INDUSTRIAL CARBON AND GRAPHITE

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Introduction and Physical Properties

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INTRODUCTION

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This is a Conference on the Industrial Uses of Carbon and Graphite. If there has been tardy recognition of the importance of this material with its astonishing range of properties, the world of science may well be excused. The several remarkable allotropic modifications in which the element carbon occurs, and the bewildering and dazzling variety of compounds formed by carbon that constitute organic chemistry are in themselves so fascinating scientifically and important commercially that the industrial applications of carbon in what one might term the inorganic sense could well be overlooked. True, much of what we regard as inorganic carbon is in fact organic hydrocarbon of very high carbon content; in its structure and formation it has much in common with polymer chemistry. Gradually the importance of industrial carbon and graphite is appealing to the engineer.

The use of carbon by man has been of great historical significance since earliest times. Carbon black, or lampblack, has a venerable story as a pigment. The dissemination of knowledge by the written word and later by the printed word owes much to carbon in this form. Analysis of ink from an Egyptian inkstand of the 16th century B.C. indicated carbon as the essential ingredient. Later, but not less important in human evolution, Caxton's presses operated with inks containing lampblack. The Chinese are credited not only with the early use of carbon as a pigment, but also with the invention of gunpowder. This invention too, in peace and in war, has been of significance in our history. The discovery that coal would burn must be of great antiquity. The wider exploitation of coal as a source of energy may fairly be regarded as a major factor in the industrial revolution that occurred one to two hundred years ago. And now we have the impact of the discovery of a new source of energy, in nuclear fission. Here too, the discovery is one of great significance in human evolution and here, too, carbon has been found a material of great value.

Indeed, the recent demand for graphite in considerable quantities and of exceptional quality has provided great stimulus to the industry and to the scientists concerned with an understanding of nuclear reactions. This Conference and the one held earlier this year at Buffalo owe much to this stimulus.

As with much of our industry of long tradition, an air of mystery and secrecy has surrounded the skill of the craftsman from time immemorial into the 20th century. Many of the papers which follow are the fruits of our attempt at a scientific unravelling of the mystery of what has been literally a ‘ black art ’. What is today called ‘ know-how ’ has long been treasured by those whose skills have contrived technical processes. In the making of gunpowder the Codex Germanicus of 1350 recommended the wood of the lime or of the poplar for charcoal burning. Earlier, that pioneering scientist and great chemist of the 13th century, Roger Bacon, realized that soft, light woods gave suitable charcoals capable of ready ignition. He specified young hazel tips as a starting material, a recommendation that is apparently still observed. He left his formulae not in patents or trade secrets, but in Latin anagrams.

Nor are our techniques in the preparation of some raw materials significantly different from what they were many years ago. The basic principles for manufacturing lampblack have not changed through the centuries. A typical plant for making lampblack of the 1940's was adequately described by the Roman architect, Vitruvius, in 25 B.C.

If the use of lamp black and charcoal is of great antiquity, modern industry has conjured up remarkable new applications. From 1830 onwards, the files of British patents contain references to the high quality of rubber compounded with lampblack. In 1904 the first successful compounding of black, rubber and sulphur was made at Silvertown in the East End of London, and the enhanced value of the rubber tyre in the automobile industry dated from that experiment. Today upwards of 2000 tons of carbon black are being produced daily and, of this total, more than 90% is consumed by the rubber industry. As an interesting reflection on the use of carbon in explosives, some lampblack is being used today in association with liquid oxygen for blasting purposes.

Charcoal, too, has found new applications. Experiments starting in the late 18th century, particularly those of de Saussure, revealed the remarkable adsorptive properties of this form of carbon. Today we recognize the value of adsorptive chars in gas and liquid purification or recovery.

