

d_0 = density of filler per unit volume of bulk material
 $d - d_0 = \rho$ of binder
 $\bar{I} = \rho$ of binder and coke after it has been compressed

PHYSICAL PROPERTIES OF CARBONS AND THE FORMULATION OF THE GREEN MIX*

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The dependence of different physical properties of carbons and polycrystalline graphites upon the porosity introduced in the manufacturing process is analyzed. The apparent (bulk) density, d , of the material is a function of two variables: the density of the coke filler, d_0 (mass of filler per unit volume of bulk material), and the density of the binder coke, $(d - d_0)$. Making a number of simplifying assumptions as to the distribution of the binder coke and as to the statistics of the interparticle contacts, the following relations are derived: For the moduli of elasticity, rigidity and volume expansion, $E = E_0 d_0^z (d - d_0)$; for the mechanical strength, $S = S_0 d_0^y (d - d_0)$; and for the electric and heat conductivities, $1/\rho = (1/B) d_0^x (d - d_0)^{-1}$. It is shown that the exponents must satisfy the relations $x = z + \frac{1}{2}$ and $y > z$. The coefficients E_0 , S_0 and $1/B$ are proportional to the respective values for the dense material; S_0 is inversely proportional to some fractional power of the radius of coke particles. Adaptation of the formulas to cases of different binder-coke types, coke particles with internal porosity, non-equiaxed particles and mixture of particles of two sizes are discussed. It is further shown that the formulas derived make possible an analysis of a carbon from which information can be obtained as to the formulation of the original mix. The method is illustrated by using data obtained by K. Hong on the elastic modulus and electric resistivity for a batch of extruded baked carbon rods, for which it is found $E = 4 \times 10^{11} (d - 1.26)$ dynes/cm² and $1/\rho^2 = 2 \times 10^5 (d - 1.28)$ mho²/cm². A consideration of the limitations imposed on the relative values of d_0 and $(d - d_0)$ by the manufacturing process (compression of the green mix) leads to predictions as to the optimum conditions for the mechanical strength, elastic moduli and conductivities.

I. INTRODUCTION

The ultimate aim of investigations of carbons and graphites is the complete understanding of the dependence of their properties on their structure, and the clarification of the nature of the forces and of the mechanisms involved in their formation. When and if this goal is attained, the manufacturers' task of preparation of carbons with well-defined properties for different uses will be greatly simplified. At present there seem to be two main areas where answers have to be obtained: One is the dependence of the final microstructure on the starting organic material and the heat-treatment procedures, and the relation

between the microstructure and the different physical and chemical properties of the material. As can be seen for instance from this volume, studies are being pursued in this direction. The second area covers the problems of the dependence of the properties of the final material on the formulation of the mix, that is, on the relative amounts of binder and filler, particle sizes used and their shapes, and finally on the processing procedures like extrusion, molding and so forth. No fundamental work has been done in this field, the existing information being mostly of an empirical nature.

Most of the physical properties are strongly dependent on the porosity of the material. In the case of carbons one finds two distinctive types of porosity. One is of a

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very fine type, composed of small inter-crystalline spaces mostly formed in cooling and due to the extreme anisotropy of single crystallites. This is the unavoidable microporosity, which depends on the type of microcrystalline structure and actually has to be considered a part of microstructure¹. The other porosity is of a much coarser type; in cokes it consists of bubbles formed during setting, with a wide size distribution depending on the conditions prevailing at that time. In manufactured carbon materials, a macroporosity is due to the method of preparation and is quite uniform throughout the material. Most of the physical properties depend so strongly on this porosity, that a more precise comparison of the real properties of, for instance, two different carbons is possible only if both carbons are made with exactly the same type of porosity (this is in general very difficult, if not impossible). Some authors have tried to circumvent this difficulty and reduce their data by multiplying them by the ratio of the apparent to the real densities (this ratio is equal to the effective cross section of the material) or by some whole or fractional power thereof. Among American manufacturers, there is a widely-used empirical formula which states that the electrical conductivity of a carbon is proportional to the cube of the apparent density. In Great Britain, a corresponding fourth power law was obtained². Actually, no formula of this kind can be correct, since the physical properties do not depend on the amount of porosity only; equally important factors are the shape of the pores and their distribution, neither of which is considered in such an expression. The general problem of the influence of porosity on physical properties is a complicated one; as has been

shown recently by Kerner³, it can be solved in principle. However, great mathematical difficulties are met when a specific application is attempted.

The aim of this paper is to consider a simplified model of a porous material which has approximately the type of porosity met in carbons, and which is so simple that it can be treated by elementary mathematics. The starting point is the observation that carbons as manufactured are essentially two-component systems: They are composed of the filler coke (amount per unit volume d_0) and the binder coke (amount per unit volume $d - d_0$). These two quantities will be the two main variables used throughout the paper. In Part II a simplified model of a filler made of spheres is considered; it is shown in Part III how this and other special assumptions can be dropped and the formulas generalized for other less specialized cases. Part IV-A contains a discussion of application of the formulas to a study of the composition of an unknown carbon and some corresponding experimental results are reported. Finally, in Part IV-B, the limitations of the standard method of preparation of carbons are considered from the point of view of the established relationships.

It has been mentioned by the author in a previous paper¹ that the interaction of the binder with the filler might not be limited to just a relation of components in a mechanical mixture, but that the binder might penetrate the particles and as a result alter their structure. This view was prompted by some earlier experimental results of the writer, and finds support in more recent ones by Collins⁴. Such an interaction represents a typical cross-problem between the two broad areas of research mentioned in the

¹ S. Mrozowski, This volume, page 31.

² G. H. Kinchin, Proc. Roy. Soc. (London) **A217**, p. 9 (1953).

³ E. H. Kerner. Reports to the U. S. Atomic Energy Commission NYO 6105 (Jan. 12, 1955) and NYO 7151 (Oct. 15, 1955).

⁴ F. M. Collins, This volume, page 177.

beginning of the introduction. Another cross-problem is the influence of grinding and particle size on the growth of the microstructure in the heat-treatment process⁵. Such cross effects are in most cases of a secondary importance and will not be considered in this paper. In cases, however, where they are not of a secondary, but of a primary importance, as for instance in the case of the thermal expansion⁴, the predictions of the simplified model do not seem to agree with observations. It is possible that a consideration of the internal stresses in the model might bring some clarification of these special cases.

II. SIMPLE MODEL OF A POROUS CARBON

A. Elastic Constants

In order to derive the dependence of the elastic modulus of a carbon with apparent density d , on the amount of filler per unit volume d_0 and of the binder coke per unit volume $d - d_0$, it will be assumed that all particles are round and are of the same size, and that they are uniformly coated with binder in the mixing process. The thickness of the binder layer ϵ' can be calculated from the relation

$$\frac{4}{3} \pi [(r + \epsilon')^3 - r^3] d_B / \frac{4}{3} \pi r^3 d_p = W/100 \quad (1)$$

where r is the radius and d_p the density of the material of the particles, d_B the density of the fluid binder and W the binder proportion used in the mix (W parts by weight of binder per 100 parts by weight of the filler). It will be assumed that the density of the particles and that of the binder after it has been coked is as high as can be obtained considering the unavoidable microporosity; that is, equal to \bar{d} . This density is considerably lower than the real density d_r of the carbon crystallites¹. When the binder is coked, the thickness of the binder coke layer

⁵ Such effects were observed by S. Mrozowski and H. T. Pinnick (unpublished). See footnote 1, page 196.

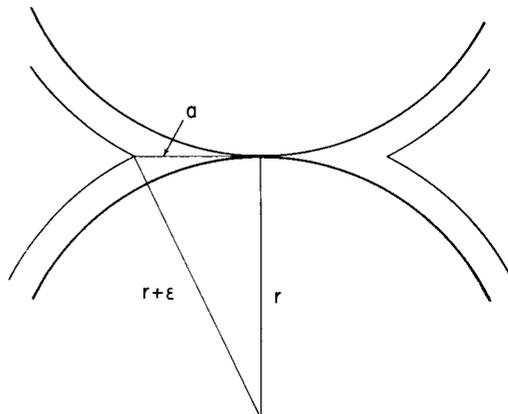


FIG. 1. Diagram showing the width $2a$ of a binder-coke bridge connecting two particles of filler.

decreases from ϵ' to ϵ , and ϵ is given by the relation similar to (1)

$$[(r + \epsilon)^3 - r^3]/r^3 = \eta W/100 = (d - d_0)/d_0 \quad (2)$$

where η is the coke yield of the binder. The decrease in the thickness is due to two factors: $d_B \rightarrow d_p$ and $\eta < 1$. For a practical case of 30 parts binder and a 60% yield, one finds from (2) $\epsilon \sim 0.06r$, that is a quite thin binder-coke layer surrounding the particle. In the following, higher order terms in ϵ/r will be neglected, and the corresponding corrections originating from this approximation will be discussed later.

