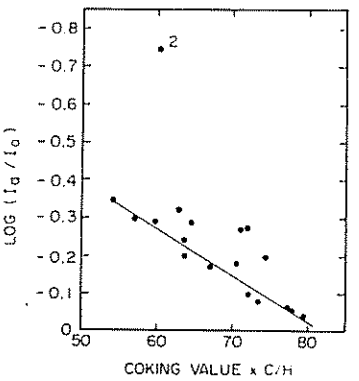

FIG. 4. A relation of the energy absorbed at 2μ and the characterization factor I[5] for coal-tar pitches.

IV. DISCUSSION

Recent studies have indicated that the nature of the Q.I. phase of a coal tar pitch is of considerable importance in determining the structure and properties of the carbon obtained upon coking the pitch[8]. Results discussed in this paper re-emphasize the importance of the Q.I. phase and also show the feasibility of rapidly measuring the result of its presence by infrared absorption. The results presented in this paper also lead to suggestions for new processing procedures in converting tar to pitch, if certain properties are desired in the carbon which will ultimately be produced from the pitch.

It is generally recognized that coal tars contain dispersed solid material, largely colloidal, but ranging in size up to coarse, dispersed particles. The coarser carbonaceous material, for the most part, is carried over from the material being carbonized. The colloidal material, for the most part, consists of complex hydrocarbons of high molecular weight. These complex hydrocarbons either are derived directly from the decomposition of the coal or are derived through the dehydrogenation and condensation of smaller aromatic molecules coming from the coal.

[17] J. M. Davidson, E. M. Woodruff, and H. H. Yoshikawa, *Proc. Fourth Carbon Conf.*, Pergamon Press (1960) p. 599.

The latter process, in the case of anthracene, is discussed by Kinney, Nunn, and Walker[18]. The amount of this dispersed solid material is usually taken as that phase which is insoluble in quinoline close to its boiling-point. Obviously the amount of this material reported for any pitch is a function of the solvent which is selected for the measurement.

Of importance is the finding shown in Fig. 1. For a conventional, high-temperature coal tar pitch (pitch 14), the material soluble in quinoline has negligible infrared absorption at 2μ. Conversely, the Q.I. phase is responsible for all the absorption. As discussed by Pinnick[19], this absorption is primarily caused by the promotion of electrons out of the π-band of the molecular solid and into the conduction band. Electronic absorption will occur at a particular infrared wavelength, only if the energy of the photon, $h\nu$, is equal to or greater than ϵ, where ν is the infrared frequency and ϵ is the energy gap in the solid between the filled π-band and the conduction band. At 2μ, $h\nu$ equals 0.62 eV. The conclusion is, then, that none of the organic compounds in the quinoline soluble (Q.S.) phase of pitch 14 have energy gaps equal to or less than 0.62 eV. Conversely, the Q.I. phase does contain some material with an energy gap equal to or below 0.62 eV. Pinnick[19] shows that the width of the energy gap decreases with increasing heat-treatment temperature (and increasing platelet size) for a carbonaceous material. Obviously, it would be fortuitous if the carbonaceous material just at the dividing line between Q.I. and Q.S. had an energy gap of 0.62 eV. It is, therefore, concluded that material of lower molecular weight in the Q.I. phase does not absorb at 2μ but that at some point in the molecular-weight (or platelet-size) distribution in the Q.I. phase, electronic absorption commences.

From electron gas theory, it is possible to estimate the magnitude of the energy gap as a function of the number of carbon atoms in a molecule (or platelet). Considering an electron wave in two dimensions, the theoretical transition energy for an electron is given as

$$\epsilon = \frac{(n+1)h^2}{8m}\left(\frac{1}{a^2}+\frac{1}{b^2}\right)$$

where n is the number of π-electrons in the molecule, h is Planck's constant, and m is the mass of an electron. Further for a symmetrical platelet, $a = b$; and in turn a and b are assumed to equal $n \times 1.39$ Å[20], where 1.39 Å is the carbon–carbon bond length. To the author's knowledge, ovalene ($C_{32}H_{14}$) is the largest symmetrical molecule on which experimental energy gap data are available. Akamatu and Inokuchi[20], from optical absorption measurements, report $\epsilon = 1.2$ eV. From the above equation, assuming one π-electron per carbon atom in ovalene, ϵ is calculated to equal 1.24 eV—a figure in surprisingly good agreement with experiment. Using the above equation, it is calculated that $n = 62$ when $\epsilon = 0.62$ eV. That is, a symmetrical molecule (platelet) containing 62 π-electrons would be expected to absorb radiation strongly at 2μ. Such a molecule could be $C_{62}H_{20}$, having a molecular weight of 765 and platelet diameter of *ca.* 13.3 Å.