If the industrial use of coal as a fuel is recognized as a landmark in the history of man, so too has been the rise of the coal distillation and extraction industry. Starting as it did with gas production, it provides today the raw materials for so much of chemical industry. The papers that follow are concerned primarily with one facet of this, namely the fabrication of carbon artefacts from the by-products of the distillation of coal and of petroleum. This manufacture has been often described in recent years and it will not be necessary to do more than to refer very briefly, first to the raw materials, and second to the process for producing carbon shapes. Mixtures are prepared by blending carbon powder with a binding medium, usually coal tar or pitch. For the powders, bituminous coal or anthracite is occasionally used, but for the most part, the starting material is coke, derived either directly from coal or from pitch produced in the distillation of coal, or as a residue from petroleum distillation. In earlier times, use was made of carbon produced in gas-making retorts, particularly of the horizontal type, but this source of supply is rapidly dwindling. These hard forms of carbon are calcined to remove residual volatile matter and are crushed and ground to provide grist with suitable particle size distribution. For certain purposes, suitable addition of fines may be made in the form of lampblack, carbon black or natural graphite. As lampblack is produced by the incomplete combustion of coal-tar products and occasionally petroleum, it can be seen how dependent this whole industry is upon coal and oil.

The various powders are blended and binder material, usually ground pitch, is added in the correct proportion and the mixture turned for some time in a heated mixer. This ‘ green ’ mixing is pressed to the appropriate shape either by compression moulding or more often by extrusion. Extrusion pressure can vary, but is usually of the order of one ton per sq. in. The green carbon shapes are baked under non-oxidizing conditions and follow a heating schedule intended to produce the maximum amount of coke from the pitch or other binder and at the same time avoid the cracking of what is virtually a ceramic body. Ring ovens are commonly used for this purpose and are usually fired by producer gas. The maximum temperature to which the carbon is taken is between 900 and 1300°, depending upon the use to which the carbon is to be subsequently put.

Plumbago or black lead has been known for a very long time and valued as a writing medium and also for its smearing and slipping properties. That it was not a compound of lead and was, in fact, carbon was not demonstrated until the late 18th century and it was at this time that the name ‘ graphite ’ was first given. It must certainly have been observed by early workers on electric carbon arcs that the carbon sticks after use were tipped with graphitic material. In 1893, Gerrard & Street patented a process for making graphite by submitting carbon to the heat of an electric arc. Three years later, Acheson took out his master patent on the graphitizing process, which has remained the standard commercial process ever since. He had found, when making silicon carbide by heating together sand and coke in an electric furnace, that if the furnace became overheated, silica distilled out and graphite was left behind. The accepted procedure today is to pack carbon blocks, prepared and gas-baked in the manner already described, in a mass of granular coke and to pass an electric current through this mass, raising the temperature to not less than 2500°. This process of graphitization causes molecular rearrangements and decomposition of residual hydrocarbons, removal by distillation of many impurities, and crystal growth in which the carbon atoms are rearranged in a lattice that corresponds more closely with that of natural graphite, the higher the temperature to which the material is taken. This so-called artificial graphite, while never as unctuous and highly crystalline as the natural product, has most of the physical properties that one attributes to graphite and finds wide industrial application.

Carbon and graphite have a unique range of properties which are widely exploited in the electrochemical and electrothermal industries. Carbon is highly refractory, not melting under normal pressure, has a low thermal expansion giving it great resistance to thermal shock, is relatively inert in the chemical sense where oxidizing materials are absent, and is a reasonably good conductor of electricity and, in graphitic form, of heat.

It is interesting to note that the applications of fabricated carbon and graphite have, to a large extent, been associated with the use of electricity. When Sir Humphrey Davy first struck an electric arc between two electrodes, he used two sticks of charcoal. The arc, brilliant as it was, must have been spluttering and noisy. This arc has been used as a source of light ever since, though with ever-improving quality of electrodes. Many will remember its use in street lighting and for searchlights and, today, in cinema projection. Another long-standing, more obvious use of carbon in the electrical industry is the carbon brush used as a current collector on a rotating surface.

With such properties, it is not surprising that carbon and graphite electrodes are widely used in the electrolytic production of chlorine, sodium, caustic soda and other chemicals, in electric furnaces for producing calcium carbide, ferrous alloys, phosphorus, and particularly in the production of metals such as aluminium, magnesium and titanium. Not only are electric furnaces used for producing high-alloy steels which require close control in their manufacture, but they are also in increasing use for producing ordinary steel where hitherto the open hearth process has been used.

