Pyrolytic Film Resistors: Carbon and Borocarbon

By R. O. GRISDALE, A. C. PFISTER, and W. van ROOSBROECK

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1. INTRODUCTION

AN IDEAL resistor would possess a resistance precisely adjusted to value and constant with time, temperature, voltage and frequency under all conditions of use in the application for which it is intended. Wire-wound resistors, which early references to "resistance helices" suggest were the first to be employed, approach the ideal in a number of respects. The advent, however, of applications requiring resistors with high values of resistance, of smaller size, and of greater stability over augmented ranges in operating conditions soon made the realization of the ideal more difficult. Moreover, despite great progress in the development of resistance alloys and in the drawing of fine wires from them, the growth of the communications and electronics industries necessitated the development of resistors smaller and cheaper than can be produced from wire and possessing different characteristics. Non-metallic resistive materials were accordingly introduced, even though some of these possess electrical and mechanical properties which are comparatively less stable. The industries now require resistors having the advantages of the non-metallic types and which at the same time are highly precise and stable. The problem, thus, is that of imparting precision and stability to non-metallic resistive materials or of employing metallic ones in new ways.

Oxides, sulfides, nitrides, carbides and non-metallic elements such as carbon, germanium, and silicon are among the many materials which have been employed in making resistors.[1] While some of these can be fabricated precisely as materials, it has become increasingly apparent that, to meet the complex requirements of modern circuitry, these materials must further be employed in specific geometrical forms. Thus, the trend towards use of increasingly higher frequencies requires that the resistive material be employed in film form in order to avoid resistance instability resulting from the "skin effect" or from excessive values of reactance. The film type of resistor possesses particular advantages for high frequency applications,[2, 3] and great effort has therefore been expended in the development of films of various resistive materials, including metals and alloys.

Metal films, produced chemically or by high-vacuum evaporation, have been studied extensively. Pure elemental metals have temperature coefficients of resistance larger than are desirable and considerable attention has consequently been given to the use of thin alloy films of lower temperature coefficient. But even though certain such alloys have specific resistances considerably greater than pure metals, their resistivities still are so low that exceptionally thin films must be employed in order to obtain high values of resistance. The specific resistance and its temperature coefficient for these thin alloy films may depart radically from those characteristic of the bulk metal: The apparent specific resistance may be larger than that of the bulk metal by orders of magnitude, and the temperature coefficient of resistance is often negative and of large magnitude. Associated with these differences, which can be ascribed to departures in structure from that of the bulk metal, there is a decreased stability of the electrical characteristics of the films. Because of this, very thin metal films cannot be employed, and film resistances* of 500 to 1,000 ohms seem to represent the present usable upper limit. However, within these limits metal alloy films can, with care, be made to yield stable resistors. Other "metals" such as germanium and silicon have also been investigated; and, while films of very high film resistances have been produced from them, the temperature coefficients of resistance are large and contact potentials at the film terminals are most troublesome.

Study of metal film resistors has thus led in the present day, as earlier, to the necessity of employing non-metallic materials of high specific resistance in the fabrication of resistors. Of the many materials studied over the years, carbon has proved to be the most generally satisfactory, both because it possesses a relatively high specific resistance and because it can readily be produced in film form.

One widely employed method of producing carbon film resistors involves the application of a carbon-laden liquid "paint" to the surface of a suitable insulating substrate and subsequent curing of the paint film to impart the requisite conductivity and mechanical stability. The carbon particles employed may be of graphite, petroleum coke, coal, channel or furnace carbon blacks, or of combinations of these. Matrices of greatly varied types have been employed, ranging from organic materials such as phenolic, urea-formaldehyde, and silicone resins to low melting inorganic glasses. The film resistance of such films is markedly dependent on the nature of the paint vehicle, on the type of carbon pigment, and on the curing conditions.

It is characteristic of carbon-pigmented films that their resistances represent the integrated contributions of a large number of single contacts between carbon particles embedded in an essentially insulating matrix. Such contacts, while not "loose" in the sense of similar contacts in the telephone

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* The "film resistance", or the resistance for a square of the film measured between opposite edges, depends only on the resistivity of the material and the thickness of the film.

transmitter, are still difficult to control and reproduce. The film resistance depends principally on the contact areas and on the elastic properties of the contact assemblage. These areas, in turn, depend on the shrinkage of the matrix during curing; on differences in the thermal expansion coefficients of the matrix, the particles, and the base; on cold flow of the matrix after curing; on its swelling through liquid absorption; and on other factors, all of which affect the stability and temperature coefficient of resistance.

