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Crystallite growth in graphitizing and non-graphitizing carbons

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[Plates 3 and 4]

An investigation of the structure of carbons of different origin treated at temperatures between 1000 and 3000° C has shown that the graphitizing and non-graphitizing carbons form two distinct and well-defined classes. The differences in structure are apparent from the earliest stages of carbonization, and may be attributed mainly to the formation at low temperatures, in the non-graphitizing carbons, of a strong system of cross-linking uniting the crystallites. This leads to a random orientation of the crystallites in a rigid, finely porous mass. In the graphitizing carbons the cross-linking is much weaker, the structure is more compact, and neighbouring crystallites have a strong tendency to lie in nearly parallel orientation.

It is shown that crystallite growth occurs by the gradual displacement of whole layer-planes or even of groups of layer-planes. The pre-orientation existing in the graphitizing carbons facilitates this process, enabling the rearrangement of the layer-planes to take place by small stages. It is the principal factor favouring crystallite growth in the graphitizing carbons. In the non-graphitizing carbons crystallite growth is impeded both by the strong cross-linking between neighbouring crystallites and by their random orientation.

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INTRODUCTION

The structure of carbons formed by pyrolysis of organic materials depends not only on the temperature of preparation, but also, to a very large extent, on the **nature of the starting material**. From some substances synthetic graphite can be prepared at about 2200° C, while others show no trace of the true graphite structure, even after heating to 3000° C.

It is of interest to inquire what are the factors which favour or hinder the development of the graphite structure when the highly disordered carbons which are obtained by pyrolysis at 1000° C are heated to higher temperatures, and hence to attempt to learn something about the mechanism of the crystallization. With this object a survey has been made of the structure of carbons of widely different origin heated to temperatures between 1000 and 3000° C.

A brief summary of some aspects of the work has already been given (Franklin 1950*a*, 1951*a*). The results are here described more fully and their interpretation is discussed.

Attention has been confined to the solid residues of carbonization in the condensed phase—the formation of carbon blacks has not been included in the present study. Carbons prepared at temperatures **below 1000° C** are also excluded, since, in general, these contain **too much oxygen or other impurity** for the direct application of quantitative X-ray analysis.

Before describing the results of the present work it will be convenient to summarize some of the general features of the structure of carbons, and to establish certain definitions.

It has long been known that the structure of all non-crystalline black carbons bears some relation to that of graphite. The X-ray diagrams of even the most disordered carbons show diffuse bands approximately in the position of the (002) and (100) graphite lines. Warren (1934) was the first to show directly, by applying the Fourier transform to the diffraction pattern of a carbon black, the presence of layer-planes of graphite-like structure in a non-crystalline carbon. Biscoe & Warren (1942) showed that carbon blacks have a two-dimensional, or cross-lattice, structure. That is, the graphite-like layers are stacked in parallel groups but are not otherwise mutually orientated. Apart from the (00*l*) reflexions such carbons show only two-dimensional (*hk*) bands (Warren 1941). There is no trace of the (*hkl*) (*l* ≠ 0) graphite lines, showing that the three-dimensional structure of crystalline graphite is absent. These carbons, in which **the graphite-like layers lie in parallel groups but are not orientated as in the crystalline structure of graphite**, will be referred to as **non-graphitic carbons**.

On heating *certain* non-graphitic carbons to temperatures between 1700 and 3000° C, the graphite-like layers show a tendency to become mutually orientated as in crystalline graphite. This is revealed in the X-ray powder diagrams by a modulation of the two-dimensional (*hk*) bands, leading, at a later stage, to the development of diffuse (*hkl*) (*l* ≠ 0) graphite lines, the diffuseness of the lines decreasing as graphitization increases. These structures of intermediate type, which show deformed (*hk*) bands or diffuse (*hkl*) (*l* ≠ 0) lines—that is, in which the three-dimensional graphite

structure is partially developed—will be called *graphitic carbons*. A description of their formation and structure has been given elsewhere (Franklin 1951b).

Those non-graphitic carbons which, on heating to temperatures between 1700 and 3000°C, form graphitic carbons will be called *graphitizing carbons*; those which, on heating to 3000°C, show no homogeneous development of the graphitic structure will be called *non-graphitizing carbons*.

It will be seen below that these two classes of carbons are sharply defined, and that there exists also a third intermediate class.

A detailed investigation of the structure of one non-graphitic carbon, prepared by *pyrolysis of polyvinylidenechloride at 1000°C*, has already been described (Franklin 1950b). As a result of quantitative measurements of the total X-ray scattering, extending from very small to very large angles, it was shown that in this substance 65% of the carbon was in the form of graphite-like layers highly perfect in structure but only 16 Å in diameter, and the remaining 35% was in a form so disordered as to give only a gas-like contribution to the total X-ray scattering. Of the small graphite-like layers, about 45% showed no parallelism and 55% were grouped in parallel pairs with an inter-layer spacing of 3.7 Å. It was further shown, by means of a Fourier transform of the low-angle scattering, that the elementary particles in this highly porous carbon were of about the same dimensions as the diameter of the graphite-like layers, and that the mean distance between neighbouring particles was about 25 Å.

This substance is now known to be a *non-graphitizing carbon*. The above detailed study therefore provides direct proof that even those carbons which do not form graphite at high temperatures consist, in the main, of truly graphite-like layer-planes, and not, as has sometimes been suggested (Riley 1947; Zachariasen 1949), of a different structural modification involving a three-dimensional network on the atomic scale.

Similar measurements have now been made on this and other carbons heated to temperatures up to 3000°C. It is found that the structure of all *non-graphitic carbons* can be described in terms of the same parameters. Their X-ray diagrams can all be satisfactorily interpreted by supposing the existence of only small, perfect, graphite-like layers together with, in some cases, a certain proportion of highly disordered material. The diameter of the graphite-like layers, their grouping and mutual orientation, the inter-layer spacing and the proportion of carbon in a non-organized state vary from one carbon to another.

METHOD

The experimental methods used in this investigation have all been described previously (Franklin 1950b, c, 1951b), and only the briefest summary will be given here.

The carbons

All carbons were heated to 1000°C for 2 hr. in a laboratory tube furnace, in an atmosphere of nitrogen purified by passage through alkaline pyrogallol and over reduced copper oxide at 300 to 320°C. They were subsequently heated to higher

temperatures in an induction furnace, samples of up to six different carbons being heated simultaneously in a series of small flat carbon crucibles which were stacked vertically and held centrally in a carbon tube through which a current of argon was passed. The maximum temperature was maintained for 15 to 20 min., except where otherwise stated.

X-ray measurements

For all quantitative measurements, vacuum cameras of diameter (i.e. sample-film distance) 76 and 125 mm. were used, with $\text{Cu } K\alpha$ radiation obtained from a bent-quartz focusing monochromator. For the photographs taken to show preferential orientation in thin flakes (cf. figures 11 and 12, plates 3 and 4) filtered $\text{Cu } K\alpha$ radiation was used, and the camera was not evacuated.

Recorded intensities were corrected for absorption, polarization, and the variation of the angle of incidence and the sample-film distance. Measurements at low angles were corrected for the influence of the finite height of the X-ray beam (Guinier & Fournet 1947; Franklin 1950c).

To estimate and subtract the Compton scattering in the more diffuse diagrams, the absolute intensity scale was established from a consideration of both the shape and intensity of the (11) band, as previously described (Franklin 1951b). The proportion of non-organized carbon was also estimated by this means.

The apparent layer diameter, L , was obtained from the shape of the (11) band using the Warren (1941) equations, and the apparent number of layers per parallel-layer group, M , from the integral breadth of the *corrected* (002) and (004) bands (Franklin 1950b). For all measurements of the inter-layer spacing the carbons were mixed with a small quantity of powdered quartz, and the distance of the (002) maximum from the nearby (101) quartz line was measured photometrically.