This was the picture of the carbon industry ten years ago. The magnitude of the industry had already won recognition in textbooks on industrial chemistry and it was evident, as I wrote in 1949, 'that there are many applications in which carbon is invaluable and no doubt many more will be found'. Such a one has now appeared in the field of nuclear energy. In the thermal reactor as it has emerged in the post-war years, there was need for a material with good moderating properties to reduce to an effective level the energy of neutrons produced by fission of ^{235}U, and which had at the same time a low capture cross-section for neutrons. Of the relatively few materials that could be considered, graphite had the advantage of ready availability, with a known production technology, a reasonable price and easy handling and machining properties. The requirement of large tonnages of pile graphite for nuclear reactors has stimulated a great expansion of the industry with a corresponding increase in the study of its technology and of the physical and chemical properties of this material. This series of papers was arranged in the belief that the subject now merited ventilation before a scientific society. That this belief was justified is evident from the number of papers and the many people who have come forward with such a wealth of new information.

There has been academic study of carbon for many years, but the stimulus now provided from the engineering need reveals many unsolved questions of technology that call for intensive scientific research.

Why is it that petroleum coke is pre-eminent as a starting material for high quality graphite? Pitch coke is equally good in making some varieties of amorphous carbon aggregates, but is inferior when heated to make graphite. Some years ago a theory was put forward that carbons fell broadly into two classes, the graphitizable and the non-graphitizable. All experience showed this to be an oversimplification. A graduation of graphitizability is more likely and evidence is not lacking for this.

What constitutes the ideal binder for carbon making and how important one way or the other is the residual volatile content of the carbon powder? Reasonable technical *cum* economic compromises are attained in practice, but no one can claim that our knowledge on these matters is satisfactory.

The true density of graphite is 2·26. Artefacts can be produced with densities from 1·0 upwards. For many purposes, a density approaching the theoretical maximum is highly desirable, yet in practice it is difficult to exceed 1·8.

One unusual and valuable property displayed by graphite is that of increasing mechanical strength with rise of temperature. But what is the physical explanation of this?

There are certain basic problems associated with the structure of carbon that are taking time to unravel. As so often happens, one or two fundamental papers give a good working picture but the real truth is always elusive. Debye & Scherrer in 1917 concluded from their *X*-ray studies that amorphous carbon is degraded graphite, with crystallites so small that they could not be produced from graphite by mechanical means. Then in 1924 Bernal, and independently, Hassel & Mark, arrived at the graphite crystal structure with which we are familiar. Since then, and right up to today, many qualifying papers have appeared.

There are today many other techniques that are being applied to the study of carbon. Electron spin or paramagnetic resonance can also be used to study the effect of temperature and of gases on the behaviour of various carbons.

Measurements of magnetic susceptibility are contributing to our knowledge of the structure of carbon. Electron microscope and electron diffraction techniques have revealed something of the nature of the surface and thin films of carbon have been examined optically and electrically.

The key to much of our understanding will come from a better knowledge of the thermal properties and much study has been devoted to this.

The varying degree of perfection in attaining the ideal graphite structure still remains something of a mystery. It is temperature-dependent—that is the basis of the graphitizing process—but many other factors are involved; the nature of the starting material, with its chemical composition, its method of preparation, and above all, the role of adsorbed oxygen and other gases and vapours. The surface oxides of carbon have been studied by several generations of chemists. Much work was done on charcoals as adsorbents and many types of acidic and alkaline carbon–oxygen complexes were postulated. Are we any nearer a true understanding? This problem may well condition combustion behaviour of different carbons; it was raised in connexion with lubrication and bearing properties by the abnormal behaviour of carbon brushes operating at high altitude; it may be relevant to the vexed and unsolved question of how carbon black reinforces rubber; and it may well play an important role in the nuclear engineering of today in determining the conditions of mass transfer of carbon in a stream of coolant gas.