In view of the complex nature of such composite conductors it is a noteworthy achievement to have attained the reproducibility and general reliability characterizing present-day carbon composition resistors of the film type. Nevertheless, these resistors suffer serious shortcomings, inherent in their structures, among which are numerically large and variable temperature coefficients of resistance, lack of availability to close and constant tolerances, relatively low power handling capacity, and poor stability with time, temperature and humidity. In addition, such resistors exhibit noise, many times greater than thermal noise, which is characteristic of contact assemblages; and they also frequently exhibit appreciable voltage coefficients of resistance.

In order to provide a carbon film free from most of these undesirable properties, the production of homogeneous carbon films by the pyrolysis of hydrocarbon vapors has been widely studied,[1] and it is with these that the present work is concerned. The production of carbon films by the thermal decomposition of hydrocarbon materials, even though unintentional, was probably effected in antiquity; and, before the present century, the use of such pyrolytic carbon films as resistors was suggested. It is only in roughly the past two decades, however, that pyrolytic carbon resistors have been commercially available, principally in Europe; but their production has been based largely on "art" without quantitative information concerning the films themselves. The purpose of this paper is to present more specific information on the structures and properties of these films and to describe the bearing of this information on the production and properties of pyrolytic carbon resistors of improved stability and enlarged fields of application. A particular object of the present paper is to describe the recent development of the borocarbon resistor wherein modification of a pyrolytic carbon film by the incorporation of boron permits the production of non-metallic resistors which are equivalent or superior to the wire-wound type.

Pyrolytic carbon resistors[1, 4, 5] comprise homogeneous carbon films, of specific resistance appreciably greater than for metallic resistance alloys, which are produced or deposited on suitable refractory bases in continuous films of thicknesses controllable over a wide range. The specific resistance of the carbon even in the thinnest films is essentially the same as in bulk, so that purely geometrical or mechanical factors determine the minimum usable thickness. The resistors can be produced in values ranging from a fraction of an ohm to tens of megohms, and, in certain versions, they exhibit exceptionally high order of stability.[5] Because of the relatively high specific resistance of carbon, the "skin depth" at high frequencies exceeds that of the thickest films employed, so that there is no increase in resistance due to skin effect. This, coupled with the fact that film configurations of inherently low reactance can be employed, permits advantageous use of these resistors at very high frequencies. Further, when suitably protected from oxidation, pyrolytic carbon films can dissipate very large amounts of power per unit area without permanent change, which is of particular advantage for certain high frequency uses.[3]

Despite their otherwise favorable characteristics and growing acceptance, pyrolytic carbon resistors have been inferior to wire-wound varieties because of the relatively large magnitudes of their temperature coefficients of resistance. This relatively large absolute magnitude of the temperature coefficient of resistance, which is always negative, has served as a deterrent to the use of pyrolytic carbon resistors where their characteristics would be otherwise suitable. It has now been found, however, that the incorporation of a few percent of boron in pyrolytic carbon films reduces the temperature coefficients of resistance to values smaller than are available, on the average, in wire-wound types. Further, this improvement is accompanied by an increased time stability of resistance value. As a result of these improvements it now appears that the borocarbon resistor, which will undoubtedly find widespread use, possesses the stability of resistance value of the wire-wound type for most applications and surpasses it for some.

2. The Production of Pyrolytic Carbon Films

2.1 *The Technique of Pyrolysis*

Pyrolytic carbon films are produced over the surfaces of suitably refractory and chemically stable objects inserted into a heated enclosure in the presence of a hydrocarbon gas or vapor. These films, which result from the pyrolysis or "cracking" or thermal decomposition of the hydrocarbons, depend in their nature and properties both on the pyrolyzing conditions and on the characteristics of the supporting surface. The pyrolysis may be carried out by maintaining a suitable vapor pressure of the hydrocarbon in an otherwise evacuated furnace or by employing a suitable carrier gas to dilute the hydrocarbon and to transport it through the furnace at atmospheric pressure. Both techniques have been studied, and no observable differences in film properties were found; but, because of their greater simplicity, carrier-gas systems operating at atmospheric pressure were employed in the work to be described. The principal reasons for this choice are that continuous coating systems can be employed and that accurate and readily adjustable control of the composition of the furnace atmosphere can be maintained.

The furnace employed in producing pyrolytic carbon films over the surface of cylindrical ceramic rods may, for example, be either of the batch type,[6, 7] or the continuous type,[8, 9] through which the rods are passed in sequence. In each case, suitable precautions are necessary in order that tightly adherent, clean films be produced on the rod surfaces.

Figure 1 shows a furnace of the batch type suitable for small scale production. In the batch process, a rotating or oscillating gas-tight refractory core is employed as the pyrolyzing chamber. Into this core is loaded a quantity of cylindrical ceramic rods, or ceramics of other shapes, together with a quantity of silica sand or other granular material which serves to support the rods and to prevent damage to them or to the core as they are tumbled. This "floating" material also has an influence on the quality of the film, and on the rate of carbon deposition. In a static process, where the rods maintain fixed positions in the furnace during coating, it would be virtually impossible to achieve the requisite uniformity in coating conditions. This is, in part, due to the fact that the composition of the atmosphere is dependent on the length of time it remains in the furnace, or, in other words, on its velocity and the actual path it transverses through the coating chamber. Rotation or oscillation of the core with the resultant random tumbling of the rods ensures that each of these is, on a statistical basis, exposed to the same deposition conditions as any other.