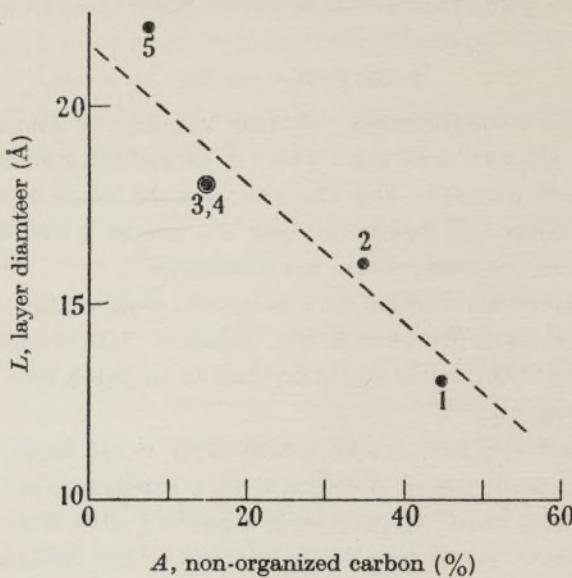
RESULTS

The non-organized carbon

Carbons prepared by pyrolysis of organic substances at 1000°C are found to contain, in general, groups of from two to four parallel graphite-like layers, of diameter less than 20 \AA , together with a certain proportion of non-organized carbon giving only a gas-like contribution to the total X-ray scattering. On further heating, the layer diameter, L , increases and the percentage of non-organized carbon, A , decreases, while there is, at first, little change in M , the mean number of layers per parallel-layer group (determined from the integral breadth of the *corrected* (002) band). Thus, at this stage of the carbonization process, the principal structure change consists in the growth of the small graphite-like layers at the expense of the non-organized carbon.

The relationship between L and A is shown in figure 1. There is apparently a single relationship for all the carbons studied, A becoming too small to be measured when L exceeds about 25 \AA . This relationship suggests some similarity in the kinetics of the formation of the graphite-like layers in the different carbons. Nevertheless, even at this early stage of the carbonization process, important differences in the development of the structure as between one carbon and another are

apparent. Among the carbons prepared at 1000° C the proportion of non-organized carbon varies from 15 to 45 %, while L varies from 13 to 18 Å, and M from 2 to 4.5 (see below).



point	1	2	3	4	5
substance	C_6Cl_6	$(C_2H_4Cl_2)_n$	sugar	$(C_2H_3Cl)_n$	$(C_2H_2Cl_2)_n$
temperature (°C)	1000	1000	1000	1000	2000

FIGURE 1. Relationship between the percentage of non-organized carbon, A , and the diameter, L , of the graphite-like layers.

Growth of the parallel-layer groups

When no measurable quantity of non-organized carbon remains, with further increase of temperature both L and M increase. But the relative values of L and M , and the temperature required to produce a given value of either, vary widely from one carbon to another.

The results are given in table 1. In figure 2, where L is plotted against M , two classes of carbons can be clearly distinguished. The upper curve in the figure contains the *non-graphitizing carbons*, and includes those treated at temperatures up to 3000° C. Among the non-graphitizing carbons are the oxygen-rich, low rank coals, sugar charcoal, and the char prepared by pyrolysis of polyvinylidenechloride. These substances show, even after heating to 3000° C, no trace of homogeneous development of the three-dimensional graphite structure. (It will be seen below that many non-graphitizing carbons form, in a separate phase, a small proportion of graphitic carbon.) The layer diameter does not increase to more than about 70 Å, nor the number of layers per parallel group to more than about twelve.

The lower curve in figure 2 contains the *graphitizing carbons*. These include a pitch coke, a petroleum coke, cokes prepared from coking coals, and the char obtained by pyrolysis of polyvinylchloride. The results shown in the figure are for graphitizing carbons heated to temperatures up to only 1720° C, a temperature

TABLE 1. VALUES OF THE NUMBER OF LAYERS PER PARALLEL GROUP (M) AND THE LAYER DIAMETER (L) FOR NON-GRAFHTIZING AND GRAFHTIZING CARBONS HEATED TO DIFFERENT TEMPERATURES (T)

substance	T ($^{\circ}\text{C}$)	M	L (\AA)
non-graphitizing carbons			
polyvinylidenechloride	1000	2.0	16
(commercial product)	2000	2.4	22
'Saran'	2140 (2 hr.)	3.8	38
	2160	4.1	35
	2700	5.6	40
	3000	7.7	50
sugar charcoal	1000	2.4	18
	2160	5.4	40
hexachlorobenzene	1000	2.1	13
coal, 82.4 % carbon (Northumberland)	2160	7.4	47
coal, 83.1 % carbon (Yorkshire)	3000	11.6	65
	2850	9.8	57
graphitizing carbons			
polyvinylchloride	1000 (2 hr.)	4.5	18
	1000 (13 hr.)	4.9	27
	1220	8.8	30
	1480	15.5	40
	1720	33	63
petroleum coke	1000	4.1	22
	1220	9.9	35
	1480	13.0	40
	1720	31	66
pitch coke	1220	9.6	35
	1480	13.4	40
Welsh coking coal	1460	12.1	40

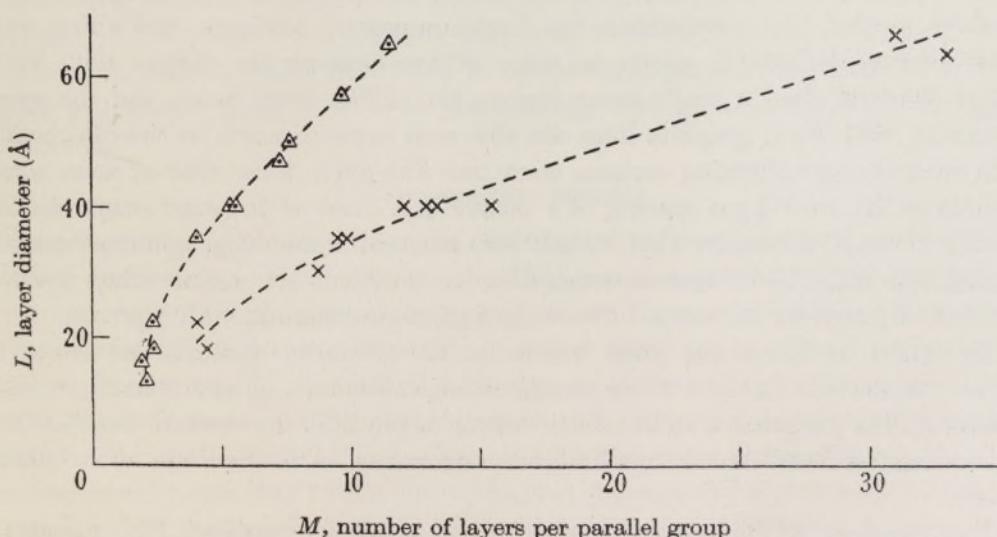


FIGURE 2. Relationship between the layer diameter, L , and the number, M , of layers per parallel group for graphitizing (\times) and non-graphitizing (Δ) carbons.

sufficient to produce, in these carbons, a layer diameter of about 70 \AA and parallel-layer groups containing about thirty layers. With further increase in temperature both L and M increase rapidly and graphitization sets in (Franklin 1951*b*).

It is seen in figure 2 that the graphitizing and non-graphitizing carbons can be clearly distinguished, even in the early stages of the carbonization process. The graphitizing carbons are those which, at 1000°C , have approximately four layers per parallel group, while for the non-graphitizing carbons prepared under the same conditions M lies between 2.0 and 2.5. As long as L is less than about 25 \AA and there remains an appreciable quantity of non-organized carbon, increasing temperature causes L to increase with little change in M . When L exceeds 25 \AA , M increases very much more rapidly with respect to L in the graphitizing carbons than in the non-graphitizing carbons.

Two-phase and three-phase graphitization

Many non-graphitizing carbons, after heating to temperatures between 2000 and 3000°C , contain a small proportion of graphitic carbon. The mechanism of the formation of this will be discussed later, but it must be emphasized that it is quite distinct from the partial development of the graphite structure in the graphitizing carbons. In the graphitizing carbons there is, throughout the graphitization, a single solid phase. A certain proportion of the graphite-like layers, distributed more or less at random throughout the mass, are orientated with respect to neighbouring layers as in crystalline graphite. The X-ray diagrams show deformed (hk) bands or diffuse (hkl) ($l \neq 0$) lines (Franklin 1951*b*). When graphitic carbon is formed in the non-graphitizing carbons, on the other hand, it appears as a separate phase in the X-ray diagrams. In particular, the (002) line is composite. Superimposed on the diffuse band given by the small groups of parallel layers in the non-graphitic carbons there appear either one or two fine lines.