Many of these questions and problems are the subject of the papers which follow and one can expect that the discussion, also reported and to which the major part of the time of the Conference is devoted, will do much to elucidate what we know and what still remains to be found out.

It is especially gratifying that there is a wide variety of papers devoted to the technology of production and that there are so many reports from users, from which one can expect also to gain much greater insight into the behaviour of carbon under varying conditions of use. It will be surprising if this too does not contribute to our understanding and to delineate the lines of further research. Graphite is a unique material available to the engineer of today. We are on the threshold of new developments in carbon technology. The urge to make dense or impervious graphite has been with us for some years. Impregnation with pitch and rebaking was but a poor compromise, unlikely to be effective to any great depth and causing only a marginal increase in density. For chemical use, impregnation with a phenolic or melamine resin provides reasonable sealing of pores, with a limitation to use under 200°. Much more is now known about pore structure. New preparative methods are on the way, such as the pyrolytic carbon film about which much is said later. The next few years will no doubt see impervious graphite, the possibility of welding graphite, of making it resistant to oxidation, and perhaps casting it to shape. Greater use will undoubtedly be made of the anisotropy of graphite and of irradiation effects, either to modify its properties or perhaps as an energy store.

THE NATURE OF ARTIFICIAL CARBONS

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After an introductory discussion of the complexities of the micro-structure of carbons (intercrystalline bonding, micro-porosity and frozen-in stresses) the type of information obtained from a study of carbon powders under pressure is reviewed. The picture of a compressed powder is applied to estimate the macro-stresses created in an artificial carbon during baking as a result of shrinkage of the binder coke. The same picture is used to develop a model of a bonded carbon material, which permits expression of most of the physical properties in the first approximation as simple functions of two variables: the packing density of the filler particles and of the relative amount of binder coke. It is further shown that this two-component model must be refined to include the different types of interaction between the binder and the particle cokes; changes in the order of processing operations change not only the geometrical relations but also lead to changes in micro-structure and micro- and macro-stress distribution and consequently affect all the physical properties of the filler and binder cokes. The existence of a possible correlation between the Youngs modulus of solid rods and the elastic expansion of carbon powders is indicated.

I. Introduction

If one defines an artificial carbon as any carbon material which has been produced as a result of some action of man, almost all carbons known to and studied by us would fall into this class, with the exception of natural graphite. This last material is highly treasured by the investigator, but it will be so only until someone learns how to produce sufficiently large single crystals in the laboratory. Actually a glance at the titles of the papers presented at this Conference shows that all of the papers are concerned in one way or another with properties of artificial carbons. Furthermore, all these papers represent inquiries into the nature of these carbons, the nature being something not yet even superficially understood. An apology therefore is needed for using such a broad and also misleading title for this paper: neither will the nature of the artificial carbons be disclosed, nor will all the information concerning the properties of such carbons be collected and reviewed. It is proposed just to describe in this paper the work which we are carrying on at the University of Buffalo; the general purpose of this presentation being to illustrate the basic philosophy guiding us in our investigations by discussing some of our victories and defeats, and furthermore, to show how seemingly minor changes in the processing technique can lead to greatly different final materials, thus raising doubts as to the validity of many comparisons or conclusions.

Carbons form a separate class of solids with a multitude of micro- and macro-structures, mainly determined by the type of original material the carbon was made from, but which are also the result of modifications introduced by and during the manufacturing process. The physical and chemical properties of these materials depend in a very complicated way on the properties of the fundamental units, that is, of the carbon crystallites, on the nature of boundaries of these crystallites and on the way the neighbouring crystallites are hooked to each other, the latter two being by far the most important factors for all of the properties of the non-graphitized carbons and also for many of the polycrystalline graphites. One can safely say that the availability of a complete quantum-mechanical solution of the structure of an infinite graphite crystal would not greatly advance the understanding of carbons today; first because of the boundary problems and furthermore because there are good reasons to suspect that the graphitic planes of small crystallites do have considerably different properties from the infinite graphite lattice plane. Since little help can be expected for the time being from a quantum-mechanical approach, one is left with the other alternative, that is, with a well-designed concentrated experimental attack supported by simplified models adaptable to simple evaluations of parameters introduced in setting up these models. In view of the complexities of the problem, in order to establish the approximate validity of models, their predictions should be checked against as many measurable properties as possible. Only then should refinements of the models be introduced. In this paper some of our attempts following this kind of attack will be described.