When the green mix is extruded or molded, particles get into direct contact; with the release of pressure, the mix expands due to elasticity of the particles. In baking, the particles support each other until the binder is solidified. It seems therefore reasonable to assume that the particles remain always in direct contact⁶ in a carbon and that they are linked by bridges of coked binder, as shown schematically in Fig. 1. The width of the bridge (radius a),

⁶ Actually it has been found experimentally by the writer that, due to shrinkage of the binder, coke particles in the baked state are being compressed with forces ranging up to several hundred lbs/inch². These results will be published at a later date.

taking (2) and neglecting higher orders in ϵ is

$$a = \sqrt{(r + \epsilon)^2 - r^2} \sim \sqrt{2r\epsilon} \sim \sqrt{2r^2(d - d_0)/3d_0} \quad (3)$$

When two particles connected by a narrow bridge (low binder content) are subjected to a tensile or compressive stress along the line connecting their centers a change in length will occur, due primarily to the strains developed in and around the bridge. The distance between the centers of the two particles can be divided into two parts: The length of the bridge, $2fr$ (where f is a fraction of the order of $\frac{1}{4}$), and the rest of the distance, $2r(1 - f)$. A compressive or tensile force F will create a total change in length $(1/\bar{E})(F/\pi r^2)2r(1 - f)$ in the particle, and a change in length $(1/\bar{E})(F/\pi a^2)2fr$ in the bridge where \bar{E} is the elastic modulus of the material with density \bar{d} . The ratio of these two quantities is proportional to $(a/r)^2(f - 1)/f$, which is small as long as $a \ll r$. For the time being, it will be assumed that the change in length is entirely due to the compression of the bridges, although for larger binder proportions the contribution of the remaining part of the particles must be considered (see below).

In a solid carbon each particle is connected by bridges with a number of neighbors. This number of contacts per particle is a function of the type of packing. For a close-packed arrangement, every particle rests on three others, this means there are three bridges per particle to be compressed. For a less dense arrangement of particles, the average number of contacts is smaller. In a simple cubic arrangement each particle presses head-on on one other particle. In the general case each of the contacts is compressed by different forces. The head-on contacts are the most contributing ones, because they are compressed the most, and because the compression occurs in the direction of compression of the piece; lateral

contacts are completely ineffective ones (it is assumed here that there are no shears; shears will be considered further below). For a disordered arrangement of particles one has to define an average effective number of contacts, n , which will include an averaging over the decomposed stresses and over the contributions from each bridge. The calculation of n is a very difficult statistical problem, the solution of which will not be attempted here. It is clear, however, that n is primarily a function of the density of packing. As a rough approximation it will be assumed that

$$n = \beta(d_0/\bar{d})^p \quad (4)$$

where p is an unknown exponent and β is a constant. By considering the simple cubic and the close-packed arrangements, one can convince oneself that for the densities found in experiments, p must be greater than 1, may be as large as 2, and β is correspondingly of the order of 4.

When a unit cube of the carbon material is compressed by a pair of forces P , the resulting change in length is due to the sum of the bridge compressions. The average distance between contacts in one particle in the direction of the compression is about equal to $\frac{2}{3}r$. Actually this distance is slightly variable with density of packing, slightly increasing when the density decreases. One can, by a similar reasoning as above, write an approximate expression

$$h = \left(\frac{2}{3}\right)r \cdot \gamma(\bar{d}/d_0)^q \quad (5)$$

where $\gamma < 1$ and $q < 1$. What is actually being done here is that most of the parameters which are difficult or impossible to calculate exactly for this problem are lumped together into the formulas (4) and (5). Dividing the length of the cube by h one finds the number of particle layers. If the total number of particles in the cube is N , then there will be $M = Nh$ particles in one layer. The total relative change in length of the cube is consequently

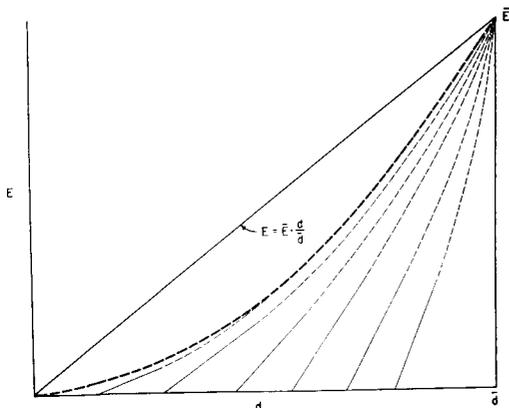


FIG. 2. Schematic diagram of the dependence of the elastic modulus E on the filler density d_0 and the binder-coke content $d - d_0$. System of lines for low binder contents is given according to Eq. (6). Thick broken line is the limiting curve for the highest E obtainable at different apparent densities d .

$$\frac{\Delta L}{L} = \frac{2fr}{\bar{E}} \times \frac{P/Nh}{n\pi a^2} \times \frac{1}{h},$$

and noting that $(\frac{4}{3})\pi r^3 N \bar{d} = d_0$, the apparent elastic (Young's) modulus is

$$E = \frac{4}{9} \frac{\beta \gamma^2 \bar{E}}{f \bar{d}^{1+p-2q}} \cdot d_0^{p-2q} (d - d_0) = \mu \bar{E} \left(\frac{d_0}{\bar{d}}\right)^z \left(\frac{d - d_0}{\bar{d}}\right) = E_0 d_0^z (d - d_0) \tag{6}$$

where $z = p - 2q$ is of the order of about 1, $\mu \sim 4$ and $E_0 \sim \bar{E}$ (since $\beta \sim 4$, $\gamma \sim 0.8$, $f \sim 1/3.5$, $\bar{d} \sim 2$). Due to fluctuations in the distribution of particles the actual value of E_0 might be somewhat lower than \bar{E} ($\mu \sim 3$).

The apparent elastic modulus E is independent of the particle size. This is as was to be expected, because for a porous substance such a physical property should not depend on the absolute dimensions of the pores, but only on their shape, distribution and total volume, provided that the physical property is determined for pieces large in comparison to the size of pores. The formula (6) gives important information: E is directly proportional to the

binder-coke content. In Fig. 2, E is plotted as a function of the apparent density d . Since (6) was derived assuming a low binder content, straight lines are not extended beyond binder coke contents $(d - d_0) \sim 0.3$ to 0.4. All the curves should tend for higher d 's toward the value \bar{E} for $d = \bar{d}$, since for the binder filling all pores no differentiation according to different d_0 should be noticeable (assuming a perfect bond between the binder and particles; see Sec. III A). Corresponding light broken curves are drawn in Fig. 2. It is easy to see that the elastic constant for a carbon of density d can have any value between 0 and $\bar{E} \cdot (d/\bar{d})$, depending on the shape and distribution of pores. The highest value of E will be obtained when the pores are infinite cylinders parallel to the direction of the stress. Any variation in the cross section of these cylinders will lead to stress concentrations, hence to an increased change in length and thus to a decrease in the apparent modulus E . For the type of porosity assumed in this section the maximum values of E are given by the heavy broken curve—this is a limiting curve which probably corresponds to about spherical pores distributed at random as far as long range order is concerned but not as far as neighbors are concerned (distribution similar to distribution of atoms in an amorphous substance like glass). Values below this curve are obtained when local constrictions are present.

It is quite remarkable that experiments yield straight lines of the type (6) up to quite high binder proportions (see Part IV). Equation (6) holds over a wider range of $(d - d_0)$ than the original assumptions would lead one to expect, due to a fortunate compensation of corrections. First, the width of the bridges increases with $(d - d_0)$ more slowly than according to (3), when higher order terms in ϵ/r are not neglected (correction 1). On the other hand, the interfering presence of neighbors (number

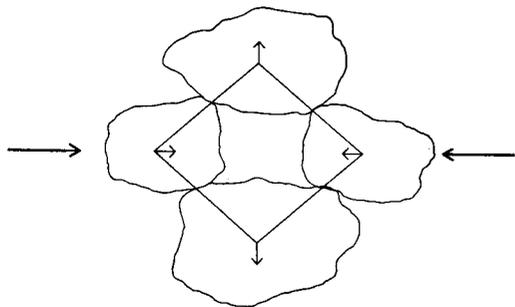


FIG. 3. Diagram showing the type of deformations occurring in the carbon under compressive stress which contribute to the apparent value of the Poisson ratio.

of contacts) makes the thickness of the binder layer increase faster than given by (2) (correction 2). Furthermore, for higher binder proportions the contribution of the changes in length of the particles themselves (their part $2r(1 - f)$) cannot be neglected (correction 3). A more detailed consideration of these three corrections shows that 1 and 3 balance about correction 2 for not-too-large binder contents.

In this whole discussion shearing deformations were not considered. Deformations of the kind given in Fig. 3 are probably very common; shears and compressions occur at the same time. A consideration of shears will lead to the same type of relationship (6) because displacements will be again proportional to the length of the bridges and inversely proportional to their cross sectional areas. The constant E_0 however will not be just proportional to \bar{E} , but will involve, in addition to \bar{E} , the modulus of rigidity \bar{G} (inverse E_0 equal to some sum involving the inverse \bar{E} and inverse \bar{G}). As a result E_0 will be lower than the previously estimated value.