This phenomenon has been observed for all except one of the non-graphitizing carbons studied. The exception is the Northumberland low-rank coal which, even after heating to 3000°C , shows no trace of fine lines on the diffuse (002) band. Sugar charcoal gives a single sharp line on the diffuse (002) band, and the corresponding (hkl) ($l \neq 0$) graphite lines are also seen superimposed on the (hk) bands. The other non-graphitizing carbons show two fine (002) lines. One of these corresponds to the inter-layer spacing of a carbon in a state of incipient graphitization (about 3.425 \AA) (Franklin 1951*b*), and the other to a highly graphitized carbon. Again, the (hkl) ($l \neq 0$) lines corresponding to the latter are visible when the proportion of graphitic carbon is sufficiently high (more than about 1%).

Examples of composite (002) bands in non-graphitic carbons are shown in figure 10, plate 3. In table 2 the results of measurements on such bands are summarized. The proportion of the total carbon responsible for each of the fine lines was estimated from the relative integrated intensities of the lines and of the diffuse band.

Two features of the results seem to be of particular interest. The integrated intensity of the fine lines in any given carbon is almost independent of the temperature of preparation, once the temperature at which the fine lines first appear

has been exceeded. When there are two fine lines, the relative intensity of the graphitic fine line increases with increasing temperature of treatment, while that of the non-graphitic ($3\cdot425\text{ \AA}$) decreases, but the total content of the two remains approximately constant. That is, at a certain temperature (or in a certain temperature range) there is formed, in a non-graphitizing carbon, a certain proportion of graphitic or graphitizable carbon, and this proportion is not appreciably increased when the temperature is further raised.

TABLE 2. TWO-PHASE AND THREE-PHASE GRAPHITIZATION

substance	temperature (°C)	position of sharp peak (\AA)	content of sharp peak, % total carbon
polyvinylidenechloride (commercial product 'Saran')	2140 (2 hr.)	3.426	1.3
	2140 (5 hr.)	3.427	2.2
	2160	3.362	1.0
		3.429	2.0
	2700	3.357	0.6
		3.424	1.6
	3000	3.359	1.5
		3.426	1.7
sugar charcoal	2160	3.39	3.7
	2700	3.36	3.8
	3000	3.36	4.2
coal, 83.1 % carbon (Yorkshire)	2950	3.361	3.2
		3.425	1.5
			4.7

The other point of interest is the high degree of graphitization in the graphitic fraction. The degree of graphitization is given by the position of the (002) line (Franklin 1951b). The spacing, 3.36 \AA , observed for the fine line in the non-graphitizing carbons even for a temperature of preparation as low as 2160°C , is attained, in the graphitizing carbons, only near 3000°C . Thus the small proportion of graphitic carbon which is formed in certain non-graphitizing carbons is *more highly graphitized* than is a true graphitizing carbon heated under the same conditions.

Fine-structure porosity

In comparing the X-ray diagrams of different carbons prepared at 1000°C , a further distinction between the graphitizing and non-graphitizing carbons is at once apparent. The non-graphitizing carbons are those which show a broad and intense low-angle scattering. This indicates that there are important variations of electron density within the solid, the dimensions of the homogeneous regions being of the order of some tens of Angströms; the solid probably contains a large volume of extremely small holes. In general, when a highly porous carbon is formed at low temperatures (below 500°C) the greater part of the porosity is preserved on further heating; when the carbon is formed in a relatively compact form it remains compact at high temperatures. The compact carbons are graphitizing, and the porous carbons are, in general, non-graphitizing.

Low-angle scattering

The low-angle X-ray scattering has been used to study the size and distribution of the effective elementary particles in the highly porous polyvinylidenechloride chars. The results obtained with the 1000°C char have already been described (Franklin 1950b), and are here compared with similar measurements on samples prepared at higher temperatures.

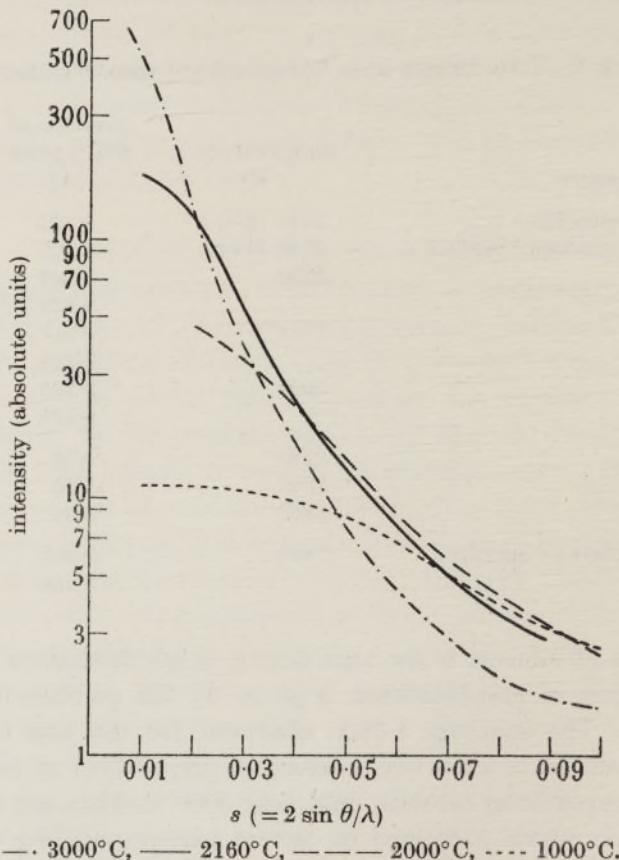


FIGURE 3. The low-angle scattering of polyvinylidenechloride chars; the (corrected) experimental intensity curves.

The intensity curves, corrected for the height of the X-ray beam and other geometrical factors, are shown in figure 3, where unit intensity is the independent (gas) scattering. The Fourier transform has been applied to each of these curves in order to obtain the mean spherical particle distribution.

The Fourier transform of the low-angle scattering curve gives the radial distribution of the elementary particles in just the same way as that of the complete scattering curve gives the radial distribution of the atoms. The conclusions which can be drawn therefrom are, however, less precise for the low-angle scattering, owing to the unknown form factor (Ewald 1940) of the particles. To obtain a sharp atomic density function, approaching that which would be given by point atoms, it is usual to divide the observed high-angle intensity curve by the square of the atomic scattering factor. To perform the corresponding operation for the low-angle

scattering, it would be necessary not merely to know in advance the size and shape of the particles and hence to calculate their mean spherical form factor, but also to assume that there is no preferential orientation between neighbouring particles; this, in view of the stratified character of the carbon structure, is highly improbable. The Fourier transform has therefore been applied directly to the corrected experimental intensity curves. The resulting density function, $\rho(r)$, is necessarily highly diffuse, but the position of the first maximum gives a useful indication of the mean inter-particle distance, and the first minimum corresponds roughly to the particle diameter.

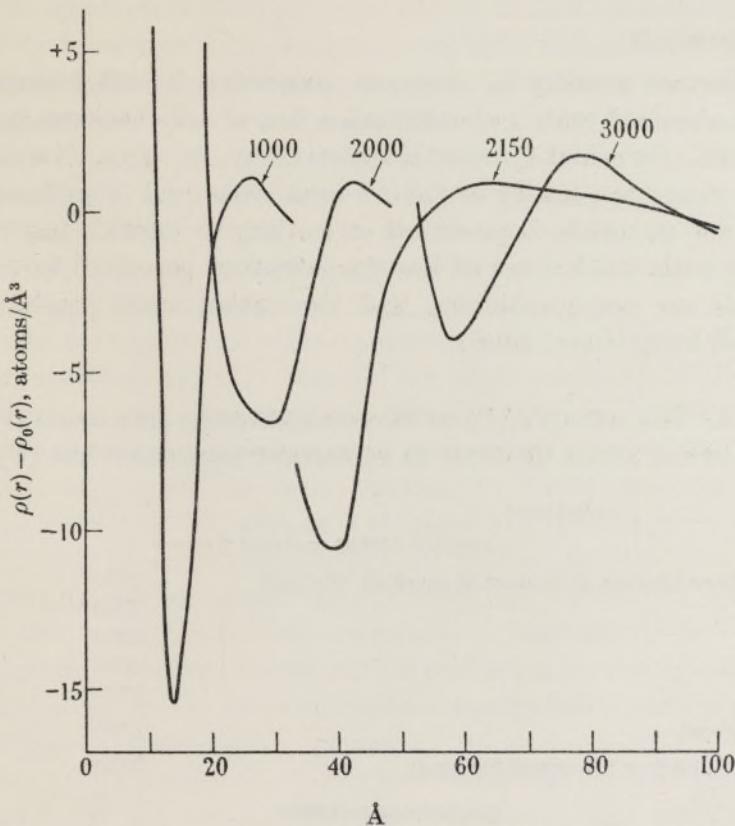


FIGURE 4. Fourier transform of the low-angle scattering of polyvinylidenechloride chars.