With the furnace core loaded with ceramic rods and sand, it is brought to the desired temperature—usually from about 975 deg C to 1300 deg C—while being flushed with an inert gas such as nitrogen before admission of the hydrocarbon. When temperature equilibrium is attained, the coating gas is admitted and permitted to flow for the requisite time. The hydrocarbon supply is then shut off and the furnace core cooled while a flow of oxygen-free nitrogen is maintained. It has been found that, if this procedure is followed, clean, uniform and strongly adherent carbon films can be produced successfully on a commercial basis.

In Fig. 2 is illustrated a typical continuous furnace,[9] which consists of three zones through which the ceramic rods to be coated are passed automatically in sequence. The first of these has been termed a "preheating" zone and its purpose is to raise the rods to a temperature at least as high as that of the next following "coating" zone before they come into contact with the coating gases. Through this preheating zone there is maintained a flow of an inert gas, such as nitrogen, moving in the same direction as the rods and emptying into the coating zone. At the junction of the preheating and coating zones the coating gas is admitted at high velocity through small jets so disposed as to facilitate thorough mixing in the furnace atmos-

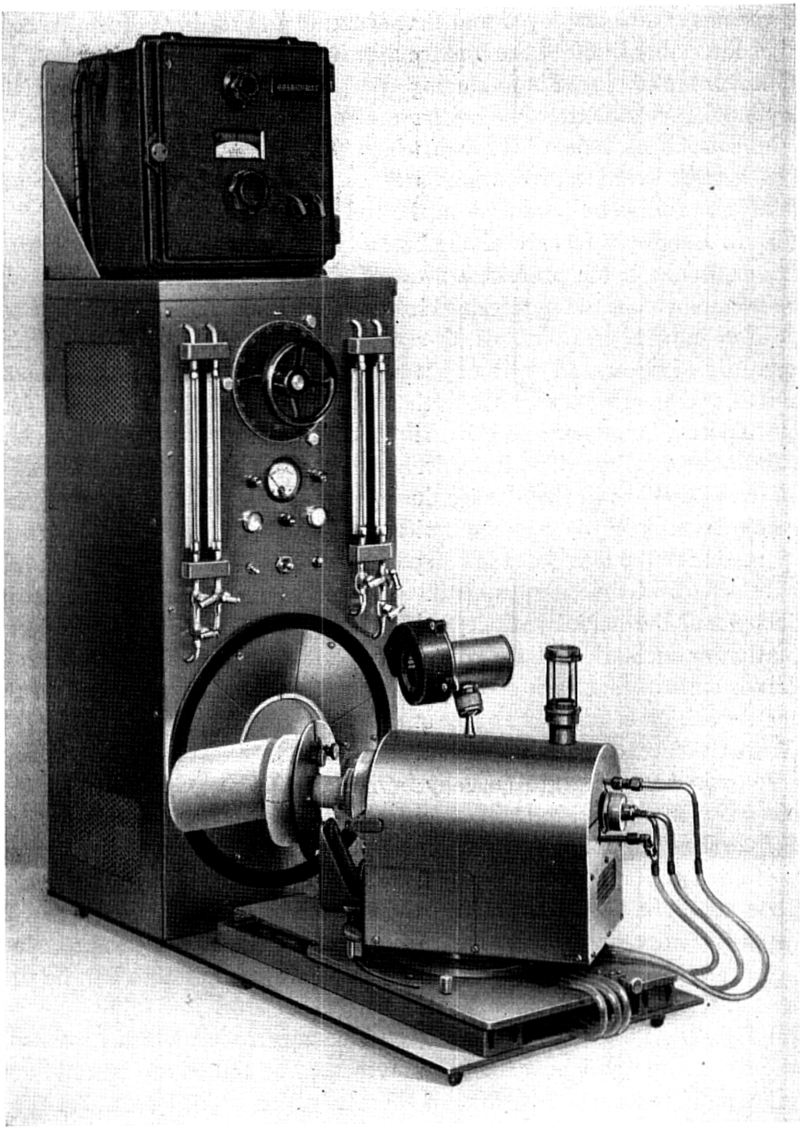

Fig. 1—A typical small scale rotating batch type furnace employed in the production of pyrolytic film resistors.

phere. The linear velocity of gas passing through the coating zone is made smaller than that through the preheating zone by expanding the coating-zone diameter. This, together with the higher temperature of the preheating