From the point of view of a single bridge the mechanism of deformation occurring in a carbon under shearing stress is very similar to that under a compressive one. A formula of the type (6) should apply therefore for the modulus of rigidity, with a corresponding constant G_0 . Again in

this case both constants \bar{E} and \bar{G} will be involved in G_0 , since in each bridge compressions and shears occur simultaneously. Furthermore, shears will contribute also in the case of dilations. For a cubic or close-packed arrangement of spheres there will be no shear stresses in the bridges. But, when a disordered arrangement of particles is subjected to a uniform pressure from all sides, there will be many bridges sheared. Consequently again the modulus of volume expansion K will have to conform to (6) with a constant involving both \bar{E} and \bar{G} . In order to find \bar{E} and \bar{G} separately at least two independent measurements performed on the same carbon piece will be necessary (for instance E and G), provided the relative contributions of \bar{E} and \bar{G} in each case were known from a theoretical treatment of a corresponding statistical problem.

It is easy to see that the Poisson ratio σ must be composed of two parts, of which one is independent of, and the other dependent on, the amount of binder coke. On one hand, there will be a transverse change in length due to stresses in the particles: $\sigma = -(\Delta L_y/L_y)/(\Delta L_x/L_x)$, where the change of length $\Delta L_y/L_y = -(\bar{\sigma}/\bar{E})(P/M\pi r^2)$ occurs due to the presence of the stress throughout the central cross section of the spheres, and $\Delta L_x/L_x = (2fr/\bar{E})(P/Mn\pi a^2)(1/h)$ occurs due to the compression and shears of bridges. Substituting both expressions one finds

$$\begin{aligned}\sigma' &= (\bar{\sigma}/2fr)(nha^2/r^2) \\ &= (4\bar{\sigma}\beta\gamma/9f\bar{d}^{p-q})d_0^{p-q-1}(d - d_0).\end{aligned}$$

On the other hand, deformations of the type Fig. 3 give a contribution σ'' which is independent of the binder-coke content because $\Delta L_y/L_y$ and $\Delta L_x/L_x$ both depend on $Mn\pi a^2$ in the same way. However, σ'' depends on d_0 and is smaller for higher filler-densities d_0 (less open structures).

Consequently the Poisson ratio is in the first approximation

$$\sigma = u \cdot d_0^{p-q-1} (d - d_0) + \sigma''(d_0) \quad (7)$$

All three moduli E , G and K tend to zero when the binder content decreases to zero; this is as it should be in view of the well-known relations $K = E/3(1 - 2\sigma)$ and $G = E/2(1 + \sigma)$. One can see that all three will be strictly proportional to $(d - d_0)$ as long as the variation in σ can be neglected. Essentially, the part of σ variable with $d - d_0$ is a second order quantity, of the same type as the corrections occurring at higher binder-coke contents, and causing deviations from the linearity required by eq (6).

The formula (6) is expected to hold for static deformations as well as for time dependent ones, as long as the wavelength of the wave is much longer than the dimensions of coke particles.

B. Mechanical Strength and Creep

When a carbon yields under stress, the process of yielding has to occur in the bridges, because there the stresses are the highest. Consequently when one wants to estimate the rate of creep and plastic flow at high temperatures, for the dense carbon material, one has to consider that the stresses in the bridges are higher than the applied one in the ratio $1/Mn\pi a^2$ and the deformations are higher than the measured one by a factor $1/f$. Thus in order to compare different carbons, knowledge of the binder-coke proportion is necessary.

A break occurs exclusively through the binder. Consequently the fracture stress S has to be proportional to the area of the break, that is, to $Mn\pi a^2$. Substituting the values from (3), (4) and (5) one finds

$$\tilde{S} \sim \frac{2\beta\gamma}{3d^{1+p-q}} d_0^{p-q} (d - d_0) \quad (8)$$

The particle size does not appear in this relation, because it has been assumed that all the bridges are under equal stress and are equally strong. Thus the strength is proportional to the total area being separated irrespective of the area's subdivision into islands of different cross sections. For a perfect regular lattice-like arrangement of particles, the strength will be very high; it will be considerably lowered by the presence of faults in the structure. On the other hand, in a disordered arrangement of particles as is obtained in extrusion or molding, there is no need to look for localized faults in the structure since there are faults everywhere throughout the material. After all, due to the disordered character of the distribution, there are fluctuations in the numbers of bridges per unit cross section of the material. The average deviation in number of contacts per unit cross-sectional area is $\Delta(Mn) = \sqrt{Mn}$, therefore the local stresses deviate in average by $\overline{\Delta F} = P(Mn - \Delta(Mn))^{-1} - P(Mn)^{-1} \cong (P/Mn) (\Delta(Mn)/Mn)$, and since $F = P/Mn$, the relative deviation $\overline{\Delta F}/F = 1/\sqrt{Mn} \propto (r^2/d_0^{(1+p-q)})^{\frac{1}{2}}$ is proportional to the size of the particles. The spread of the deviations so obtained is much too high, because the contacts are not statistically independent and the fluctuations in their numbers are strongly restricted by particle interferences. This is another statistical problem, a very difficult one, of which no solution will be attempted here. If one assumes, however, that the actual spread is proportional to some kind of function of the same ratio (r^2/d_0^{1+p-q}) , and considers the maximum deviation $\Delta F/F$ which with almost certainty will be existing in a piece of given dimensions, one will find that the actual strength $\tilde{S} \cdot [1 - (\Delta F/F)]$ is also a function of this variable. If, in a restricted range, it is approximated by a factor $d_0^{(1+p-q)s}/r^{2s}$, where s is some unknown exponent, then

$$S \sim (1/r^{2s})d_0^y(d - d_0),$$

where $y = (p - q)(1 + s) + s$. (9)

Since as far as it is known the strength of carbons with different particle sizes varies only weakly with the size, s must be small. If one takes $s \sim \frac{1}{6}$, then the expected value of y is about $\frac{4}{3}(1 + \frac{1}{6}) + \frac{1}{6} = 1.8$. Experiments on the strength of carbons, each carbon made from particles of a different size, will yield the exponent s ; a series of experiments on elastic modulus and tensile strength as a function of d_0 would lead then to the estimate of the exponents p and q .

It is well known that for carbons the crushing strength is much higher than the tensile strength. This is undoubtedly due to the fact that in crushing, local failure of a bridge might lead to a displacement of a particle into a new position in contact with its neighbors in which it might still support some stress; consequently a local failure does not always lead to a large increase of the stress on the neighboring particles and to an avalanche type failure. It is therefore to be expected that the exponent y should be slightly higher than the one for the tensile stress case, and the difference would be representative of the statistical mending collaboration of particles not present in case of tensile stress.

Finally it should be remarked that since particles do not contribute to the strength even at quite high binder contents, a correction of type 3 (from IIA) is not present in this case and consequently the relation (9) is not expected to hold up to as high binder-coke contents as relation (6). The curve for strength should, after a linear portion, start gradually curving upward.

C. Flow Properties

The flow of electric current and the flow of heat through a solid are governed by the same type of differential equation. This means that if for one of the con-

ductivities the porosity factor is found, the same factor can be used for the other conductivity. One reservation must be made, namely, that this is not true in the microscopic dimensions comparable to the size of crystallites, because the anisotropy of the crystallites is much larger in the case of the electric conductivity. However, in all carbons, even in the very well-graphitized ones, the crystallite size is still usually small in comparison to the size of binder-coke bridges, and therefore this in general will not lead to any measurable difference in the porosity factor. The heat convection through the pores when gas is present and the heat transport by radiation at high temperatures are factors to be taken into consideration when the two conductivities are compared.

When electric current is flowing through a body of a nonuniform cross section, the resistance cannot be simply calculated without solving the differential equation for the distribution of the electric potential throughout the material. It has been shown, however, that when there is only one very strong constriction present the resistance of the body is almost exclusively due to the resistance to the flow through this constriction.⁷ This is the so-called spreading resistance, which for a circular constriction of radius a is equal to $\bar{\rho}/\pi a$ where $\bar{\rho}$ is the resistivity of the dense material. If the binder content is low, the widths of the bridges between the particles are small ($a \ll r$) and the resistance of a carbon piece will be due to the spreading resistances in the bridges. The total resistance ρ of a unit cube will be equal to the resistance of each bridge multiplied by the number of bridges connected in series (number of layers m is given by $1/h$) divided by the number connected in parallel ($Mn = Nhn$). Consequently using (3), (4) and (5)

⁷ See the book by R. Holm, *Electrical Contacts*, Almqvist and Wiksells, Uppsala (1946).

$$\rho = \frac{1/h}{Nhn} \cdot \frac{\bar{p}}{\pi a} = \frac{\omega \cdot \bar{p}}{(d_0/d)^x [(d - d_0)/d]^{\frac{1}{2}}} \quad (10)$$

$$= \frac{B}{d_0^x [d - d_0]^{\frac{1}{2}}}$$

and where ω , B and x are constants and $x = \frac{1}{2} + p - 2q$. For the values of coefficients previously taken, $\omega \sim 0.35$ and $x \sim \frac{3}{2}$; probably ω is somewhat smaller, maybe about 0.3, because the bridges are not circular. Irrespective of the exact values of the exponents p and q , the model predicts that $x = \frac{1}{2} + z$, a prediction which can be checked experimentally. Again in (10), as in (6), the result is independent of the size of the particles. This is to be expected from general similarity considerations, but it will hold only so long as all, even the largest particles are dense.