Akamatu and Inokuchi find experimentally that factors other than increasing molecular weight are of importance in decreasing the energy gap. These factors include the presence of quinoid structure and pyridine rings. For example, indanthrone, $C_{28}O_4N_2H_{14}$ (molecular weight = 442) has an energy gap of 0.65 eV from optical absorption measurements[20]. However, Martin and Nelson[15] give as a typical chemical analysis of the Q.I. material (by wt. %): C, 92.9; O, 0.8; and N, 0.8. This means that the compounds in the Q.I. fraction of pitch contain a relatively small number of quinoid groups and pyridine rings, which would result in a lowering of

[18] C. R. Kinney, R. C. Nunn, and P. L. Walker, Jr., *Ind. Eng. Chem.* **49**, 880 (1957).

[19] H. T. Pinnick, *Proc. 1st and 2nd Carbon Conf.*, U. of Buffalo (1956), p. 3.

[20] H. Akamatu and H. Inokuchi, *Proc. Third Carbon Conf.*, Pergamon Press (1959), p. 51.

their energy gaps. Therefore, a platelet size of *ca.* 13 Å would appear to be necessary before a molecule in the Q.I. phase absorbs strongly at 2μ.

From this discussion, it now appears possible to present a qualitative picture of coal tar pitch on the basis of the platelet size of the molecules and crystallites present in the pitch. This picture is given in Fig. 5, say for a

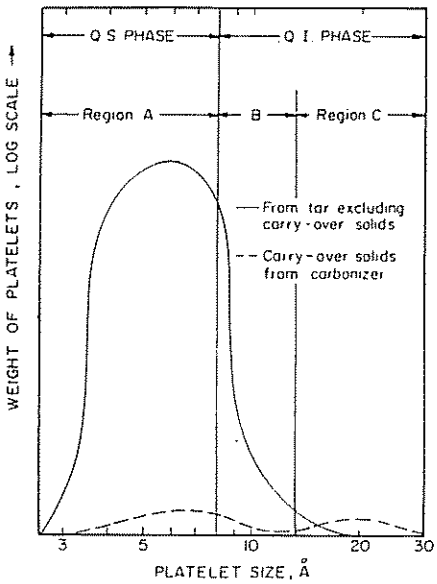

FIG. 5. Qualitative picture of coal-tar pitch on the basis of weight distribution as a function of platelet size of molecules and crystallites present.

pitch with a Q.I. content of 10%. About 90% by weight of such a pitch consists of 3 (platelet size of *ca.* 4 Å) to 7 (platelet size of *ca.* 8 Å) ring aromatic compounds, according to Franck[3]. The whole pitch is composed of material derived from tar, exclusive of carry-over solids, and carry-over solids from the carbonizer, as previously discussed. Obviously the distribution of platelet size in both materials depends upon the processing conditions used and the starting coal. The distribution of platelet size for the carry-over solids was assumed similar to that shown by Diamond[21] for a bituminous coal carbonized at 800°C. According to Fig. 5, a coal-tar pitch can be divided into three major regions —a Q.S. fraction which does not absorb at 2μ (region A), a Q.I. fraction which does not absorb at 2μ (region B), and a Q.I. fraction which does absorb at 2μ (region C). The latter fraction is composed of non-carry-over and carry-over material.