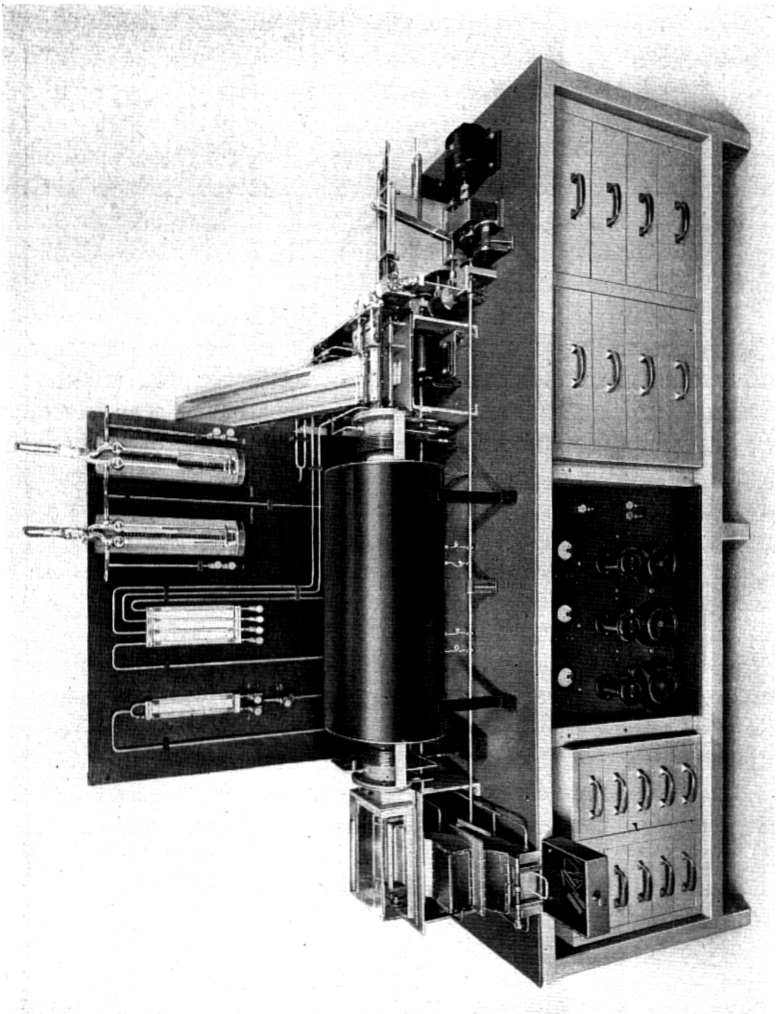

Fig. 2—An automatic furnace of the continuous type employed in the production of pyrolytic film resistors. Two parallel rows of ceramic blanks are rotated while passing from right to left through this furnace.

zone, prevents entry of the coating gases into the preheating zone either by flow or by diffusion.

From the coating zone, the coated rods enter a "cooling" or "after-heating" zone, during passage through which they are brought very nearly to room temperature. Through this zone, in a direction countercurrent to that of the rods, there is maintained a flow of oxygen-free nitrogen, or of this with small additions of hydrogen, since it has been found virtually impossible adequately to deoxidize commercial nitrogen except by the addition of a small amount of hydrogen and passage over a catalyst such as palladinized alumina prior to thorough drying and admission to the cooling zone. To prevent entry of coating-zone gases into the cooling zone, the counterflow of gas through this zone is maintained at a higher linear velocity. All gases admitted to the furnace are exhausted at the junction between the coating and cooling zones. To produce circumferentially uniform films on the rods they are rotated about their axes as they advance through the furnace.

At reasonably high hydrocarbon concentrations in the atmosphere, an opaque fog is formed over most of the coating zone cross-section in both the batch and continuous furnaces. Immediately surrounding the rod surfaces or other surfaces on which deposition takes place, however, there is a fog-free region, called the conduction zone, which is the zone in which the transfer of heat from the surfaces to the gas occurs by conduction rather than by convection. The well-defined outer edge of this conduction zone is thus considered to be the boundary of the region of generally streamline flow in the body of the furnace atmosphere, with the conduction zone, contiguous to the hot surfaces, being a more viscous, stationary region in which diffusion processes are operative. The fog consists of minute particles of sooty and tarry substances which do not penetrate the conduction zone appreciably and which, therefore, do not deposit appreciably on the rod surfaces. The cause of this behavior is that the surface temperature of the rod exceeds that of the body of the gas; and, under the influence of this temperature gradient and the associated viscosity gradient, the heavier particles of soot and tar tend to diffuse away from the surface. If this temperature gradient is reversed, as by the introduction of a cool rod into a hotter gas, then there is produced on its surface a soft and easily removed sooty coating. It is for this reason that, in the continuous process, the ceramic rods are preheated before entry into the coating zone and that the carbon-coated rods are protected in the cooling zone from contact with furnace effluents of higher temperature.