The Fourier transform curves are shown in figure 4, where $\rho(r) - \rho_0(r)$ is plotted as a function of distance, $\rho_0(r)$ being the mean macroscopic density. In table 3 the results shown in figure 4 are compared with the values of L , the diameter of the graphite-like layers, obtained from the shape of the (11) band. It is clear that, throughout the series, the position of the first minimum is approximately equal to, and that of the first maximum slightly greater than, L .

This important result shows that for all temperatures up to 3000°C the small groups of parallel graphite-like layers in this non-graphitizing carbon are approximately coextensive with the elementary particles. That is, the growth of the layers is limited by the limited growth of the particles, thus confirming that the non-graphitizability of the carbon is related to its finely porous structure.

TABLE 3. POLYVINYLDENECHLORIDE CHARS: COMPARISON OF THE LAYER DIAMETER (L) WITH THE POSITIONS OF THE FIRST MINIMUM AND FIRST MAXIMUM IN THE FOURIER TRANSFORM OF THE LOW-ANGLE SCATTERING CURVES, FOR DIFFERENT TEMPERATURES OF PREPARATION (T)

T (°C)	L (Å)	first minimum (Å)	first maximum (Å)
1000	16	14	26
2000	22	28	42
2160	35	39	65
3000	50	57	78

Density measurements

The fine-structure porosity is, of course, observable by other simple methods, and, for the carbonized coals and anthracites, has already been studied by means of measurements of true and apparent densities (Franklin 1949). It was shown that the large fine-structure porosity of the low-rank coals (and of anthracites), which exists in the raw materials, is preserved on heating to 1600°C, and that the less porous coking coals yield cokes of low fine-structure porosity. Accordingly, the low-rank coals are non-graphitizing and the coking coals graphitizing. (The anthracites will be discussed later.)

TABLE 4. THE DENSITY (D) OF NON-GRAFHTIZING AND GRAFHTIZING CARBONS AFTER HEATING TO DIFFERENT TEMPERATURES (T)

substance	T (°C)	D (g./cm. ³)
non-graphitizing carbons		
polyvinylidenechloride (commercial product 'Saran')	1000	1.59
	2160	1.19
	2500	1.32
	2700	1.30
	3000	1.38
sugar charcoal	3000	1.79
coal, 82.4% carbon (Northumberland)	1000	1.72
graphitizing carbons		
polyvinylchloride	1000	1.99
	1480	2.15
	2310	2.23
	3000	2.25
petroleum coke	1000	2.00
	1480	2.10
pitch coke	1480	2.06

The relationship between graphitizability and fine-structure porosity is illustrated by the density measurements quoted in table 4. These were made by the float-sink method, by dropping a few grains of the dry carbon into mixtures of benzene, carbon tetrachloride and bromoform. These liquids do not penetrate into the fine pores of carbons heated to 1000°C or higher (Franklin 1949), and the difference between the measured density and the true density gives therefore a

direct indication of the fine-structure porosity. The true density lies between 2.20 and 2.26 g./cm.³ for the graphitic carbons, and between 2.0 and 2.20 g./cm.³ for the non-graphitic carbons.

The coal series

It has been shown that the graphitizability of a carbon is apparently related to its colloidal or fine-pore structure. Carbons with a large fine-structure porosity are non-graphitizing and the compact carbons are graphitizing. The question therefore arises as to how carbons having a pore structure of intermediate type will behave.

The colloidal structure of coals in relation to their rank (or carbon content) has been extensively investigated by Bangham and his collaborators (*Conference, etc.* 1944) who showed that the fine-structure porosity and inner surface tend to decrease on passing from the low-rank coals to the coking coals, and to increase again with increasing rank among the steam coals and anthracites. It was therefore decided to investigate the graphitizing behaviour of coals intermediate in rank between the (graphitizing) coking coals and the (non-graphitizing) oxygen-rich low-rank coals, with a view to finding how the transition from a graphitizing to a non-graphitizing carbon takes place.

Measurements were made on chars prepared from two Welsh medium-coking coals. The fine-structure porosity and the low-angle scattering of such chars are greater than those of chars prepared from the strongly coking coals and less than those of chars prepared from the low-rank coals. Their graphitizing behaviour is also found to be of intermediate type. Heating to 3000°C produces only a very small degree of graphitization, such as is obtained in a true graphitizing carbon at about 1700°C. In figure 5 the curves of figure 2, representing the *M-L* relationship for the graphitizing and non-graphitizing carbons, are reproduced, and the points representing these intermediate coals are seen to lie between the two curves.

The intermediate character of these coals is perhaps more clearly seen in figure 6, where *M* is plotted against *T*, the temperature of preparation, for the graphitizing, non-graphitizing and intermediate carbons.

Thus although the majority of carbons apparently fall into two distinct classes, the graphitizing and the non-graphitizing, there exist, also, certain carbons of intermediate type.

The anthracites

The anthracites provide an exception to the rule that finely porous carbons are non-graphitizing and non-porous carbons graphitizing.

Measurements have been made on two Welsh anthracites, of carbon content 93.9 and 94.3% respectively.

It is well known that anthracites have a large fine-structure porosity, and it has been shown (Franklin 1949) that this porosity is preserved on heating to 1600°C. In accordance with this, the X-ray powder diagrams of the anthracites heated to temperatures between 1000 and 2000°C closely resemble those of the non-graphitizing carbons. However, on heating to temperatures above 2500°C the anthracites are more highly graphitized than any other graphitizing carbon investigated.

Numerical results are given in table 5 and in figure 5. The transition from the non-graphitizing to the graphitizing type of diagram occurs in the temperature range 2000 to 2500°C (for a period of $\frac{1}{4}$ hr. at the maximum temperature). The values of M and L recorded for this range represent only approximate mean values, since the detailed form of the intensity curves shows clearly that the structure is in reality far from homogeneous during the transition stage.

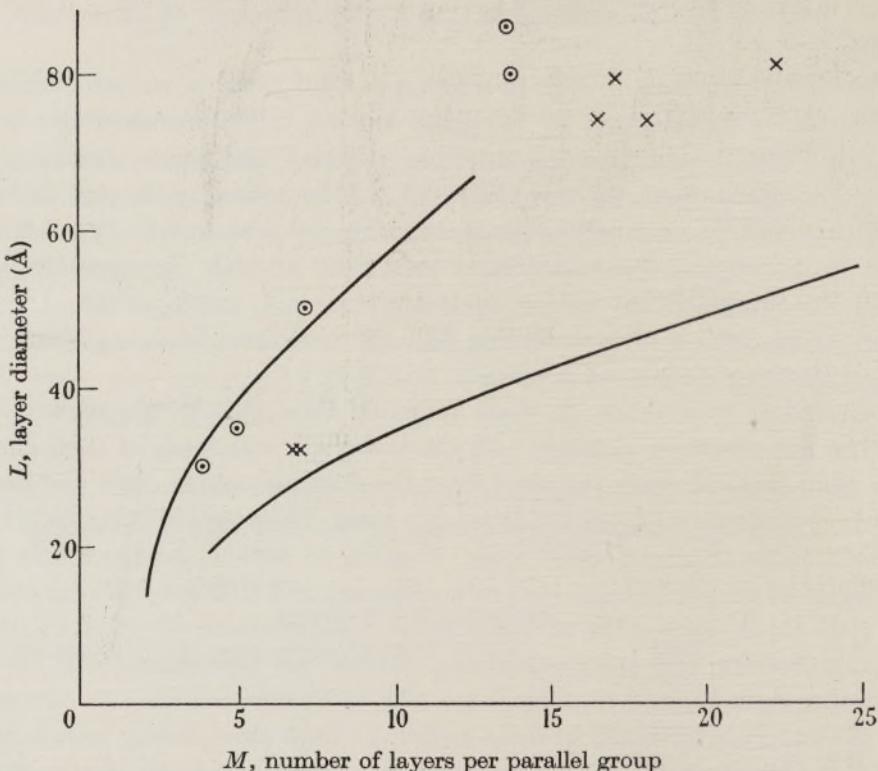


FIGURE 5. Relationship between L and M for the intermediate coals and anthracites. The curves represent the results obtained for the graphitizing and non-graphitizing carbons (figure 2). \times , intermediate coals; \circ , anthracite.