With this concept in mind, the results presented in Fig. 2 can be understood. The total amount of Q.I. material (given as $W_B + W_C$) does not determine the extent to which the pitch absorbs at 2μ; rather the extent of absorption is determined by the amount of material in region C, that is, W_C. Therefore, one equation would not be expected to correlate the results between log (I_0/I_b) and Q.I. for a collection of pitches. Several examples of large deviations from the line drawn in Fig. 2 can be considered. In the case of pitch 4, a substantial amount of Thermax black was added to increase the Q.I. content. Thermax has an average crystallite diameter (platelet size) of *ca.* 35 Å[22] and would, therefore, be expected to absorb strongly at 2μ. For pitch 4, then, the ratio $W_C/(W_B + W_C)$ is considerably greater than for an average pitch, resulting in its absorptivity per unit of Q.I. being also above average. In the case of pitch 2, bituminous coal was digested in heavy anthracene oil to increase Q.I. As shown by Friedel[23], electronic absorption begins to appear at *ca.* 1.9μ for a Bruceton vitrain. Further, the energy gap for this coal was established at *ca.* 1.5 eV (corresponding to 0.8μ)[23]. From the previous discussion, the energy gaps for the compounds in the heavy anthracene oil[24] would be

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[21] R. Diamond, *Proc. Third Carbon Conf.*, Pergamon Press (1959), p. 367.

[22] H. Kuroda and H. Akamatu, *Bull. Chem. Soc. (Japan)* **32**, 142 (1959).

[23] R. A. Friedel, *Proc. Fourth Carbon Conf.*, Pergamon Press (1960), p. 321.

[24] P. J. Wilson, Jr. and J. H. Wells, *Coal, Coke, and Coal Chemicals*, McGraw-Hill (1950), p. 374.

expected to fall in region B of Fig. 5, making the ratio $W_C/(W_B + W_C)$ considerably lower than that for an average pitch. Pitch 2, then, should show an absorptivity per unit Q.I. which is less than that shown by the average pitch.

Figures 3 and 4 show that there is a relation between the extent to which a pitch absorbs at 2μ and some of the properties of the carbon produced from the pitch. In line with the previous discussion, this would appear to be reasonable. Upon carbonization, the Q.I. material (particles) in region C which is dispersed throughout the pitch is heated by absorption of photons. These particles would then be expected to serve as the nuclei for dehydrogenation and condensation of the surrounding Q.S. material. This should result primarily in an enlargement of the Q.I. particle size as the amount of Q.I. material in the pitch is increased. This result has been confirmed by Wilt and co-workers[8]. They measured the specific surface area of the Q.I. phase of pitches as a function of the Q.I. content of the pitches. They found, for example, that for a particular high temperature pitch, having a Q.I. content of 12.4 wt. %, the Q.I. phase had a surface area of 15.9 m^2/g of Q.I. This pitch was then thermally treated to increase its Q.I. content to 35.0 wt. %. The Q.I. phase now had a surface area of 8.0 m^2/g of Q.I. The increase in particle size which would be predicted from the surface area results was confirmed by photomicrographs.

Low-angle X-ray scattering results of Pollack and Alexander[9] indicate that at least a portion of the Q.I. phase of coal tar pitch is quite porous and heterogeneous. They report a specific surface area of ca. 40 m^2/g of Q.I. While Pollack and Alexander do not give the Q.I. content of the pitch from which the Q.I. phase was removed, Wilt and co-workers[8], by gas adsorption measurements, report a maximum surface area of only 22.9 m^2/g for a pitch with 2.4 wt. % Q.I. Probably the pitch with which Pollack and Alexander worked had a higher Q.I. content and consequently a lower surface area for the Q.I. phase than 22.9 m^2/g Q.I. Apparently, therefore, the Q.I. phase contains porosity which is inaccessible to the adsorbate during low temperature surface area measurements.

The extent of crystallite ordering in the Q.I. particles which promote carbonization of the Q.S. phase should be of importance in determining, in turn, the nature of crystallite growth and arrangement in the Q.S. phase. Such an effect is indicated from the X-ray diffraction data of Table V and considerations on processing of the pitches. Consider, for example, the pitches produced from coal tar D. Pitches 14 and 15 were produced from the unfiltered tar which had a Q.I. content of 10%. On the other hand, pitches 16, 17, 18, and 19 were produced from the filtered tar, which had a Q.I. content of 3%. Filtration of the tar would be expected to remove preferentially the coarser carbonaceous material —the carry-over material. That this is the case, is shown by consideration of the values for percentage ash in pitches 14–19, given in Table II. Pitches 14 and 15 have considerably higher ash contents than pitches 16–19. Since the ash content of the carry-over material is expected to be high, its removal by filtration should lower the ash content of the resultant pitch, as observed. It is of interest, then, to note that the crystallite alignment in the cokes produced from filtered pitches 16–19 is significantly greater than the alignment produced in pitches 14 and 15. The conclusion drawn is that the carry-over material on which carbonization of the Q.S., in part, occurs, presents sites for crystallite growth which are inferior to those found on the non-carry-over material. It is suggested that the non-carry-over nucleating material (or the colloidal material as previously called) has a more ordered structure and less porosity than the carry-over material.