II. The complexities of the micro-structure of carbonized materials

The first necessary step in formation of a carbon material from any carbonaceous well-defined chemical compound or mixture of compounds is its polymerization. Other processes might precede this setting, like that of aromatic condensation in heated tars or pitches, or evaporation but essentially no carbon would be formed if the material would not polymerize. The structure formed in this process of polymerization is the skeleton which will determine its behaviour in the further heat treatment. As the carbonization proceeds, peripheral groups are being driven off and as the remaining carbon structures become hooked together by direct carbon–carbon bonds, they approach each other closely, large rearrangements occurring during this process of shrinkage.* These new structures are statistically the most probable ones to be formed from the original ones as a result of the haphazard thermal vibrations of the polymeric structure. Thus the structure of each carbon is a direct result of the original structure of the polymer and, although many carbon structures might look very much alike as to their *X*-ray diffraction pattern, there will be, strictly speaking, as many carbon structures as there are starting polymeric materials. It is therefore easily seen that any classification of carbons based on any one or even several physical properties, can provide only a broad framework from which striking exceptions can be expected to be found in experiments. For instance, the calcined anthracite coal coke is hard and would seem to belong to the poorly graphitizing class of carbons, but when heat treated to temperatures above 2500° becomes soft and graphitizes easily. It seems that what one needs for establishing a better framework are methods to study in some detail the nature and distribution of the intercrystalline bonds. The broad classification of all carbons into soft, hard and carbon blacks (the first two being called by Franklin 'graphitizable' and 'non-graphitizable'), which to some extent reflects the history of their formation (from fluid, solid and from gaseous phase), is really an admission of our inability to see clearly the details of the structure.

The structure formed by the carbonization of the polymer is pretty rigid, the rigidity increasing as the material is being carbonized and the gases driven out (see the end of Section VI). In further heat treatment the material shrinks again until all the disordered phase is consumed by the crystallites, that is for soft cokes up to about 1400°, beyond that expanding slightly with increase of temperature, but at a much lesser rate than the expansion of single crystallites would require.[1] Evidently the growth of crystallites relieves the stresses created by their expansion by such rearrangements in the structure that their expansion occurs preferentially into the pores. This rearrangement process leads, therefore, to a more complete filling of the space by the carbonized material. When, and if, suitable rearrangement is not possible, the expansion stresses, if sufficiently great, will result in cracking the material. For instance, for very small particles, the crystallite growth is arrested at approximately $\frac{1}{4}$ of the particle diameter; above the corresponding temperature stresses are created which, not being relieved, lead to a breakage of the particles. Corresponding popcorn-type structures were found by Akamatu & Kuroda in graphitized fine carbon-blacks and reported recently at the Third Carbon Conference in Buffalo. In graphitized Thermax, cracked-off shells from the surface of particles were observed by Boehm.† The mechanism of growth of the microcrystals in carbons is certainly very complicated and not yet understood; its main feature, however, an asymptotic growth to a definite average size-distribution characteristic of a given heat-treatment temperature, must be connected in some way with this process of release of expansion stresses.

One must also keep in mind that the turbostratic crystallites in the carbon material are probably very imperfect. For instance, in the course of formation of large planes by coalescence of smaller ones, the planes might be left with many sites unoccupied, which will remain so up to the temperatures at which the holes will be able to diffuse out from the crystallites (>2000°). Even for high heat treatments (>2500°) there will be dislocations present (for instance, screw dislocations formed when two crystallites join in slightly twisted position) which will be locked in the structure, partly due to the stabilizing influence of the peripheral bonding to other crystallites.