2.2 *Process Variables Controlling the Rate of Carbon Deposition*

The thickness of pyrolytic carbon films is dependent not only on the nature of the hydrocarbon employed, but also on its concentration in the gases admitted to the coating chamber, on the temperature of this chamber, and on the duration of pyrolysis. The rate of deposition of carbon is independent of this duration except during the first moments of deposition when the initial deposits formed serve to catalyze subsequent reaction, whose steady state is ordinarily quickly achieved. In Fig. 3 the film resistance of carbon films produced in a batch furnace is shown as a function of the duration of deposition. Included in the figure is a scale giving the film thickness which, as discussed in a later section,* is inversely proportional to the film resistance over the range shown. The linearity of the relationship thus bespeaks a constant deposition rate.

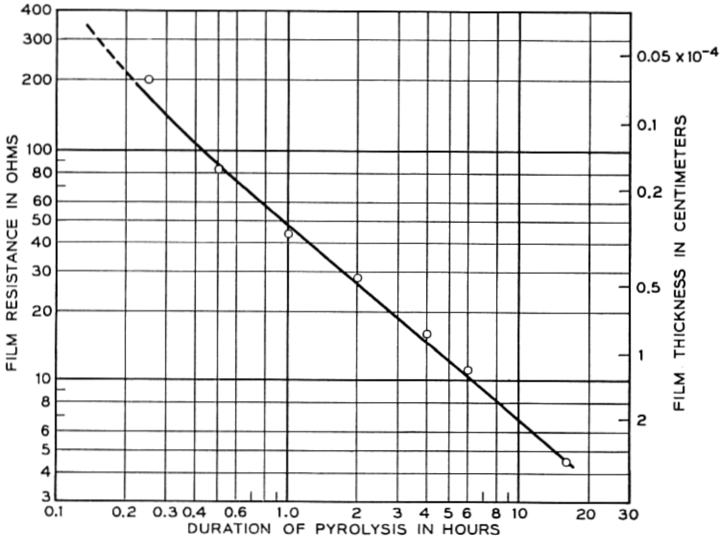

Fig. 3—Dependence of the thickness of carbon films on the duration of pyrolysis at 1000 deg C and 30 per cent methane concentration. Film thickness expressed in terms of film resistance.

The pyrolyzing temperature, more than any other single condition, determines the actual rate of deposition of pyrolytic carbon. Figure 4 gives the film resistance for a given duration of pyrolysis, inversely proportional to the deposition rate, in a continuous furnace as a function of temperature in dynamic equilibrium and illustrates the need for precise temperature control when films of constant and reproducible film resistance are to be produced.

Increase in the hydrocarbon concentration in the furnace atmosphere increases the rate of carbon deposition, as is shown by Fig. 5 for the case of methane, which gives the dependence of film resistance on concentration for

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* See Section 5.4.

a fixed duration of pyrolysis. It will be noted that the rate of deposition is not proportional to the concentration, a change in concentration by a given percentage producing a greater change in rate of deposition at low concentrations than at high.

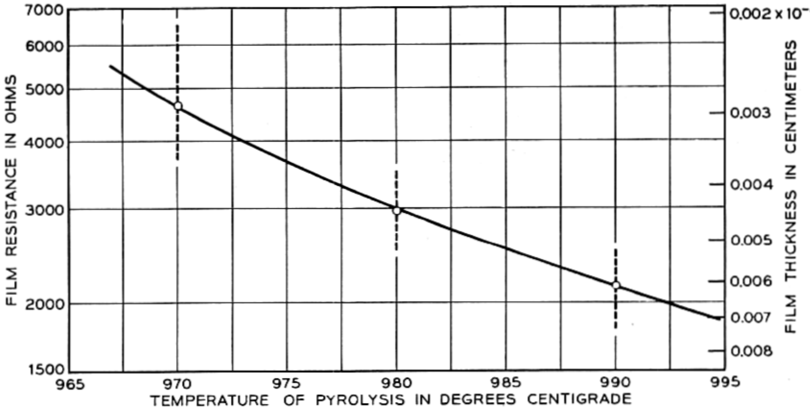


Fig. 4—Dependence of the rate of carbon deposition on pyrolyzing temperature at 4.5 per cent methane concentration and for constant duration of pyrolysis. Rate of deposition expressed in terms of film resistance.