When $1/\rho^2$ is plotted against apparent density, straight lines should be obtained

$$1/\rho^2 = (1/B^2)d_0^{2x}(d - d_0) \quad (11)$$

A system of such straight lines is very similar to that shown in Fig. 2; the limiting heavy broken curve, however, will have more curvature than in the case of the elastic modulus. A good idea of the nature of the limiting curve can be obtained from the envelope of the system of lines (11) (See Fig. 4). If the equation of the envelope is $1/\rho^2 = f(d)$, its value for a particular d is given by the maximum value of (11) for any d_0 , so

$$\frac{\partial}{\partial d_0} \left(\frac{1}{\rho^2} \right) = \frac{2xd_0^{2x-1}}{B^2} \left(d - \frac{2x+1}{2x} d_0 \right) = 0,$$

for $d = d_0(2x + 1)/2x$. Since the slope of the tangent to the envelope must be equal to the slope of (11),

$$(\partial/\partial d) \cdot f(d) = (1/B^2)d_0^{2x} \propto d^{2x},$$

and $f(d) \propto d^{2x+1}$. Consequently, $x = \frac{3}{2}$ corresponds to a relationship $\rho \propto 1/d^2$, $x = 2$ to $\rho \propto 1/d^{2.5}$. The empirical rule $\rho \propto 1/d^3$ originates probably from the fact that

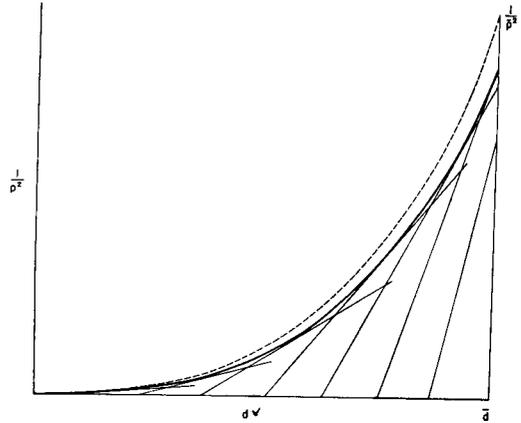


FIG. 4. System of lines corresponding to Eq. (11) with their envelope. The thick broken line is the limiting curve for the highest $1/\rho^2$ obtainable at different apparent densities d for a binder coke identical with the filler coke.

manufacturers try to get the best products for each density thus corresponding closely to the envelope of the system of lines. It seems, however, that they find more difficulty in obtaining the optimum at lower densities. Anyway, the considerations given above represent a partial vindication of the empirical rule still used by a number of manufacturers.

At high binder-coke contents, similar to the case of the elastic moduli, the straight line relationship (11) extends to quite high proportions due to a similar compensation of corrections. With increasing binder content and decrease of the spreading resistance, the resistance of the particles comes into play; the formula $R = \bar{p}/\pi a$ loses its validity and the resistance of the particle-bridge system decreases more slowly with increase of a than according to the formula. Again as in IIA by more detailed considerations one can convince oneself that this correction, with the correction for higher order terms in ϵ , helps to balance the effect of interference of neighboring particles (correction 2).

The permeability of a carbon to a fluid flowing through the pores should show an

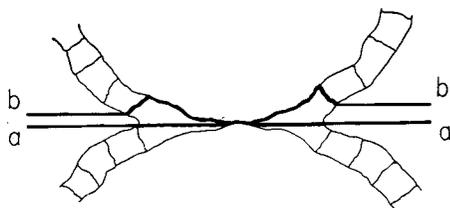


FIG. 5. Diagram illustrating the two types of fracture occurring through binder coke bridges. The cracks in the binder layer due to shrinkage in baking are indicated.

inverse relationship with the binder-coke and filler contents to the one for the electric or heat conductivity. The constrictions which determine the resistance to flow have a quite-complicated shape for the model here discussed. Unfortunately, even for simpler types of constrictions, there are no formulas which would permit a derivation of a general relationship as in the cases of the physical properties considered above. In spite of this drawback, the problem is worth looking into.

III. SPECIAL CASES AND REFINEMENTS

A. *The Nature of the Binder*

Fig. 4 shows that when the lines (11) are extrapolated to the density $d = \bar{d}$ the resistivity found in the limit is higher than the actual resistivity of the dense material. This is probably due to the fact that for increasing binder contents, the actual curves in Fig. 4 do not cross with each other but bend upwards crowding in the region between the envelope and the limiting broken curve. Now all the equations in Part II were obtained assuming the binder forming dense coke in the bridges and being well bonded to the particles. In experiments, however, it is very seldom that one uses a binder from which the original filler coke was made; furthermore, even if such a binder is used, it does not produce in baking a dense shell around each particle—a shell which has the same average low resistivity and high strength as the

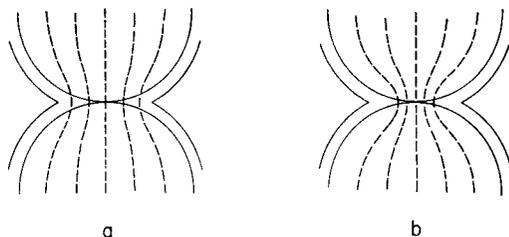


FIG. 6. Distribution of flow lines for the electric current flowing across a binder bridge (a) when the binder coke has the same conductivity as the particle coke, (b) when the binder coke is less conductive than the particle coke.

particle coke. This is because in baking the binder coke shrinks greatly and as a result the binder layer becomes full of minute cracks.⁷ Furthermore, the binder might not adhere too well to the surface of the particles for the same reason, and still less well when the crystalline structure of the binder coke differs greatly from the structure of the filler coke (differences in thermal expansion). Let us see what the modification of the formulas obtained in Part II will have to be in order to take care of these effects.

Fractures might occur either across the bridge through the binder or along the surface of the particle (Fig. 5). In either case the stress necessary must be proportional to the area of the bridge. Consequently formula (9) will hold, but with a coefficient representing the decrease in strength of the bridge due to cracks and due to poor adherence to the particle, in comparison to the dense binder-coke material. Thus the coefficient will always be smaller than 1. Similarly a coefficient smaller than 1 must be used in (6), the deformation of the carbon being larger than for dense binder material due to an increased relative mobility of particles (cracked bridges). In addition, the constant \bar{E} will not be exactly equal to the elasticity of the binder material because of the contribution of the deformations of the particles themselves. \bar{E} will be therefore a mixed constant. In the case of

the electrical resistivity the spreading resistance is determined by the radius of the cross section of the constriction. For a binder with a higher resistivity than that of the particles, the flow lines will be more crowded toward the center (see Fig. 6) and the constriction will act as if it would have a smaller radius; thus an effective radius can be introduced which is equal to the actual one multiplied by a factor smaller than 1. Equation (10) will again hold with such a correction factor, $\bar{\rho}$ being the resistivity of the filler coke. This time, however, different lines will cross, since for lower d_0 's the curves tend with increasing d to lower $1/\rho^2$ limits—the situation will more closely correspond to the one in graph Fig. 11, with the envelope representing the limiting curve. If the same kind of filler is used with several different binders, a relative effectivity coefficient can be found for each binder coke and for each heat treatment. Clearly, such an approach becomes inadequate for relatively highly-conductive binder cokes, because of the change in the character of flow (little flow through the particles).

The surface tension might have a tendency to widen the bridges beyond the size calculated from (3). This effect however would be noticeable only at very low binder contents, and under these conditions other effects occur which destroy the agreement of the theoretical formulas with experiment anyway.⁸

B. Porosity of Particles *dr. Shape*

For each definite type of porosity there is a corresponding limiting curve on the graph S vs d (and the other similar graphs E and $(1/\rho^2)$ vs d) which encloses all the possible values of S . When a coke of a bulk density d is ground, breaks occur mainly through the large-sized pores; as

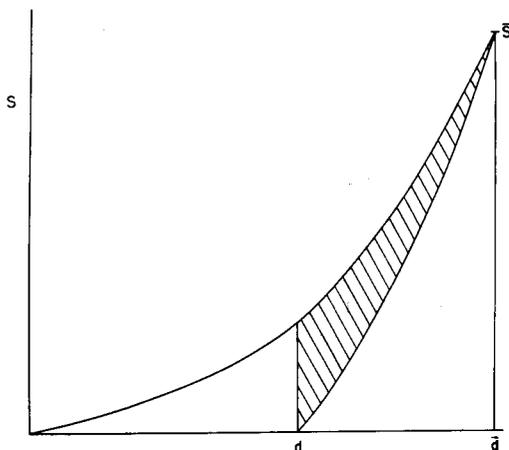


FIG. 7. Diagram illustrating the gradual increase in density and strength of coke particles in the process of grinding, starting from a material of density d .

a result the apparent density of the particles becomes higher and also the particles with the lowest values of S are eliminated. The particles become smaller and at the same time more and more homogeneous; they concentrate in a band (Fig. 7) which decreases in width, all values tending toward the limiting value \bar{S} .