It is very probable that after sufficiently long soaking time at the maximum temperature all the stresses created in heating are relieved. When the carbon is cooled, however, the microcrystallites shrink mostly in the c-direction and thus lead to formation of another complicated pattern of internal stresses (tensile and compressive). In the absence of plastic flow, these stresses are not relieved and remain frozen-in in the material, except in the regions where they were so

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*As evidenced for instance by the loss of sharpness of the (002) diffraction ring in soft cokes in the heat treatment range 500°–800° (see for instance reference 2, Fig. 5 and p. 42).

†Private communication.

great that this led to opening of internal cracks. The frozen-in stresses are reversible: they disappear when the material is heated to the original heat-treatment temperature, and reappear when it is cooled. They are responsible for the increase of the strength of carbons with temperature,[1] and probably also for the increase in the elastic modulus. Their importance will be stressed again in later sections (III, VI) in connexion with other experiments.

In cooling, tiny voids are also opened. This is the so-called unavoidable porosity—a system of small open spaces adjacent to each microcrystallite, this system of pores being a part of the carbon structure as much as the crystallites themselves.[2] The existence of these micropores is very important, for instance, as far as the influence of impregnation on the thermal expansion and the formation of residual compounds of carbon are concerned (Section VI). On the other hand it is of minor importance for transport phenomena (the transport occurring mostly along graphitic planes) and also for any effects depending on the number of peripheral carbon-carbon intercrystalline bands in general (strength, creep, etc.).

The system of partly aligned (or disaligned) turbostratic (or graphitic) crystallites hooked to each other at the peripheries by scattered valence bonds, with a system of frozen-in stresses added to the existing peripheral bond strains, and including the unavoidable microporosity, constitutes the carbon material as formed in the process of heat treatment whose physical properties one would like to investigate first. Unfortunately carbons so formed possess a disordered macroporosity (bubbles and cracks) and very few successful experiments can be performed with such pieces of coke. To achieve uniformity one has to grind the coke to a definite particle size (or sizes) and then either study the properties of the so-prepared loose powder directly or form a carbon by addition of binder and investigate the solid piece having a controlled uniform porosity. Neither approach is very satisfactory, because one does not obtain *direct* information as to the *real* properties of the material, and furthermore because the material one investigates might not be the *same* as the original one. In order to interpret intelligently the results of such studies one has to answer a number of questions: How does one draw conclusions as to the real properties from results of such investigations? Does the ground material have the same properties as the original one? How is the binder coke distributed throughout the carbon? What is its contribution to different properties investigated? What is the effect of the binder on the ground material? These are some of the many challenging questions we have been concerned with for some time and which I should like to discuss briefly in this paper.

III, Carbon powders[3,4]

Since many carbons are produced in particulate form (carbon blacks), it was felt that the properties of carbon powders should be thoroughly studied in an effort to find methods for determination of at least some of the physical properties of the particles. Carbon powders, compressed in glazed porcelain cylinders by the use of plungers, were investigated at room temperature under compressions ranging from 10 to 6000 lb./in.^{2}. For pressures above 100 lb./in.^{2} the results do not depend on the initial preparation of the sample (shaking or just pouring). On a log–log plot, the volume V *versus* pressure P relation yields a straight line with a negative slope m for the initial compression (1) of about 0·1–0·2 (in some cases even higher; for instance, for Carbolac, 0·3). The linear relation seems to be a consequence of the statistical mechanism of the volume change: jumps of particles into new positions occurring when the local force becomes higher than the frictional resistances (or resistances to breakage of the sharp corners). When the pressure is gradually released, the powder expands, the volume–pressure relation being again linear, but having a lower slope (2); subsequent application of pressure yields another straight line with an intermediate slope (3). The two last operations can be repeated many times and the same lines obtained; the non-identity of the two lines is caused by frictional hysteresis (locked-in transverse pressures). For cokes, the percentage expansion after a complete release of pressure P is about proportional to $P^n/D^{1/4}$, where n is about 0·5 to 0·65 and D is the average diameter of the particles. The size dependence for highly graphitized cokes and the behaviour of carbon blacks are less regular. The mechanism of the expansion is not clear, but the similarity to the electrical resistivity in the pressure exponent, n, and in the size dependence is striking and might become the clue for unravelling its nature.