The importance of the physical structure of the nucleating material on crystallite growth of the Q.S. phase is also shown by results on

other pitches. In pitch 4, Thermax was added to increase the Q.I. content. From Fig. 3 it is seen that crystallite alignment in the coke from this pitch is considerably greater than that predicted from results on the more conventional pitches. The conclusion is that Thermax has a degree of crystallite ordering similar to that of the non-carry-over material in the Q.I. and superior to that of the carry-over material.

The strikingly high crystallite alignment shown by the coke from pitch 2 is of considerable interest. The coke was produced from a filtered tar, which has been shown to aid alignment to some extent. However, the intensity of the (002) X-ray diffraction peak from this coke was 50% higher than that of the best coke produced in the usual manner from a filtered tar. It is suggested that the explanation rests in the effect of structure of aromatic compounds in the Q.S. phase on their crystallite growth. Kinney[25] has shown the strong effect which the structure of aromatic compounds can have on the graphitizability of the cokes produced therefrom. Anthracene is highly graphitizable. Phenanthrene, an angular isomer of anthracene, is poorly graphitizable. This suggests that the crystallite alignment in the coke produced from anthracene is appreciably greater than that for the coke produced from phenanthrene. Many of the compounds identified by Franck[3] in coal tar are angular in shape and on the basis of the results with phenanthrene, probably do not produce cokes with high crystallite alignment. Apparently in the case of pitch 2, the heavy anthracene oil, added to the tar, contained substantial amounts of aromatic compounds (including anthracene) from which a coke of high crystallite alignment resulted. Further the aromatic structure of the digested bituminous coal had not yet undergone severe cracking and may, therefore, have yielded upon carbonization a coke of better crystallite alignment. From X-ray studies, Diamond[26] concludes that the compounds present in coal are, in the main, isodimensional (or symmetrical). Such compounds would be expected to result in good crystallite alignment upon slow carbonization. Certainly the importance of the structure of the aromatic compounds in the Q.S. phase on subsequent crystallite growth is clearly evident with the lignite pitch 5. This pitch, which on the basis of absorption at 2μ, should yield a coke of high crystallite ordering, to the contrary, yielded a coke having the lowest crystallite ordering.

The results of Charette and Bischofberger[5], relating compressive strength to the product of coking value and C/H of the pitches are at least, in part, understood on the basis of Figs. 3 and 4. As discussed previously, the relation shown in Fig. 4 indicates that electrode compressive strength should increase with increasing absorption at 2μ by the pitch. Increasing absorption at 2μ by the pitches has been shown, however, to result in poorer crystallite alignment in the cokes produced. Since poorer crystallite alignment almost invariably results in the carbon having a greater strength[1], the correlation of Charette and Bischofberger is reasonable.

V. CONCLUSIONS

On the basis of this work, it appears that much more research should be done studying methods to modify the carbonization behaviour of coal tar pitches. In particular, the effect of changing the heterogeneity of sites on which new coke formation from the Q.S. phase occurs during carbonization should be investigated. The extent of both physical and chemical heterogeneity of the sites could be of importance. The physical heterogeneity could be changed through differences in heat treatment temperature of

[25] C. R. Kinney, *Proc. 1st and 2nd Carbon Conf.*, U. of Buffalo (1956), p. 83.

[26] R. Diamond, *Phil. Trans. Roy. Soc. (London)* **A252**, 193 (1960).

carbon blacks before their introduction into a tar. The chemical heterogeneity could be changed by exposing the carbon blacks to different atmospheres either during or after their heat treatment. The possibilities of modifying the mode of crystallite growth of the Q.S. phase during carbonization by the introduction of different aromatic compounds into the tar should also be investigated.

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