Particles formed by grinding have in general no definite geometrical shape—one might inquire if this fact does not invalidate the formulas of Part II derived for spherical shapes. One can easily see that in the derivation of the thickness of the binder-coke layer, instead of the surface of the spheres the actual surface of the particles should be introduced. Not all the bridges between particles are round, but again in general only the average total cross-sectional area of the bridges is of importance except for the case of the conductivities, where, however, the constriction resistance of a noncircular bridge can be also estimated (see next section, C). Going through the formulas of Part II in detail, one finds that although the specific values of different coefficients will be changed, the general dependence of the

⁸ See the following paper by E. J. Seldin, this volume, page 217.

physical properties on d and d_0 will not be modified. It will be shown below that this is true also when the internal porosity of particles is considered.

Two kinds of porosity for particles has to be distinguished: The accessible and the inaccessible pores. The accessible ones are connected with the surface and some of them are really only pits in the surface which might be considered as pores (when deep) or as a part of the outer surface shape (when shallow). If the fractional space occupied by these pores is δ and by the inaccessible ones Δ , then the apparent density of the particle is $d_p = \bar{d}(1 - \delta - \Delta)$. This value of d_p has to be used instead of \bar{d} in the calculation of ϵ from (2) and in (4) and (5). Part of the binder which entered the accessible pores in mixing will remain there and change into coke, thus increasing the density d_p ; the other part, pushed out in baking by the evolved gases, will coke outside and contribute to the binder-coke layer ϵ . Let the fraction of the binder remaining in pores be α . The amount of binder which fills the accessible pores being $Nv_p\delta d_B$, where $v_p = \frac{4}{3}\pi r^3$, and the amount of binder coke left in the pores being $D_i = \alpha Nv_p\delta\eta d_B$, the amount covering the particles outside will be

$$\begin{aligned} D_0 &= d - d_0 - \alpha Nv_p\delta\eta d_B \\ &= (d - d_0) \\ &\cdot [1 - \alpha\delta\eta d_B d_0 / \bar{d}(1 - \delta - \Delta)(d - d_0)] \\ &= (d - d_0)(1 - \alpha F_0). \end{aligned}$$

From (2), $3\epsilon\bar{d}/rd_p = D_0/d_0$, and proceeding further one finds that in (9) the porosity introduces a correction factor

$$S_p = S_0(1 - \delta - \Delta)^{-y}(1 - \alpha F_0). \quad (15)$$

For $y = 2$, $d_0 = 1.3$, $\eta = 0.6$, $d_B = 1.32$, $\bar{d} = 2.05$, $d - d_0 = 0.3$, the correction amounts to

$$\frac{1}{(1 - \delta - \Delta)^2} \left[1 - \frac{5}{3} \alpha \frac{\delta}{1 - \delta - \Delta} \right].$$

Since α varies between 0 and 1 according to the baking conditions, the correction

factor in the case of 10% accessible and 5% inaccessible porosity will vary from 1.38 to 1.12.

For the elastic modulus one gets a correction factor similar to (15) but with z substituted for y . Since the average modulus of the particle throughout it and also in the neighborhood of the bridges is lower due to porosity and depends on the density of the particle, about $E_p \propto \bar{E} \cdot d_p^n$ (See Part IIA, Fig. 2 and Fig. 7) a factor

$$\begin{aligned} [1 - \delta - \Delta + \alpha\delta\eta d_B / \bar{d}]^n \\ = (1 - \delta - \Delta)^n (1 + \alpha F_i)^n \end{aligned}$$

taking care of the increase of the density of the particle, must be added.

$$\begin{aligned} E_p &= E_0 \\ &\cdot (1 - \delta - \Delta)^{n-z} (1 - \alpha F_0) (1 + \alpha F_i)^n \quad (16) \end{aligned}$$

For $n = 2$, $z = 1$, and the other data the same as above, the factor varies from 0.85 to 0.74.

Finally the correction factor for the electric resistivity, assuming $\rho_p \propto \bar{\rho}/d_p^m$ turns out to be

$$\begin{aligned} B_p &= B_0(1 - \delta - \Delta)^{x-m} \\ &\cdot (1 - \alpha F_0)^{-1} (1 + \alpha F_i)^{-m} \quad (17) \end{aligned}$$

For $m = 3$, (See Fig. 4 and Fig. 7), $x = \frac{3}{2}$, and the other data the same as above, the factor is about 1.18, the same for $\alpha = 0$ and $\alpha = 1$. It is very interesting that as far as the constant B for the electric resistivity is concerned it makes very little difference if the binder stays in the pores or is pushed out.

When porous particles are used in the filler with the same density of packing (same number N of particles per unit volume), a value of d_0 lower by a factor $(1 - \delta - \Delta)$ is obtained. On the other hand, in order to have the same conditions in extrusion or molding, that is, the same thickness of binder layer ϵ' , a considerably higher proportion of binder has to be used, since the binder is taken by weight, and the weight of the porous

particles is lower, and also because some binder goes into the pores. This last effect leads to a factor $1/(1 - F_0)$ in the final $(d - d_0)$; the first one to $(1 - \delta - \Delta)^t$, where $t = z, y$ or $-x$. Carbons made from porous particles under the same extrusion conditions as from dense ones will consequently have the same or slightly greater strength $(1 - \alpha F_0)/(1 - F_0)$, slightly lower modulus

$[(1 - \delta - \Delta)^n(1 + \alpha F_i)^n(1 - \alpha F_0)/(1 - F_0)]$
and higher resistivity

$[(1 - F_0)^{\frac{1}{3}}/(1 - \delta - \Delta)^m]$
 $(1 + \alpha F_i)^m(1 - \alpha F_0)^{\frac{1}{3}}]$.

For the special case selected above the factors are respectively: 1.24 and 1 in strength, 0.9 and 0.78 in elastic modulus and 1.46 and 1.47 for the electric resistivity. One can see therefore that the electric resistivity is most affected by the presence of pores in the particles. For S and E the binder does much more good when it is pushed out than when it stays in the pores; for E and ρ the inaccessible porosity is especially bad, since it does not permit an increase in the binder content.

C. Anisotropy Due to Alignment of Particles

When particles have an elongated shape, they will tend to be aligned with the long axis parallel to the direction of extrusion. Due to such an alignment, even for particles made from a perfectly isotropic type of material, an anisotropy in the final material will be obtained.¹ In order to estimate the maximum anisotropy due to this effect one has to consider the model of spherical particles discussed in Part II and expand it uniformly in one direction in a ratio r_b/r_a . Under such a distortion all spheres change into ellipsoids with one axis equal to r_b and two equal to r_a . A cube of the material is changed into a parallelepiped with square unit cross section, but a length r_b/r_a (See Fig. 8). In result,

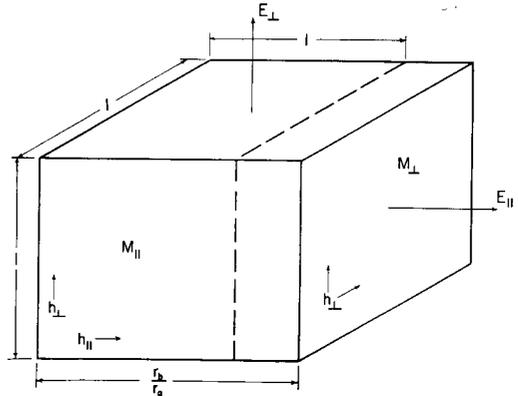


FIG. 8. Diagram explaining the relation between different quantities defined in the text for a case of ellipsoidal particles with long axis aligned parallel to one direction.

the number of particles in a unit cross section perpendicular to the direction M_{\perp} and parallel to the direction M_{\parallel} are given by expressions

$$M_{\perp} = N h_{\parallel} = \left(\frac{4}{3}\right) \gamma (\bar{d}/d_0)^3 N r_b ;$$

$$M_{\parallel} = N h_{\perp} = \left(\frac{4}{3}\right) \gamma (\bar{d}/d_0)^3 N r_a .$$

The number of contacts per particle remains the same independent of direction, but the shapes of the cross sections of the bridges change from circles along the direction of distortion to ellipses in any perpendicular direction. The distortion of the spheres does not affect the binder, which is distributed uniformly over the particle surface in a layer of thickness ϵ . If A is the average cross section of the effective bridges in the parallel direction, and B in a perpendicular direction, the elastic moduli in two directions are then

$$E_{\parallel} = \bar{E} M_{\perp} n_A A h_{\parallel} / 2 f r_b ;$$

$$E_{\perp} = \bar{E} M_{\parallel} n_B B h_{\perp} / 2 f r_a$$

and the anisotropy

$$\frac{E_{\parallel}}{E_{\perp}} = \frac{r_b}{r_a} \left(\frac{n_A A}{n_B B} \right) \leq \frac{r_b}{r_a} . \quad (12)$$

For the mechanical strength a similar anisotropy results:

$$\frac{S_{\parallel}}{S_{\perp}} = \frac{M_{\perp} n_A A}{M_{\parallel} n_B B} = \frac{r_b}{r_a} \left(\frac{n_A A}{n_B B} \right) \leq \frac{r_b}{r_a} \quad (13)$$

elastic modulus and strength

For a disordered arrangement of particles the numbers n_A and n_B are about equal and the cross sections of the bridges A and B are also equal (mostly the same bridges contribute in both cases, but B slightly larger than A and $n_A > n_B$), the factors in parentheses therefore contribute only slightly to the anisotropy. It has to be remarked that the anisotropy in strength might be greatly reduced by any macro-faults present in the carbon material, the fractures starting in a carbon not always perpendicular to the externally applied stress.