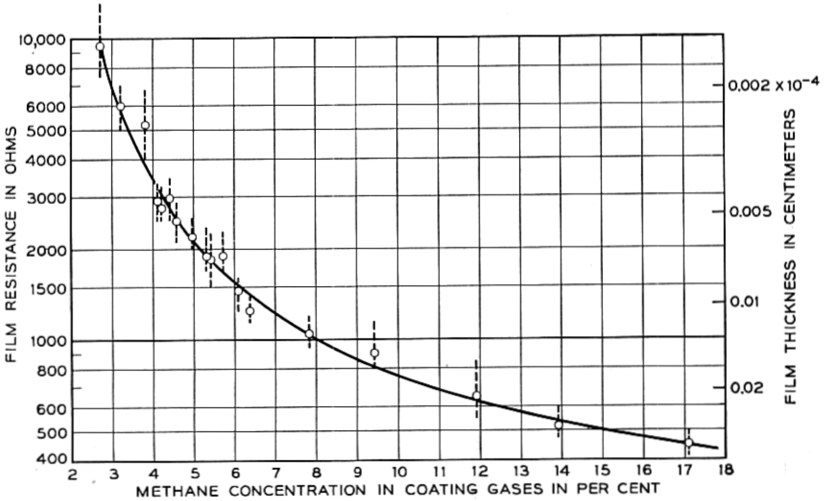


Fig. 5—Dependence of the thickness of carbon films on hydrocarbon concentration in a continuous furnace. Film thickness expressed in terms of film resistance.

The rate of carbon deposition with temperature, concentration, and duration of pyrolysis all held constant is a function of the geometry of the system, being dependent, for example, on the distance between the furnace wall and the object being coated, and particularly so if this distance is less than the thickness of the conduction zone.

While the rates of deposition associated with the film resistances of Fig. 4 and Fig. 5 are related to the corresponding absolute rates of hydrocarbon pyrolysis in the furnace atmosphere, they cannot be identified with them because of the important influence of the conduction zone, and because the rate of flow of the gases through the furnace is not specified. In fact, the rates of carbon deposition in individual furnaces are virtually independent of the rates of flow of the furnace atmospheres over wide limits, but they may differ appreciably from one furnace to the next. The viscosity in the conduction zone is so great that the rotation of an object in the furnace can be seen to drag with it the immediately surrounding gas; and it appears unlikely that this viscous gas layer is greatly altered in its thickness or other properties by any reasonable change in flow conditions of the furnace atmosphere.

The rates of carbon deposition were determined by weighing ceramic blanks before and after deposition of carbon films and are expressed in terms of weight deposited per unit area and unit time. This procedure is best suited to the thicker films, and for thin films or low rates of deposition large errors may obtain. For this reason, it has proved desirable to determine the rate of deposition from the film resistance, for which is required knowledge of the relationship between the film resistance and its thickness, and between its thickness and its mass, which involves a knowledge of the density of the carbon film. The determination of the density is discussed in a later section.

3. THE MECHANISM BY WHICH PYROLYTIC CARBON IS PRODUCED

It seems reasonably well established that the mechanism by which pyrolytic carbon is produced is not simply a surface reaction, but is related to that of the gas phase dehydrogenation and polymerization of hydrocarbons. Thus, in the case of methane, the simplest hydrocarbon, it is found that, among others, free radicals such as methyl and methylene are present in the gas phase. These combine or polymerize and the resultant products lose hydrogen to yield radicals and molecules of increasing size and complexity. Analysis of the furnace gases from the pyrolysis of methane has shown the presence of acetylene, ethane, ethylene, benzene, napthalene, anthracene and a long series of more complex materials of decreasing hydrogen content up to pure "carbon" soot itself. It thus appears that pyrolysis of a gaseous hydrocarbon involves the formation of an entire series of molecular species of progressively decreasing hydrogen contents, which are intermediates in the formation of carbon. Chemical, structural, and physical tests are, in fact, incapable of distinguishing between some of the higher members of this series and pyrolytic carbon.[10]

While the deposition of pyrolytic carbon films is not a surface reaction in the usual sense, the nature of the substrate surface can profoundly affect the reaction through its catalytic influence. For a ceramic surface contaminated with iron or other heavy metals or their oxides this influence is evidenced by the production of soft, sooty, easily removed deposits which can be formed at temperatures considerably below those normally required. There is evidence that these loosely adherent films may result through the formation of the metal carbides as intermediates.

A great variety of catalytic influences on the deposition of pyrolytic carbon films has been observed: For instance, fingerprints are very clearly "developed" by deposition of thin films, the salts in them appearing to inhibit carbon deposition. If there is back diffusion of gases from the coating zone into the preheating zone and end chambers of a continuous furnace, then several phenomena may be observed: Colloidally dispersed complex hydrocarbons may deposit on the cooler ceramic rod surfaces from the gas phase or they may be mechanically transferred to the rods by contact with already contaminated portions of the furnace mechanism. In either event, their distribution is nonuniform and the contaminated areas provide catalytic nuclei which accelerate carbon deposition in their immediate vicinities, resulting in a pyrolytic film with locally thicker areas. On the other hand, if these complex materials come into contact with certain metallic portions of the mechanism, complex organo-metallic compounds are occasionally formed, and transfer of these to the rod surface generally results in a local inhibition of deposition and hence in films with locally thin areas.