Since the electrical resistance can be measured much more precisely than the height of the column of the powder, small changes caused by creep can be investigated. For calcined cokes

(1200°) one finds at constant pressure a transient creep of a logarithmic type, the percentage change of resistance being about inversely proportional to $P^{1/2}$ (or P^{n}?). Surprisingly, no transient creep except an initial change in the first 2 seconds is observed for graphitized coke powders (2400°). For almost all of the not-too-fine carbon powders, at the initial compression the resistivity changes in inverse proportion to $P^{n}.D^{1/4}$, where $n = 0{\cdot}55$–$0{\cdot}65$. At the highest pressures deviations due to crushing are observed. When the pressure is released and reapplied, hysteresis effects of the type mentioned above in connection with the volume changes are observed (Fig. 1).

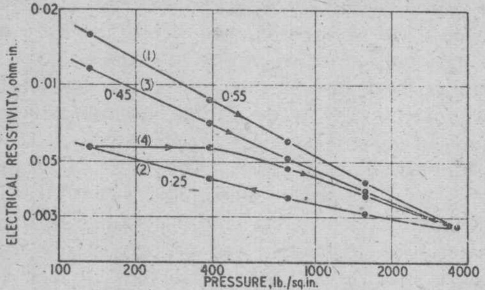

FIG. 1. *Typical graph of the room-temperature electrical resistivity of a carbon powder as a function of pressure* Curve (1)—original compression, (2)—release of pressure, (3)—compression after complete release of pressure, (4)—compression after a partial release of pressure. Texas petroleum coke heat-treated to 2400°, then ground to mesh size 100/150

It might be interesting to mention that from the differences between the corresponding curves the transverse locked-in pressures can be estimated; since, however, the mechanism of the expansion is not understood, little more information can be extracted from the consideration of these data.

This is not so in case of the initial compression. When two particles are brought together and a gradually increasing force F applied, an area of contact will be established which will increase proportionally as $F^{2/3}$ as long as the deformation is purely elastic. As soon as in any part of this area the local pressure exceeds the yield value, h, for the material, the total area, A, will have to increase faster, so that for large values of F the area will be about equal to F/h. As long as the contact area is small in comparison with the diameters of the particles, the resistance to the flow of electric current is mainly due to the presence of the constriction. It is well known that a constriction resistance is proportional to the resistivity of the material and inversely proportional to the radius of the contact area. Thus the resistance of a single interparticle contact has to be proportional to $F^{-1/3}$ for low values of F and change to $(F/h)^{-1/2}$ at higher values of F. When a powder is compressed, the number of particles in each layer increases with the total pressure due to the increase in density (by jumps as described in the beginning of this section); one can show that the resistance is also about proportional to $V^{-1/2}(= P^{-m/2})$. The comparison of these theoretical predictions with the experimental values of the exponents m and n, shows that for not very fine carbon particles one deals with the yield-type of contact areas ($n = \frac{1}{2} + m/2$). The resistance of a powder under compression is therefore proportional to the real resistivity of the material the particles are made from, and to the square root of its hardness (or yield value, h). Thus the powder resistivity is *not a measure of the real resistivity alone:* in fact, some comparisons based on the formulae discussed in Section V show that calcined cokes (1200°) have almost the same resistivity irrespective of their origin, and the differences in their powder resistivities are consequently mainly due to the differences in hardness. Using reasonable extrapolated values for the real resistivity and for the numbers and statistical distribution of interparticle contacts one finds for the microscopic hardness of calcined and of graphitized carbon particles, values of the order of 10^6 lb./in.^{2}.

Heat-treated carbon blacks (1000°–3000°) show a decreasing exponent, n, with the particle size: while for Thermax, $n = 0{\cdot}55$ is still obtained, for the smallest ones, slopes of about 0·38 are found. Evidently the force per contact ($F = PD^2$) is so small in the latter cases that the contact areas are of a pure elastic type. Theoretical considerations show that for a given packing in the elastic range, no particle-size dependence is expected; consequently the large differences in resistivities of calcined finest carbon blacks must be due to differences in real resistivities or in their elastic moduli. For the yield range a size dependence of $D^{1/3}$ is predicted, which agrees reasonably well with the experimental findings ($D^{1/4}$).