For the electrical resistance of ellipsoidal bridges one has to use the formula developed by Holm,⁷ namely $R = (\bar{\rho}/\pi\sqrt{ab}) \cdot f(\sqrt{b/a})$, where $f(x)$ is a function decreasing from 1 at $x = 1$ to about 0.85 at $x = 2$, to 0.5 at $x = 7$, and to 0.25 at $x = 20$. The function f is always smaller than 1, that is, for $a < b$ and $b < a$.

$$\begin{aligned} \rho_{\parallel} &= \bar{\rho} f_A / M_{\perp} n_A h_{\parallel} \sqrt{\pi A}; \\ \rho_{\perp} &= \bar{\rho} f_B / M_{\parallel} n_B h_{\perp} \sqrt{\pi B} \\ \frac{\rho_{\parallel}}{\rho_{\perp}} &= \left(\frac{r_a}{r_b}\right)^2 \left(\frac{n_B f_A}{n_A f_B}\right) \cdot \sqrt{\frac{B}{A}} \geq \left(\frac{r_a}{r_b}\right)^2 \end{aligned} \quad (14)$$

It appears that alignment of particles should affect the conductivities more than the mechanical properties. However, $f_A/f_B > 1$, and furthermore the effective numbers of contacts n_A and n_B are different averages in the two cases of E and ρ . The ratios found in (12)–(14) are limiting maximum values: 1) With increase of binder-coke content the anisotropy due to particle shape should decrease and disappear in the limit of the dense material; 2) Inclusion of the contribution of the particles in the cases of both E and ρ will decrease the anisotropy further below the limiting values given by the formulas; 3) Very often mixes are used in which only particles of certain sizes or a certain proportion of particles have well-defined shapes.

Since the particle shape obtained in grinding is usually the result of an internal

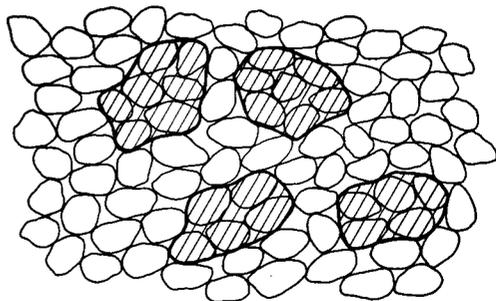


FIG. 9. Diagram representing the distribution of particles in a mix containing a small percentage of large size particles.

structure (alignment of crystallites) the anisotropy of the particles themselves has to be added to the purely geometrical effect considered in this section.¹

D. Mixture of Two Particle Sizes

When particles of two sizes (both density \bar{d}) are put into the mix the final structure of the material will be composed of the large particles surrounded by the small ones distributed with the density d'_0 (Fig. 9). If the numbers of particles per unit volume of both kinds are N_R and N_r , and their radii R and r , and furthermore if the weight ratio of both fillers is κ , then

$$\begin{aligned} \kappa &= N_R \cdot R^3 / N_r \cdot r^3, \\ d_0 &= \frac{4}{3} \pi \bar{d} (N_R R^3 + N_r r^3) \end{aligned}$$

and consequently (we shall limit the considerations to the range $\kappa \leq 1$)

$$\begin{aligned} d'_0 &= \frac{4}{3} \pi r^3 \bar{d} N_r / (1 - \frac{4}{3} \pi R^3 N_R) \\ &= d_0 / (1 + \kappa) \left(1 - \frac{\kappa}{1 + \kappa} \cdot \frac{d_0}{\bar{d}} \right) \end{aligned} \quad (18)$$

This means d'_0 is always slightly smaller than d_0 . If the binder coke is distributed so that a layer of thickness ϵ_r is on the small particles and ϵ_R on the large ones, then the binder-coke density in the regions of the groups of small particles is

$$d' - d'_0 = 4\pi r^2 N_r \epsilon_r \bar{d} / (1 - \frac{4}{3} \pi R^3 N_R)$$

On the other hand

$$d - d_0 = 4\pi\bar{d}(N_r r^2 \epsilon_r + N_R R^2 \epsilon_R) \\ = N_r 4\pi r^2 \epsilon_r \bar{d} (1 + \kappa \lambda r/R)$$

where $\lambda = \epsilon_R/\epsilon_r$. Consequently,

$$d' - d'_0 = (d - d_0) / \left(1 + \kappa \lambda \frac{r}{R}\right) \\ \cdot \left(1 - \frac{\kappa}{1 + \kappa} \cdot \frac{d_0}{\bar{d}}\right) \quad (19)$$

In Fig. 9, inside the larger particles smaller ones have been sketched in. If these smaller ones were substituted for the large ones physical properties of this material with uniform particle size would be given by the equations (6), (9), and (10) with substituted values of d'_0 and $(d' - d'_0)$ from (18) and (19). In the case of the elastic modulus, the substitution of the large ones back into the mix will have a stabilizing influence, that is, increase the modulus, but only as long as there are not too many large particles ($\kappa < 1$). In other words, the expression (6) has to be multiplied by a function $f_E(\kappa)$ such that $f_E(0) = 1$ and $f_E(\infty) = 1$, and $f_E(\kappa) > 1$ for $0 < \kappa < \infty$. The same situation exists in regard to the electric resistivity—large particles replacing groups of small ones cut down the resistivity. Consequently again, B in (10) has to be multiplied by a function $f_\rho(\kappa)$ for which $f_\rho(0) = 1$ and $f_\rho(\infty) = 1$ and $f_\rho(1)$ is a minimum. Since the factor $1 - (\kappa/1 + \kappa) \cdot d_0/\bar{d}$ varies very slowly with d_0 , for a mix with two particle sizes (6) and (11) still hold, with the difference that the coefficients E_0 and $1/B^2$ will be somewhat larger than for the case of a single size. The increase in $f_E(\kappa)$ between 0 and 1 with the slight decrease of the denominator in (19) will be partly compensated by a corresponding increase in the denominator from the expression (18). A similar consideration applies to the resistivity case; a study of the dependence of $1/B^2$ on κ with a parallel study of the function $f_\rho(\kappa)$ for the resistivity of powders might be of interest here.

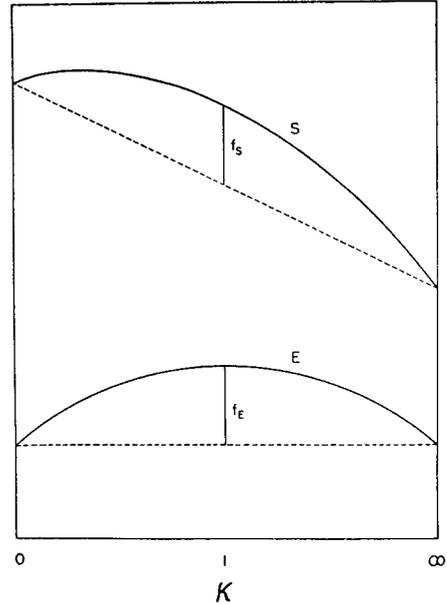


FIG. 10. Schematic presentation of the dependence of the elastic modulus and strength as a function of the relative amount of κ of large size to small size particles in the mix.

When a break occurs, the fractures will go through the binder; that is, it will look as if the break is through a material made exclusively from the smaller size particles (exactly so for $\lambda = 1$). Therefore, (9) is expected to hold with r being the radius of the smaller particles. Why there will be no increase in strength due to the presence of the larger particles can be understood from Fig. 10; although the stabilization factor $f_s(\kappa)$ is also present in this case, the change of S with size creates the apparent independence of strength from κ in the range $0 < \kappa < 1$.

IV. APPLICATIONS

A. Analysis of the Composition and Homogeneity

The formulas developed in the preceding sections have a number of important features. Most of the physical properties of carbon materials depend in a simple way on the filler density and binder-coke density, the details of the manufacturing

processes leading to the given values of d_0 and $d - d_0$ being immaterial. The final d_0 will depend on the initial compression of the mix and subsequent shrinkage in baking; $d - d_0$ will be a function of baking conditions determining the coke yield of the binder, the shrinkage and possibly the pushing out of the binder. No matter what the details of the manufacturing processes are, the knowledge of the physical characteristics determined for one carbon piece permits a prediction of the physical properties of any other carbon piece made under a variety of conditions but using the same filler and binder materials and heat treating to the same final temperature. Thus the formulas give a basis for the evaluation of the filler cokes and binders without the trouble of going into the often impossible task of making carbon pieces with identical d_0 and $(d - d_0)$'s.