TABLE 5. VALUES OF THE NUMBER OF LAYERS PER PARALLEL GROUP (M) AND THE LAYER DIAMETER (L) FOR ANTHRACITES HEATED TO DIFFERENT TEMPERATURES (T)

substance	T (°C)	M	L (Å)
Welsh anthracite, 93.9 % carbon	1460	5.0	35
	2290	13.5	85
Welsh anthracite, 94.3 % carbon	1460	4.1	30
	2070	7.2	50
	2290	13.7	80

During the transition the low-angle scattering (and fine-structure porosity) progressively disappears, and above 2500°C the anthracites form normal, compact, highly graphitic carbons.

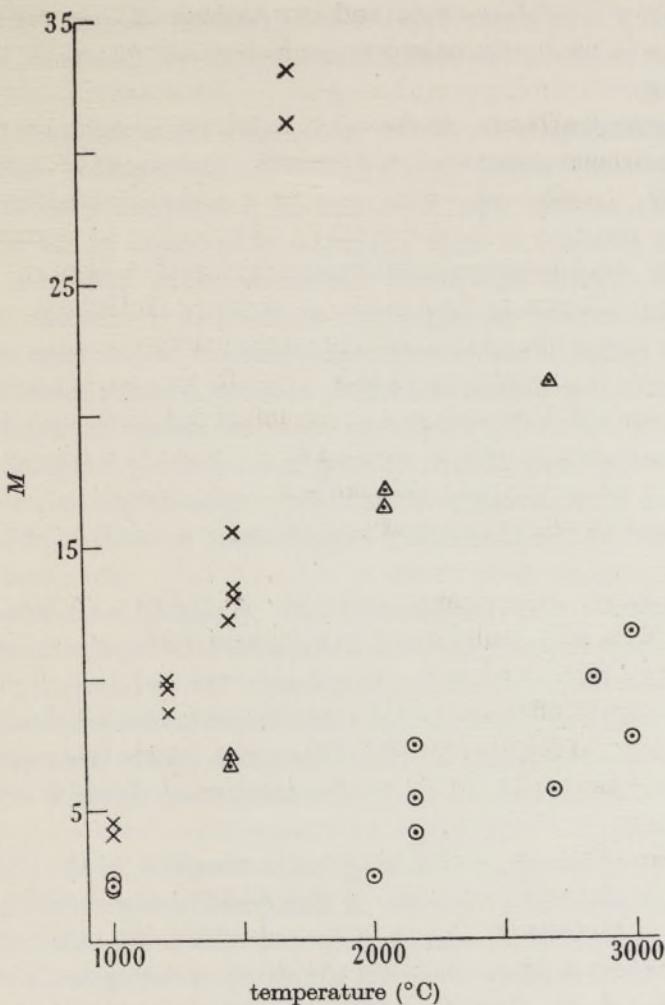


FIGURE 6. Relationship between M and the temperature of preparation, T , for the graphitizing (\times) and non-graphitizing (\circ) carbons and the intermediate coals (\triangle).

DISCUSSION

Origin and nature of the pore structure in the non-graphitizing carbons

Measurements of true and apparent densities show that the fine-structure porosity of the non-graphitizing carbons varies from 20 to 50%. Low-angle scattering measurements show that the diameter of the effective elementary particles is approximately equal to that of the parallel-layer groups, or crystallites,* that is, from 20 to 70 Å. The diameter of the fine pores is therefore not more than a few tens of Ångströms.

These fine pores must result from the formation, in the early stages of the carbonization process, of rigid cross-linking between neighbouring nuclei of carbon. The cross-linking is preserved on heating to higher temperatures, and serves to

* The term 'crystallite' is used in this discussion for the sake of brevity. It should be understood to include those parallel-layer groups in which there is no truly crystalline structure, as well as those in which the three-dimensional graphitic structure is partially or completely developed.

hold neighbouring crystallites apart and in random orientation with respect to one another, and to hinder the coalescence which would be a necessary preliminary to graphitization.

In the graphitizing carbons, on the other hand, the cross-linking must be much weaker, and the carbon nuclei formed during the first stages of carbonization must remain relatively mobile. The formation of a compact graphitizing carbon is favoured by the presence of large quantities of hydrogen in the raw material. In the pyrolysis of organic substances containing much hydrogen, the continued formation of hydrocarbon decomposition products in the interior of the structure during the early stages of carbonization prevents the carbon from 'setting' at very low temperatures; any cross-links which may be formed between neighbouring nuclei of carbon are probably subject to continual reduction and destruction, and the carbon is consequently able to develop in a relatively compact state.

The formation of a strongly cross-linked, open-structured, non-graphitizing carbon is favoured by the presence of oxygen or by a shortage of hydrogen in the raw material.

Thus, for example, polyvinylidenechloride, $(C_2H_2Cl_2)_n$, contains only enough hydrogen to combine with the chlorine to form HCl during the decomposition, and no surplus for the formation of hydrocarbons. On pyrolysis it forms an open-structured coke which solidifies at about $220^\circ C$ and is non-graphitizing. Pyrolysis of polyvinylchloride, $(C_2H_3Cl)_n$, on the other hand, yields large quantities of tar; the residue remains viscous up to about $450^\circ C$ and forms a compact, highly graphitizing carbon.

The importance of strong cross-linking in the structure of the porous carbons is revealed by their physical properties. A non-graphitizing carbon is much *harder* than a compact graphitizing carbon prepared under the same conditions. The difference in hardness is easily observed simply by grinding in a pestle and mortar a small quantity of the coarsely powdered carbons prepared, for example, at $1000^\circ C$. With increasing temperature of preparation in the range 1000 to $2000^\circ C$ the difference becomes still more marked, the non-graphitizing carbon becoming harder and the graphitizing carbon softer. Since the crystallites in both types of carbons are themselves, presumably, at least as soft as graphite, the greater hardness of the non-graphitizing as compared with the graphitizing carbons must be attributed to the greater strength of the bonding between neighbouring crystallites.

Similarly, the *thermal expansion* of a coke prepared from a coking (graphitizing) coal is about twice that of a carbonized low-rank (non-graphitizing) coal prepared under the same conditions (Bangham & Franklin 1946), and this again may be attributed to the greater strength of the cross-linking in the latter material.

The non-organized carbon

It has been shown that when carbons prepared at $1000^\circ C$ are heated to higher temperatures the change in structure consists, at first, mainly in the lateral growth of the small graphite-like layers at the expense of the non-organized carbon. This non-organized carbon is presumably attached to the edge-atoms of the graphite-

like layers, and links neighbouring crystallites one to another. X-ray measurements provide no clue as to its chemical character; it may well include both chain and ring structure, and contain some hydrogen. On heating it is presumably absorbed, atom by atom, or at least by small fragments, into the layer-planes to which it is attached, leaving, finally, only a few carbon atoms to effect each link between neighbouring crystallites.

Growth of the parallel-layer groups

It remains to consider by what mechanism the crystallites continue to grow, both in breadth and height, once the non-organized carbon has been consumed. It is, perhaps, tempting to suppose that there is some mechanism by which isolated carbon atoms or small groups of atoms could migrate from the smaller to the larger ordered units. One might imagine such a development to take place through the vapour phase, or by surface migration, or even by means of an unstable intermediate compound formed by combination of the carbon with a trace of impurity (for example, hydrogen). But it is easily shown that no such mechanism can account for the observed facts.

If the process of crystallite growth were dependent on the migration of isolated atoms or small groups of atoms from one crystallite to another, it would involve the breaking of some of the strong carbon–carbon bonds in the graphite-like layers. It would therefore be a high-temperature reaction, and have a high energy of activation and a high temperature coefficient of velocity, and the temperature range in which it occurred with measurable speed would be sharply defined and rather narrow. Instead, crystallite growth occurs with measurable speed in the whole range of temperature from 1000 to 3000°C. It is therefore necessary to suppose that the structural change which occurs at each stage renders further development progressively more difficult, the energy of activation increasing continuously as the crystallite size increases. This would be explained if *whole layer-planes*, or even groups of layers, are displaced intact during the crystallization process. As the size of the layers or groups increases, so higher and higher temperatures are required to provide sufficient energy to displace them and thus to continue the process of crystallite growth.