For the production of uniform films of pyrolytic carbon it is generally necessary to employ a substrate which is uniformly clean. Chemical methods of cleaning contaminated surfaces have not proved generally feasible, and to achieve the requisite cleanliness firing of the ceramics at high temperatures in air is usually required. Even this may not be adequate, however, and it is occasionally necessary to reject ceramics with badly contaminated surfaces.

Since the production of pyrolytic carbon involves the synthesis of progressively more complex hydrocarbons, it is natural to expect that the nature of the hydrocarbon employed would be of considerable significance. As discussed in a later section, pyrolytic carbon is graphitic in nature and thus can be considered as originating from aromatic hydrocarbons which possess similar hexagonal carbon ring structures. Isolation of benzene, napthalene, anthracene and other more complex aromatic compounds from the pyrolysis of methane is evidence that the aromatization of methane is probably an intermediate step in the production of carbon. It is therefore to be expected that the use of benzene should increase the rate of carbon deposition and this increase is observed. Similarly, the use of toluene or xylene, leading to the more rapid formation of aromatic radicals, should, as is observed, provide even more rapid deposition than does the use of benzene.

Rapid generation of free radicals, whether by catalytic surface reactions or through use of easily "ionized" hydrocarbons, is necessary for rapid deposition of pyrolytic carbon films. However, an excessive rate of generation, as from large concentrations of acetylene, leads to so rapid a gas phase polymerization that coherent surface films can be formed only with difficulty, the principal product being an "aerosol" of soot. Methane is employed in most instances because, being the most thermally stable hydrocarbon, the deposition from it can be so controlled as to yield thin and coherent films

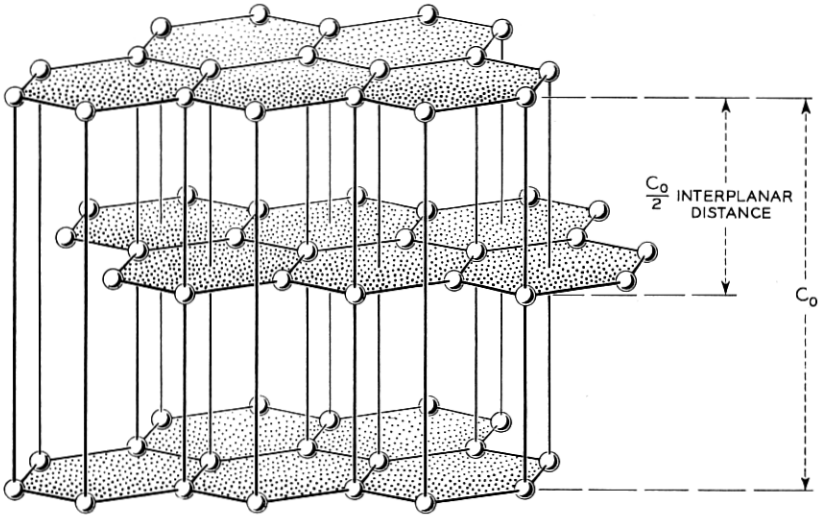


Fig. 6—Structure of the most abundant form of graphite.

4. THE STRUCTURE OF PYROLYTIC CARBON FILMS

X-ray and electron diffraction analysis of pyrolytic carbon has shown clearly that its fundamental structure is similar to that of graphite, although it differs in two respects: The lattice constants are not quite the same, and the structure possesses a greater randomness, in a sense which will presently be specified.

The hexagonal structure of the most abundant form of graphite[11] is shown in Fig. 6. The carbon atoms are arranged in parallel plane sheets, being located at vertices of hexagons in these sheets. The interatom separation in the sheets is 1.415 Å and the separation between neighboring sheets is 3.345 Å. Alternate sheets of atoms are so displaced that the repeating distance perpendicular to the layers, or along the *c*-axis of the crystal, is twice the interplanar spacing, or 6.690 Å. Other relatively rare forms of graphite differ from this form only in the way successive planes are displaced or in the repeating distance.[12]

Pyrolytic carbon consists of minute crystal packets composed of parallel plane sheets of carbon atoms in hexagonal arrays as in graphite.[13] The areas of these planes are, however, very small, their diameters generally being less than 50 Å. Associated with their small size, there are differences in lattice constants, the interatom distance within the planes being less than in graphite and the interplanar spacing being greater. The extent of these differences is dependent on the size of the crystal packet. The interplanar separation as determined in the present work and by other investigators[11, 14, 15, 16] is given as a function of the packet size in Fig. 7.