Furthermore, the analysis of the problem of porosity not only shows that different parts or regions in the carbon contribute in various degrees to a given physical property, but indicates which are the regions of importance and what changes should be made to achieve an improvement in one without adversely affecting the other properties of the material. Finally the relationships established make possible an analysis of a carbon as to the composition of its original mix and as to its homogeneity.

When the filler and the binder coke are graphitized the whole piece of carbon becomes polycrystalline graphite. If in addition both the filler and binder coke are made from the same original material (pitch), the task of differentiating between the filler and the binder coke seems a very difficult one. Actually, however, no matter how similar both materials are, the geometrical relations as expressed in the porosity formulas provide a relatively simple method for determination of the binder-coke content. All that is necessary

in most cases is to determine the value of a definite physical parameter Q and the density of the given carbon piece, to impregnate the piece with binder and re-bake it to the temperature of the original heat treatment, following which a re-determination of its density and of the physical parameter will yield a second point on the diagram Q vs d ; a straight line drawn through the two points will cut the d -axis at the d_0 value. The temperature of the original heat treatment T_0 can be easily found by heat treating the piece to consecutively higher temperatures and checking its physical characteristics—its physical properties will start to change only when one exceeds, in the heat treatment, the original temperature T_0 . Some precautions have to be observed however. When there is reason to suspect that the carbon contains some filler which at some previous time was heat treated to a higher temperature (for instance, the presence of graphite flakes) the piece should be heat treated as high as possible to insure a uniformity of graphitization. One can object here that the selected impregnant might yield coke of a different kind from the binder used originally in the mix and thus invalidate the use of our formulas. This is in general a valid objection; however, there is no such danger in the case of the electrical resistivity of materials baked to temperatures in the range 1000–2000°C, since all carbons, hard and soft ones, have approximately the same $\bar{\rho}$ in this range (as found by the author by application of formula (10) to a variety of carbon materials.)

One can avoid all the difficulties of the selection of the proper impregnant and subsequent heat treatment, by oxidizing the carbon piece in a slow stream of nitrogen containing traces of air. Since the particles of the filler are covered with the binder, it is the binder coke which is oxidized first—thus for not-too-strong oxidation levels a

change of $d - d_0$ is obtained without d_0 being affected. A uniform oxidation throughout the whole piece is essential for the application of the formulas to this case.

In the following, two examples of such an analysis are presented in Fig. 11 and 12. Two batches of 6" long rods were investigated: One batch of $\frac{1}{2}$ -inch diameter graphitized rods and another one of $\frac{1}{4}$ -inch diameter baked carbon rods obtained from the National Carbon Company. Both the electrical resistivity and the Young's modulus were determined at room temperature for each of the rods, the Young modulus being obtained by measurements of deflection in bending (the apparatus used will be described elsewhere). The measurements were performed by Mr. K. Hong. The observed scatter in densities of the original rods from the same batch is given in both figures by the length of a horizontal bar. The lower densities were obtained by prolonged heating in the not-completely-air-tight furnace at temperatures below the heat-treatment temperature. The higher densities were obtained by impregnation with the Resin C coal tar pitch binder and subsequent heat treatment. As can be seen from the figures very good straight lines are obtained: The corresponding d_0 's for the two batches turn out to be 1.22 for the graphitized ones and 1.27 for the baked ones. Taking the average d observed for the original rods, $d - d_0$ is found: 0.32 and 0.31. Assuming a 65% coke yield for the binder, the original binder proportion in the mix is found to have been 40.5 and 38 parts per 100 parts of filler. As will be shown in Part B the binder proportions found are consistent with the conditions obtainable in the compression of the green mix.

It is interesting to note that the points corresponding to the original rods follow roughly the straight lines obtained. This means that in the manufacture the main source in the scatter of densities is primarily

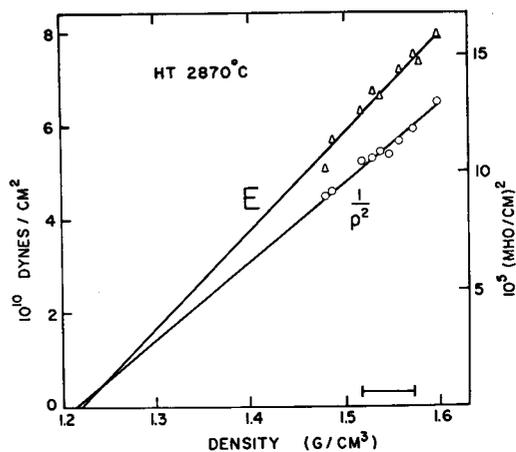


FIG. 11. Dependence of the elastic modulus and of the square of the electric conductivity on the density for a batch of $\frac{1}{2}$ -inch-diameter graphitized carbon rods, as obtained by direct measurements. The bar indicates the distribution of densities in the original batch, smaller values of d were obtained by oxidation, and larger ones by impregnation.

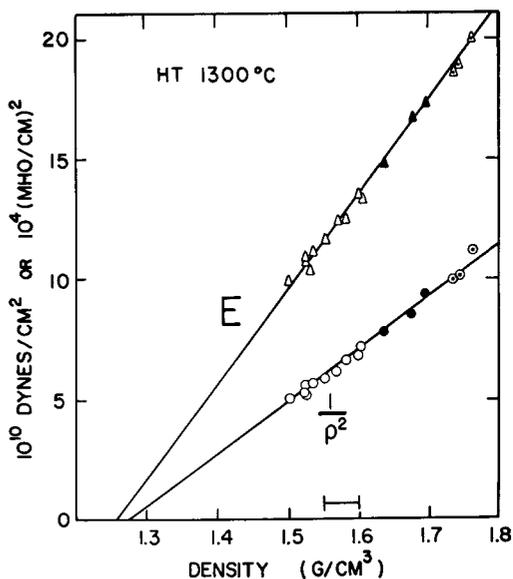


FIG. 12. Dependence of the elastic modulus and of the square of the electric conductivity on the density for a batch of $\frac{1}{4}$ -inch-diameter NCC baked rods. The bar indicates the distribution of density in the original batch, smaller values of d were obtained by oxidation, and larger ones by single and double impregnation.

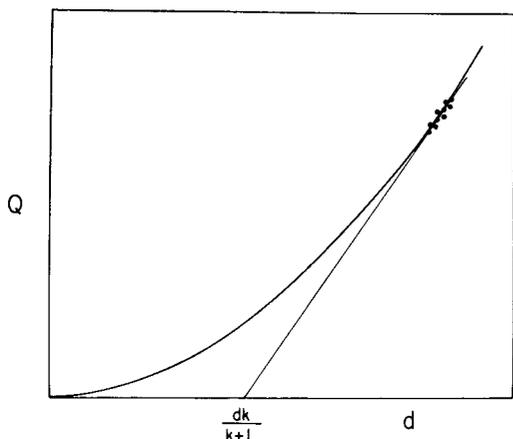


FIG. 13. Diagram illustrating the effect of different compressions on the final value of the physical parameter Q . In a limited range an apparent linear density dependence is obtained which extrapolates to an incorrect filler density $d_0 = dk/(k + 1)$.

a difference in binder-coke content. Probably in extrusion the rods carry the same binder proportion and as a result have the same d_0 (poor mixing would lead to a variation in d_0)—however in baking the binder-coke yield varies from one region to another in the baking furnace and leads to variations in the final density of the product.

When an extruded or molded piece is subdivided (the dimensions of parts being still large in comparison with the size of particles of the filler) it is found that the density d is lowest in the center of the piece. One could suspect that this is due to the compression of the green mix being greater in the neighborhood of the surface of the piece. It is easy to estimate the variation in the values of physical properties due to the inhomogeneity of compression. From equation (2) $d = d_0(1 + \eta W/100)$, therefore any expression $Q = Q_0 d_0^k (d - d_0)$ can be transformed into

$$Q = Q_0 \eta W d^{k+1} / 100 (1 + \eta W/100)^{k+1} \quad (20)$$

The variation of Q with d for a constant W is shown in Fig. 13 in the form of a thick curve. For a sample with an average

density d a nonuniformity in compression will lead in a limited range to an apparently linear dependence of Q on d with an extrapolated apparent d_0 of $d \cdot k / (k + 1)$. The presence of a nonuniformity in compression can be therefore easily discovered if two quantities Q with different exponents k are investigated; for instance, E and $1/\rho^2$ —the two lines will extrapolate to very different d_0 's with E yielding an unreasonably low value. Actually such poor distribution of compression can occur only for very dry mixes (that is, only in molding). Wet mixes will tend to produce more uniform density throughout the piece; with slightly higher d_0 on the periphery some binder will be squeezed out into regions of lower d_0 . Observed large differences in density can therefore be due only to pushing out of the binder from the center of the piece in the baking process, in addition to the effect of slight variation in d_0 . In general, simultaneous variation of d_0 and $d - d_0$ will lead to a broadening of the experimental Q vs d line into a band. However, if it should happen that the binder-coke content is high in the regions of high d_0 and vice versa, good straight lines extrapolating to densities lower than the actual d_0 might be obtained. The presence of such a variation in d_0 can be recognized by oxidation or impregnation of the batch of samples.