It has been shown that the non-graphitizability of certain carbons is associated with their finely porous structure, which results from the system of strong cross-links formed at low temperatures and holding neighbouring parallel-layer groups apart. If crystallite growth resulted from the movement of isolated atoms or small groups of atoms it is hard to see how either the pore structure or the cross-linking associated with it could be effective in preventing the process. If, on the other hand, it resulted from the movement of whole layers or large fragments, the importance of cross-linking and fine pores in retarding the process is at once explained. In a compact carbon, the conception of whole layer-planes moving by small stages seems a reasonable one; no large, abrupt movement need be involved, especially if we admit the possibility of a *slight* bending of the layers during their migration. But it is clear that when each crystallite is more or less surrounded by fine pores, as in the non-graphitizing carbons, the movement of the layers will be seriously

hindered. Similarly, strong cross-linking between neighbouring crystallites must obviously impede the movement of the layers.

Further, if a whole migrating layer-plane or group is to join itself to an existing crystallite, there is, *a priori*, a higher probability of its being fixed on the basal plane than of its becoming attached to the edge-atoms of a layer-plane; for the

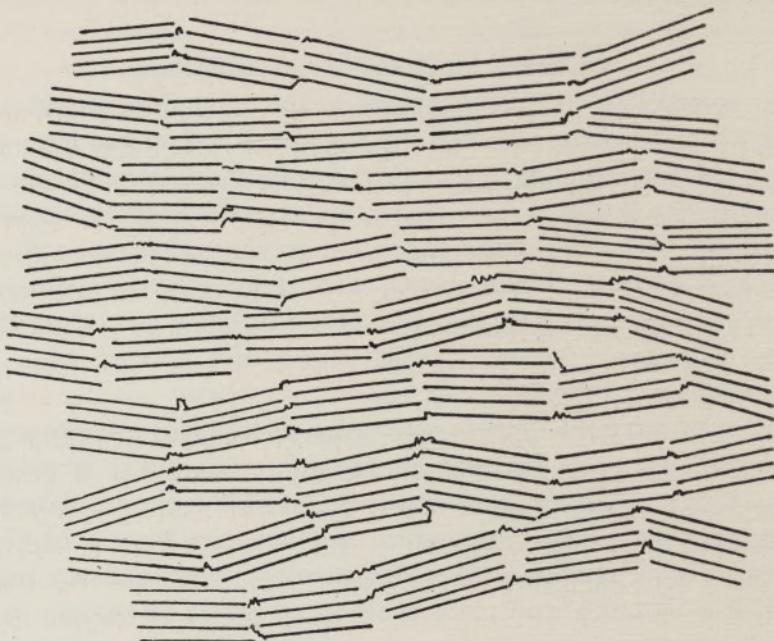


FIGURE 7. Schematic representation of the structure of a graphitizing (but non-graphitic) carbon.

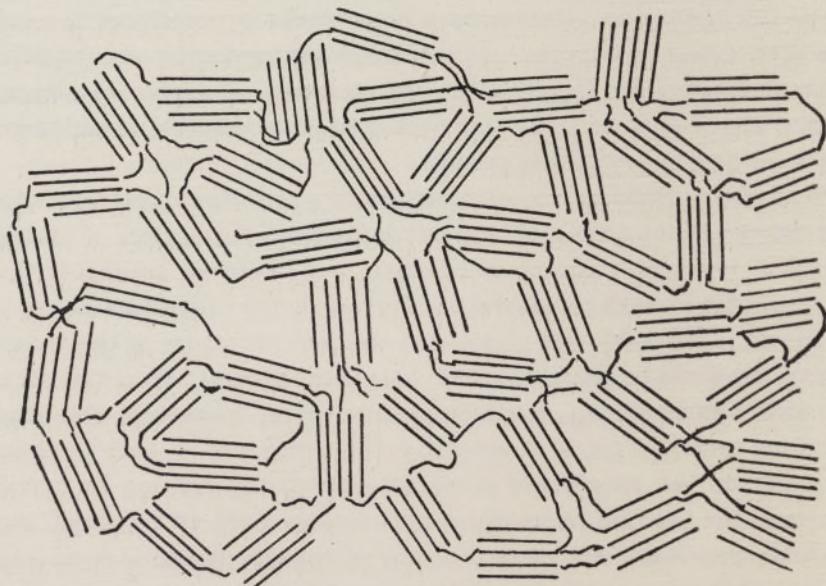


FIGURE 8. Schematic representation of the structure of a non-graphitizing carbon.

former it only requires to be parallel to, and at a fixed distance from, the basal plane, whereas for the latter it must not only lie in the correct plane, but must also adopt the correct orientation. This may, perhaps, explain why, in the graphitizing carbons, the crystallites grow in height more rapidly than in diameter. If, on the other hand, growth occurred through the movement of isolated atoms or small groups, these would tend to be fixed by the unsaturated valencies at the edges of the layers rather than on the basal planes.

Orientation of the crystallites

If crystallite growth occurs by the movement of whole layers or groups of layers, it is clear that the only way in which such large units could be supposed to move is by *gradual* shifting of position; and this could only occur easily if the layer-planes of neighbouring crystallites lie nearly parallel to one another.

In a compact carbon the shape of the crystallites alone makes a tendency to parallelism of nearest neighbours highly probable. In fact, it is found that in the graphitizing carbons a preferential orientation of the crystallites exists not only between nearest neighbours but also in the mass. For a series of carbons prepared at 1000°C small parallel-sided flakes formed at the surface of the recipient were examined. In the non-graphitizing carbons X-ray photographs revealed no trace of preferential orientation, whereas in the graphitizing carbons a strong tendency of the layer-planes to lie parallel to the surface of the flake was always observed. An example of this, the diagram given by such a flake of a petroleum coke heated to 1000°C, is shown in figure 11, plate 3.

It is seen in figure 11 that the low-angle scattering (which is very weak compared with that of a non-graphitizing carbon) is orientated even more strongly than the (002) band, and in the same direction. This indicates that such pores as exist in this relatively compact carbon are situated between the basal planes of neighbouring near-parallel crystallites, and not between the edges of the layer-planes of neighbouring groups. Such a structure is represented schematically in figure 7. The process of crystallite growth then consists, primarily, in the progressive elimination of the holes by gradual shifting of the near-parallel groups into truly parallel positions.

A schematic representation of the structure of a non-graphitizing carbon, showing the strongly cross-linked system of randomly orientated crystallites, and the resulting large porosity, is given in figure 8.

Further evidence of the importance of *orientation* as a prerequisite of graphitization is given in the following sections.

Two-phase and three-phase graphitization

When a small proportion of graphitic carbon is formed, as a separate phase, in a non-graphitizing carbon, it is in general more highly graphitized than a normal graphitizing carbon prepared under the same conditions, and the quantity formed is nearly independent of the temperature of preparation (table 2).

The phenomenon is of too general occurrence for it to be supposed, simply, that the non-graphitizing carbon is not homogeneous and contains, from the start, a small proportion of graphitizing carbon. Moreover, this would explain neither

the abnormally high graphitizability of the small proportion of graphitizing carbon nor the existence of the fine line at $3\cdot425\text{ \AA}$. (In a normal graphitizing carbon the (002) line is considerably more diffuse when the spacing is as large as this.) Nor can it be supposed that the graphitizing carbon occupies a special position in the structure of the non-graphitizing carbon, since the diameter of the structural units in the non-graphitizing carbon does not exceed 70 \AA , whereas that of the crystallites of the graphitic carbon certainly exceeds 500 \AA .

It seems that the formation of a small fixed proportion of graphitic carbon in a non-graphitizing carbon must result from the high internal stresses set up during thermal treatment. The true coefficient of volume thermal expansion of the carbon crystallites is presumably not very different from that of graphite, 27×10^{-6} (Nelson & Riley 1945). As a result of the strong cross-linking in a non-graphitizing carbon the system is constrained to have a volume expansion coefficient of only about 4×10^{-6} . This means that at 2000°C internal stresses are sufficient to cause a volume contraction of about 5 %. Even if a substantial part of this be taken up in a diminution of the pore volume, it is probable that very strong internal tensions remain. Thus, when the cross-links begin to break (either owing to tension or to normal thermal decomposition or to a combination of the two effects) the layer-planes or groups of layers set free will at once be severely compressed by the surrounding cross-linked structure under tension, and there will take place, effectively, a localized crystallization under high pressure in the interior of the solid.