The results discussed above are not changed if the particles are coated with liquid films (water, oil, hot pitch or tar). The fluids are pushed out from the contact areas and do not contribute to the resistance. When, however, chemically bonded films are present on the surface of the particles they remain in the contact areas and give rise to an extra resistance inversely proportional to the area, i.e., varying as $(F/h)^{-1}$ in the yield range. Thus a higher slope of the log ρ *versus* log P line indicates the presence of such a film.* Most of the not heat-treated carbon blacks possess resistive surface films which are removed by heat treatment to above 800°. In some cases the contributions of the constriction resistance and film resistance can be roughly determined. If the contribution of surface layers is mentioned here, this is because carbons, when ground, react with the surrounding air and become covered with an oxide film. This film results in a higher powder resistivity, but its presence is indicated by the steeper slope of the curves. Comparisons between carbon powders should be made only when such films are eliminated by heat treatment to above 800°; after all, for the comparisons to have any meaning, the slopes of all the pressure curves should be about the same.

Thus the powder resistivity method turns out to be a valuable tool for the study of the nature of the surfaces and of the mean micromechanical properties of carbons (especially when the real resistivity of the material is known beforehand). When two samples of the same calcined coke (1200°) are prepared, one by fine grinding ($\sim 1\,\mu$) and then heat treating, and the other by heat treating and subsequent grinding to the same size, the second sample has to be heat-treated again to remove the oxide film. If this is done, one finds an increasing difference in resistivity with increase of heat-treatment temperature, the first sample showing the higher powder resistivity (after heat treatment to 2400° it may increase from 60–1007 %). As studies of the thermoelectric power of such powders have shown,[5] the first type of samples has fewer carriers, this being then the main reason for the higher resistivity. The slightly more diffuse nature of the *X*-ray diffraction lines shows that the graphitization is also less advanced; the elastic expansion after release of pressure is considerably lower for the samples of the first kind. One concludes that the grinding of the already heat-treated material does much less damage† than the grinding before the heat treatment. Evidently the release of some of the frozen-in stresses in grinding and the impossibility of a build-up of larger stresses during heat treatment of small particles, are factors responsible for the change in the pattern of events, and for the resulting lower degree of graphitization.

IV. The structure of bonded carbons

When a carbon powder is mixed with a binder and the mix extruded or moulded, a structure is formed which is similar in many respects to the compressed powder. If the amount of binder is not excessive, the flow of the mix occurs by particles pushing the other particles, the expansion of the mix at the release of pressure giving evidence to this effect. The expansion is not as great as it could be because of the restraining influence of the viscous binder; before all the elastic stresses are released the binder solidifies and the system becomes similar to a powder held under a constant pressure. The magnitude of the frozen-in compressive forces can be easily estimated by comparing the electrical resistivity of the green carbon with the resistivity of the corresponding powder after release of pressure. It is true that the process of expansion of green carbon when it is removed from the container is different from the unidirectional expansion of the powder remaining inside a porcelain cylinder, in the latter case some transverse locked-in stresses remaining even after the release of the pressure. But one is concerned only with the order of magnitude of these forces; to avoid the influence of frictional hysteresis one has to extrapolate the second compression curve (type 3, Fig. 1) to lower pressures for the same powder as used in the green mix and compressed originally to about the same extent as the mix. The values of the frozen-in pressure vary within wide limits according to the cooling which occurred before the pressure was released. After a normal extrusion operation at our laboratory, ½-in. diameter rods were found to vary in resistivity over a range as shown in Fig. 2; the corresponding frozen-in pressures are estimated to be of the order 0·2 to 1 lb./in.^{2}.

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*This shows only for fine powders, since the number of contacts must be high to give a measurable contribution (proportionality with $1/D$).

†Although it does appreciable, damage as the work of Bacon has shown; one observes also a change in thermoelectric power when a solid piece of carbon is ground and the oxide film removed.[5]