B. Limitations of the Standard Method of Manufacture

When a green mix is being compressed in a molding or extrusion operation, an increasingly tight packing of the mix is produced up to a limit which is reached when all the spaces between the particles of the filler and all accessible pores are filled with the binder. When this limit is reached, no further increase in pressure will increase the packing of the mix, the extra pressure being transmitted across the mix by the almost incompressible fluid binder. Thus an upper limit exists for the density d_0

of the filler in the green mix under compression. This limit can be easily calculated. The volume available to the binder per unit volume is $V_B = [1 - Nv_p(1 - \delta)]$ but $Nv_p(1 - \delta - \Delta)\bar{d} = d_0$ and $W/100 = d_B V_B/d_0$, therefore

$$[d_0^{\max}]_{gc} = \bar{d} / \left[\frac{W\bar{d}}{100d_B} + \frac{1 - \delta}{1 - \delta - \Delta} \right] \quad (21)$$

The subscript *gc* means green-compressed. One can see that the presence of accessible porosity does not affect the limiting value; the inaccessible porosity has an effect similar to a decrease in the density \bar{d} . For a given pressure, the limit (21) might not be reachable, if the particle sizes in the filler are not properly graded—higher pressures might be required to crush some of the particles and establish better packing.

When the pressure is released the green mix expands. The expansion depends on the temperature of the mix at the time the pressure is released—a long well-cooled straight-away section in the extruder will lead to a relatively small expansion, the elastic expansion of the compressed filler being prevented by the stiffening of the binder. However, in the first stages of the baking process the binder becomes completely fluid and the filler will expand until all the elastic stresses are released. The total expansion from the compressed state to this final state, when the pressure is released, is equal to the expansion of the corresponding coke powder, compressed under pressure equal to the pressure used (if below the limiting value, above which part of the pressure is taken up by the binder). Under usual experimental conditions this volume expansion varies from 3% to 7%,⁹ being larger for more densely packed powders. Since the expansion is very roughly proportional to the square root of the compressive pressure, and

⁹ Under certain conditions powders can be prepared which show up to 50% volume expansion. Ref. 5.

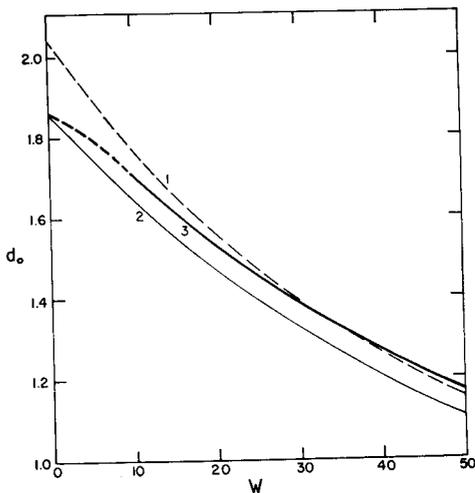


FIG. 14. Dependence of the maximum filler density d_0 on the binder proportion used: (1) in the green mix under compression, (2) after complete release of elastic stresses, (3) after the mix is baked. Curves calculated assuming $\bar{d} = 2.05$ and $d_B = 1.32$.

the packing increases proportionally to about the 0.1 power of the pressure, the use of very well-graded particle sizes is necessary in order to obtain highest d_0 's in this relaxed state.

In order to find the final limiting values of d_0 for baked carbons, a second correction to (21) is necessary. After the binder solidifies a strong shrinkage of the whole piece occurs in baking, the shrinkage being larger for the case of larger binder proportion and binder-coke yields. The exact relation is probably of a similar but reverse type to the elastic expansion; that is, approximately of a square root type (the shrinking binder producing a compressive stress). In Fig. 14, three d_0 curves are given as a function of binder content for the most-commonly-met experimental condition: The curve (1) for the green mix under compression, Eq. (21), (2) the d_0 after elastic expansion, and (3), the final curve for d_0 of the baked material. In calculating these curves it was assumed: $\bar{d} = 2.05$ (calcined coke), $d_B = 1.32$, $\delta =$

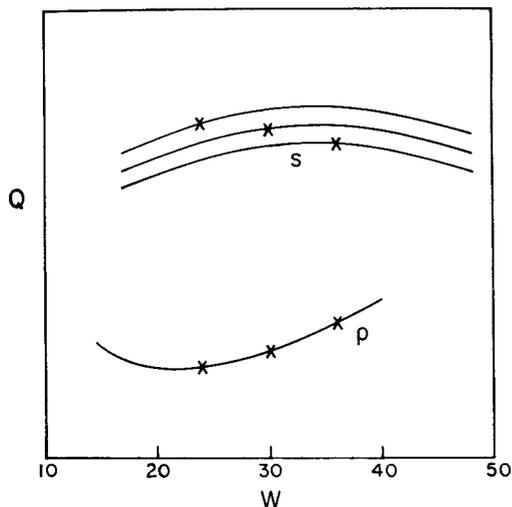


FIG. 15. Curves showing the dependence of the maximum strength S (three curves for different particle sizes) and of the minimum resistivity ρ obtainable for different binder contents W . Crosses illustrate the change in resistivity and in strength when mixes with decreasing W (increasing filler density) are used, the observed increase in strength being due to an addition of finer particles to the mix.

$\Delta = 0$, free expansion in baking and shrinkage changing, respectively, from 7% and 3% for $W = 10$ ($\eta \sim 0.6$) to about 4% and 5% for $W = 40$. The final curve (3) can be approximately expressed by

$$\text{or } \begin{cases} [d_0^{\max}]_b = a/(bW + c) \\ [W^{\max}]_b = (a - cd_0)/bd_0 \end{cases} \quad (22)$$

with the parameters for the special case considered $a = 1.92$, $b = 0.0128$ and $c = 1$.

The curve (3) of Fig. 14 can be used for cross-checking the results of the binder-coke determination presented in Part A (Fig. 11 and 12). For the estimated original binder proportions (40.5 and 38), Fig. 14 gives maximum d_0 's of 1.26 and 1.29, values which are slightly higher than the ones obtained in Part A. Evidently either the binder proportion was higher than the estimated one (and the binder coke yield lower than 65%) or the compression of the mix was not complete, or the coke particles used not completely free of porosity.

Eliminating W from (2) and (22) one finds that any quantity $Q = Q_0 d_0^k (d - d_0)$ can have the following maximum value Q_m for a given d_0 :

$$Q_m = Q_0 \cdot \frac{100b}{\eta} \cdot d_0^k (a - cd_0) \quad (23)$$

The function Q_m has a maximum at

$$[d_0^{\max}]^{\max} = ka/(k + 1)c \quad (24)$$

The corresponding Q_m is a maximum value which can be obtained for the physical quantity Q under the best experimental conditions for a carbon made according to the standard method of manufacture and without subsequent impregnation. The formula shows that the optimum values for different physical properties are obtained at very different binder proportions. The reason for the existence of a maximum is the fact that when the filler density becomes too great, the amount of binder which can be put into the mix becomes insufficient to give enough width to the bridges. (This is true even for 100% binder-coke yield, because $d_B < \bar{d}$.)

Taking for a and c the previous values, one finds that the highest electrical conductivity for a baked carbon can be obtained for $d_0 \sim 1.5$, the highest mechanical strength for $d_0 \sim 1.3$, and the highest elastic modulus for $d_0 \sim 1.1$. These d_0 's correspond to 22, 36 and 56 parts of binder, respectively, according to Fig. 14. The result in the case of the elastic modulus is unrealistic, because the straight line relationship breaks down for such a high binder content and even if it did not, it is experimentally impossible to get a good bake anyway (the binder will not stay where it is supposed to stay according to the assumptions). The optimum for strength is obtained with higher binder contents than are needed for optimum electric conductivity, as expected. The maximum at $d_0 = 1.3$ does not seem to agree with general experience, but this is because when denser fillers are used

this is achieved by mixing in smaller particles (for instance, carbon blacks) and the size factor not taken into consideration in (23) changes the relationship in favor of higher d_0 's (Fig. 15). According to (23) for electric conductivity an absolute maximum should be found for baked carbons at densities of around 1.72 (for graphitized ones at somewhat higher densities — ~ 1.76). It is significant that whenever very dense carbons are made their conductivities are found to be definitely lower than expected according to the empirical d^3 relation; this might be an indication that one is approaching the optimum in these cases. It seems that there is no good reason for trying to make denser carbons just in one single operation—impregnation of the product is

a more effective way of increasing the density with a corresponding increase in physical parameters.

In this section, only the geometrical limitations were considered. These limitations and others such as imposed by poor transfer of pressure in molding dry mixes, necessary wetness for extrudability of mixes, and difficulties in baking, leave little leeway to the manufacturer for improvements of the products (unless a different method of manufacture is used). Use of nonporous coke particles, careful grading of sizes to cut down the elastic expansion, availability of denser binders with increased coke yield (see Eq. 23) and use of not-too-low binder proportions are the main factors to be considered in this connection.