The development of such graphitic nuclei in the interior of the solid will relieve to some extent the stress in the surviving cross-linked structure. The formation of graphitic carbon will cease when the tension in the non-graphitic structure is sufficiently reduced. On heating to higher temperatures the cross-links will be more easily broken down, and hence no further stresses sufficiently great to cause graphitization will be set up. Thus the graphitic carbon in a non-graphitizing carbon is formed in a limited temperature range, and the quantity formed does not increase with further increase of temperature. It is more highly graphitized than a normal graphitizing carbon because it is crystallized under pressure.

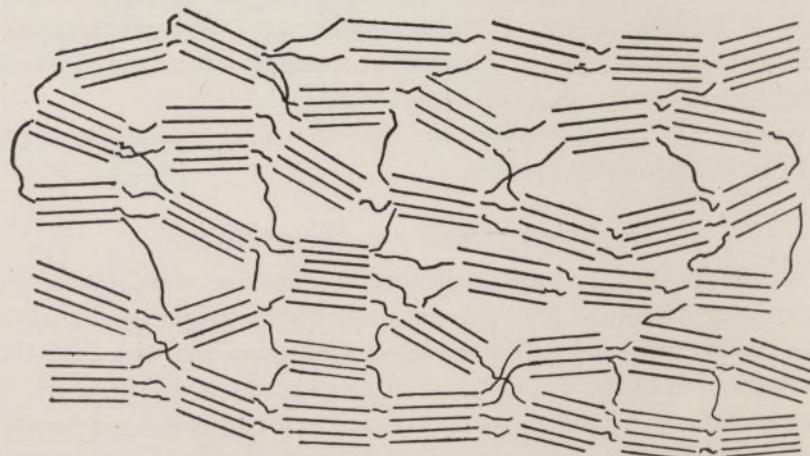


FIGURE 9. Schematic representation of the structure of a low-temperature anthracite char.

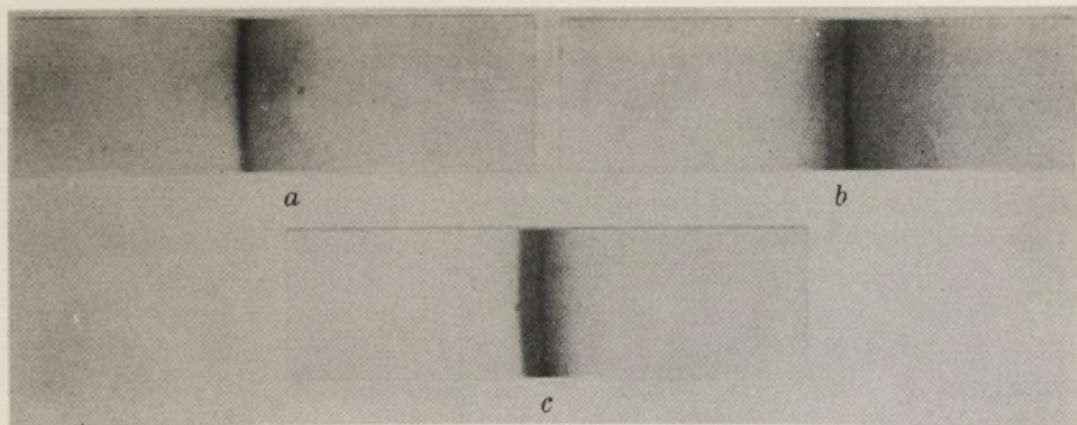


FIGURE 10. Two-phase and three-phase graphitization. *a*. Sugar charcoal heated to 3000°C. The (002) band, showing one sharp line at 3.36 Å on the diffuse band. *b*. Polyvinylidene-chloride heated to 2700°C. The (002) band, showing two sharp lines on the diffuse band. *c*. Yorkshire coal (83.1 % carbon) heated to 2950°C. The (002) band, showing two sharp lines on the diffuse band.



FIGURE 11. Petroleum coke treated at 1000°C. X-ray beam parallel to surface of flake.
Plane of flake vertical.

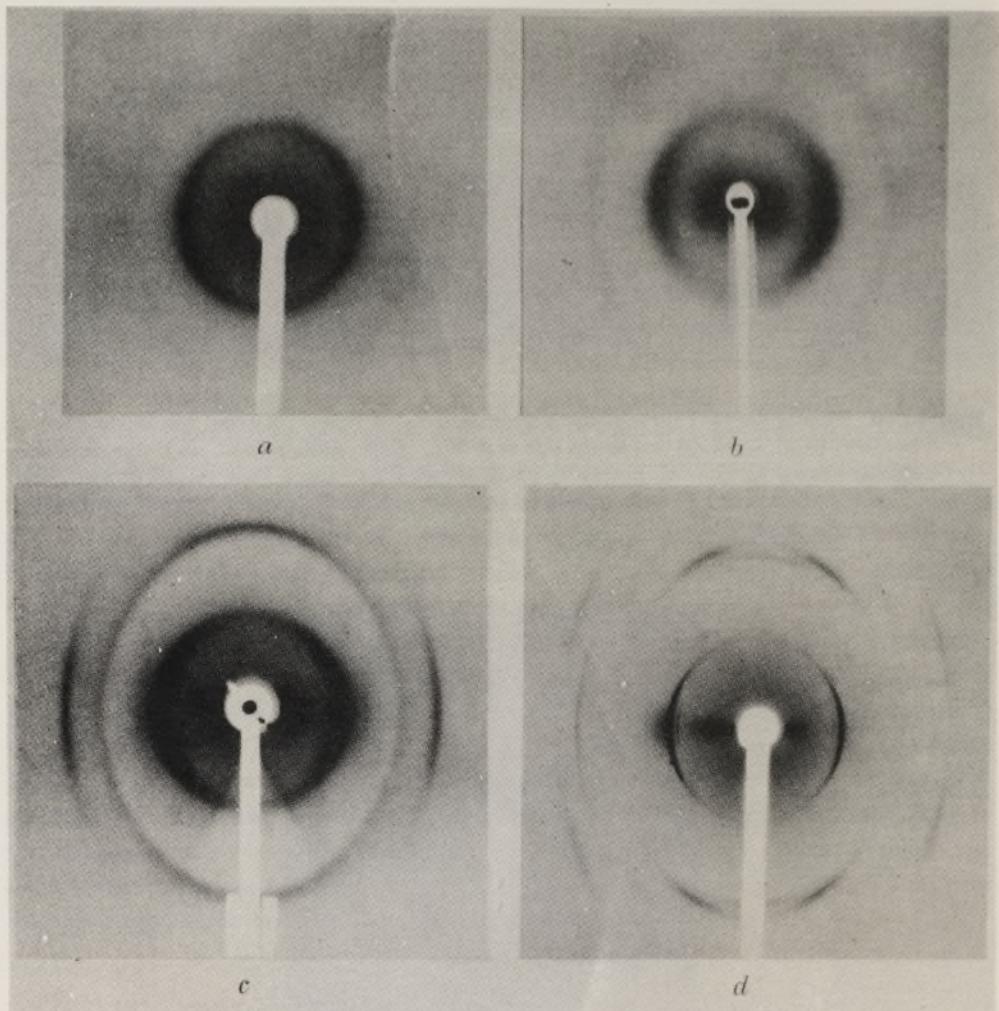


FIGURE 12. Monolith of Welsh anthracite (94.3 % carbon). X-ray beam parallel to surface of flake (i.e. parallel to bedding plane). Plane of flake vertical. *a*, raw anthracite; *b*, heated to 1000°C; *c*, heated to 2400°C; *d*, heated to 2650°C.

It will be noted that in the above explanation we admit that at sufficiently high temperatures the cross-linking in a non-graphitizing carbon is at least partially destroyed. This is confirmed by the decreased *hardness* of the carbons. Simple abrasion tests show that those non-graphitizing carbons in which a small proportion of graphitic carbon is formed are considerably less hard after heating to 3000°C than after heating to only 2000°C. Nevertheless, in spite of the partial breakdown of the cross-linking, no trace of homogeneous graphitization occurs at 3000°C. This must be because neighbouring crystallites are not *suitably orientated* with respect to one another.

That the absence of strong cross-linking is not in itself a sufficient condition for graphitization to occur at high temperatures is confirmed by the behaviour of fine-particle *carbon blacks*. All carbon blacks in which the particle size is sufficiently small are non-graphitizing. Here any cross-linking which may exist between the particles must be extremely weak, and the non-graphitizability can only be attributed to the lack of good contact between neighbouring crystallites.

Thus, in order that graphitization should occur in a given carbon, two conditions must be fulfilled. The first is that the system of cross-linking which unites the crystallites in the mass should not be too strong. The second, and perhaps more fundamental, condition is that neighbouring crystallites should be suitably orientated with respect to one another.

The anthracites

The anthracites, heated to temperatures between 1000 and 2000°C, form hard chars with a large fine-structure porosity. The pore structure greatly resembles that of chars prepared from the low-rank coals (Franklin 1949), and the X-ray powder diagrams resemble in all respects those of the non-graphitizing carbons. Nevertheless, at temperatures above 2500°C the anthracites form graphitic carbons more highly graphitized than any others obtained during the course of this investigation.

There is, however, one important respect in which the low-temperature anthracite chars differ from those of the low-rank coals or other non-graphitizing carbons. The structure of the anthracite chars is anisotropic.

The anisotropy which exists in raw anthracites is well known, the layer-planes showing a tendency to lie parallel to the bedding plane. X-ray photographs of a thin plate of Welsh anthracite, cut parallel to the bedding plane and heated to various temperatures up to 2700°C (figure 12, plate 4), show that the degree of orientation is greatly increased by thermal treatment.

It was shown above that the strong cross-linking which exists in the non-graphitizing carbons is at least partially broken down at sufficiently high temperatures. Graphitization does not occur because the crystallites are in random orientation and the pore structure remains intact. In the case of the anthracites, however, only the cross-linking hinders crystallite growth at temperatures below 2000°C. When, at higher temperatures, the cross-linking is destroyed, the orientated crystallites are in a position to unite and eliminate the holes in the structure, and graphitization follows. A schematic representation of the structure of a low-temperature anthracite char is given in figure 9.

Thus the behaviour of the anthracites, which appears at first sight to be anomalous, in reality provides strong confirmation both of the importance of cross-linking in hindering crystallite growth and of the importance of orientation as a prerequisite of graphitization.

Chemical behaviour

The above conclusions concerning the existence of strong cross-linking in the non-graphitizing carbons and in the low-temperature anthracite chars have received further confirmation from the work of Maire (1951 and private communication).

Maire studied the effect of Brodie's reagent (concentrated nitric acid and potassium chlorate) on a series of carbons prepared at temperatures between 1000 and 2000°C, and on Acheson graphite. Working under conditions such that the Acheson graphite was completely converted to graphitic acid (with an increase in weight of about 51% and with no measurable loss of carbon) he found that the other substances were divided sharply into two groups. For the *graphitizing carbons* an increase in weight of from 18 to 50% was observed, and the X-ray diagrams of the solid products showed a partial or almost complete transformation of the carbon into graphitic acid; for the *non-graphitizing carbons*, the increase in weight never exceeded 3%, and the X-ray diagram of the solid was unchanged after the reaction. The anthracite chars prepared below 2000°C behaved in this respect (as also in their X-ray powder diagrams) like the non-graphitizing carbons.

It is clear that the strong cross-linking which immobilizes the layer-planes and hinders crystallite growth in the non-graphitizing carbons and in the low-temperature anthracite chars prevents, also, the separation of the layer-planes to give the increase in inter-layer spacing (from 3.4 to 3.7 Å to 6 Å) which accompanies the formation of graphitic acid.

Later work (Maire, private communication) has provided confirmation of the partial destruction of the cross-linking in the non-graphitizing carbons heated to higher temperatures. Most non-graphitizing carbons, after heating to temperatures between 2500 and 3000°C, show, on treating with Brodie's reagent, a partial transformation to graphitic acid.

CONCLUSIONS

A study of the structure of carbons of different origin, and of the variation of the structure with the temperature of preparation, shows that the majority of carbons correspond to one of two well-defined and markedly different types.

The *non-graphitizing carbons* are formed, in general, from substances containing little hydrogen or much oxygen. On heating such substances there develops, at low temperatures, a strong system of cross-linking which immobilizes the structure and unites the crystallites in a rigid mass. The resulting carbons are hard, and their fine-structure porosity is large and is preserved at high temperatures. The elementary particles in the finely porous structure are at all stages approximately co-extensive with the crystallites, and the latter are in random orientation in the mass.

Such carbons show no trace of homogeneous development of the true graphitic structure, even after heating to 3000°C. The diameter of the graphite-like layers does not grow to more than about 70 Å, and the number of such layers per parallel group, or crystallite, does not exceed about twelve.

The non-graphitizability of these carbons results from their porous structure and the random orientation of the crystallites.

The *graphitizing carbons* are prepared, in general, from substances containing much hydrogen. The crystallites remain relatively mobile during the early stages of carbonization, and cross-linking in the mass is weak. The carbons are softer and less porous than the non-graphitic carbons prepared under the same conditions, and their crystallites are more highly developed, especially in the direction perpendicular to the layers. There is at all stages a strong tendency for neighbouring crystallites to lie nearly parallel to one another, leaving only small holes between the basal planes of neighbouring groups (figure 7). Graphitization sets in at about 1700°C and increases rapidly with increasing temperature.

There is much evidence that crystallite growth occurs by the movement of whole layers or even groups of layers, and *not* by isolated atoms or small groups of atoms. Since such large units can only be supposed to move by small successive stages, the near-parallelism of neighbouring crystallites in the graphitizing carbons is probably the most important factor responsible for crystallite growth and graphitization.

The *anthracites*, at temperatures below 2000°C, form strongly cross-linked, highly porous carbons which greatly resemble the non-graphitizing carbons. They differ from the latter, however, in that they show a strong preferential orientation of the crystallites in the mass. Thus the low-temperature anthracite chars behave in most respects like the non-graphitizing carbons; but when, at higher temperatures, the cross-linking begins to break down, the near-parallelism of neighbouring crystallites leads at once to rapid crystallite growth, and highly graphitic carbons are formed.

The small and almost constant proportion of highly graphitic carbon formed in many non-graphitic carbons at temperatures between 2000 and 3000°C is believed to result from the high internal tensions which must exist in the strongly cross-linked non-graphitic carbons at high temperatures. When the tensions are such that the cross-linking begins to break down, a localized crystallization under high pressure takes place in the interior of the solid.

To summarize, in order that crystallite growth and graphitization should occur readily in a given carbon, two essential conditions must be fulfilled. The system of cross-linking which unites the crystallites in the mass must not be too strong, and neighbouring crystallites must lie in near-parallel orientation.

I am very grateful to Dr I. G. C. Dryden and the late Dr D. H. Bangham, of the British Coal Utilization Research Association, for providing me with all the coals and anthracites used in this investigation. I wish to thank also Monsieur P. Corriez for a sample of sugar charcoal, Professor H. L. Riley for the hexachlorobenzene carbon, and the Société Carbone Lorraine for the pitch coke and petroleum coke.

I am deeply indebted to Monsieur le Professeur Ribaud for putting at my disposal the facilities of the Laboratoire de Hautes Températures, where all carbons treated at temperatures above 1000°C were prepared.

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The thermal oxidation of methylamine

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A study has been made of the kinetics of the reaction of gaseous methylamine with oxygen. Since the nitrogen atom is eliminated from the molecule in the course of the oxidation, analysis of the products formed at various stages yields evidence about the reaction mechanism which is not available in the study of hydrocarbons.

The variation of oxidation rate with time may be represented by the equation

$$\frac{dp}{dt} = B e^{Ct} + D,$$

and the influence of reactant pressures and of temperature on *C* and *D* has been determined. Inert gases do not affect the course of the oxidation, but an increase in surface inhibits the reaction to an extent dependent on the composition of the reactant mixture.

Since the later stages of the oxidation are complicated by secondary reactions, the analytical results for the early stages provide the most useful information about the main chemical reactions occurring.

The greater part of the combined nitrogen is initially converted to ammonia, but small quantities of nitrogen oxides are also formed. The fact that the concentration of ammonia is lowered and that of nitrogen oxides is raised by increasing oxygen pressure suggests that both products arise from reaction of NH₂ radicals with the original reactants. One source of these radicals is probably the breakdown of intermediate peroxides such as NH₂CH₂—O—O—H,