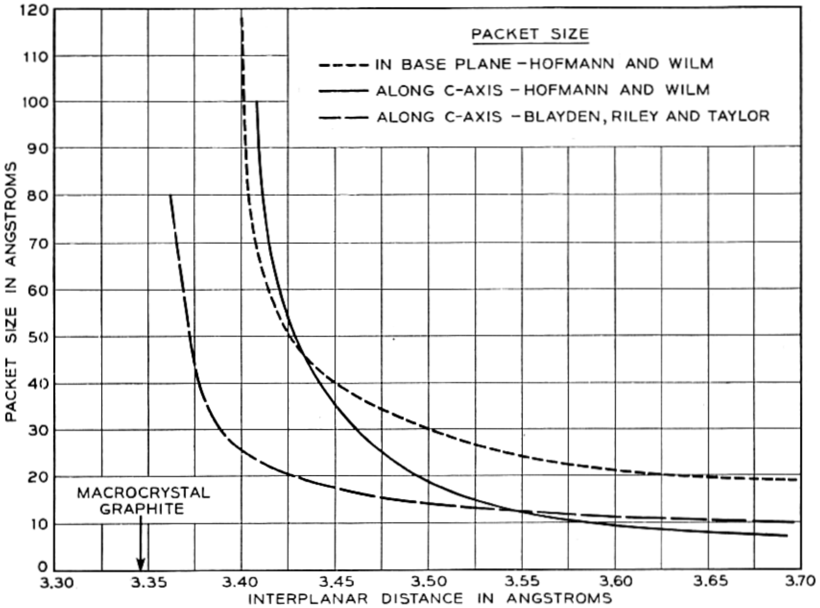


Fig. 7—Dependence of the interplanar separation in crystallites of pyrolytic carbon on crystallite size.

The average crystal packet size in pyrolytic carbon appears, for a given parent hydrocarbon, to depend principally on the rate of carbon deposition whether this rate is altered by change in pyrolyzing temperature or in hydrocarbon concentration. When the rate of deposition is changed through use of other hydrocarbons there appears also to be a correlation with packet size.

Pyrolytic carbon differs from graphite in another important respect: Whereas in graphite the atom layers lie one above the other with the atoms in successive layers in a definite relationship, those in pyrolytic carbon are randomly stacked, the only crystallographic order along the *c*-axis being the uniform separation of the layers.[13,14]

The carbon atom has four valence bonds and, in graphite, these valences are completely satisfied within the plane hexagonal network. There is no valence bonding between successive atom layers, these being held together only by relatively weak van der Waals forces. The valence bonding between carbon atoms within any one plane is of the resonance-stabilized type, with the result that there is effectively one electron from each atom left over. Some such electrons are free to move over the entire extent of the atom plane, and these provide metallic conductivity. With the larger interatomic spacing along the *c*-axis, many fewer electrons move from one plane to the next and along the *c*-axis, accordingly, the conductivity of graphite is much smaller.

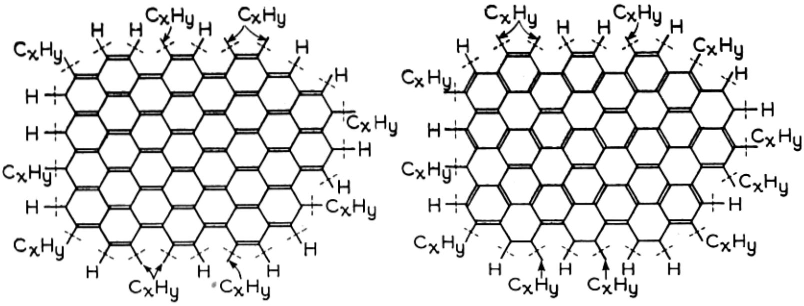


Fig. 8—Two resonance forms of the valence structure in the carbon atom layer, showing the free valences at the crystal periphery with possible bonding of hydrogen and a hydrocarbon.

Any single plane of carbon atoms in graphite may be considered to be a single giant molecule. Examination of such a plane of carbon atoms will show, however, as in Fig. 8, that it could better be considered as a free radical since there are free valences at its periphery; and these valences are quite probably satisfied by hydrogen or hydrocarbon fragments, as shown. Since the number of free valences in a graphite crystal is small relative to the total number of carbon atoms, the actual percentage of hydrogen is very small. Nevertheless, each plane of carbon atoms may be considered to be surrounded by a "hydrocarbon skin."

In pyrolytic carbon, the atom planes may likewise be considered to be surrounded by hydrocarbon skins. However, with an average diameter for these planes of approximately 25 Å, the number of free valences is appreciable relative to the total number of carbon atoms, so that the hydrogen content of pyrolytic carbon may be greater than that of graphite. This hydrogen content is primarily dependent on the temperature at which the carbon is produced, and Fig. 9 shows the hydrogen content of pyrolytic carbon films produced from methane as a function of the deposition temperature.

While the atom planes within a crystal packet are parallel to each other there is, in general, no regularity in the relative angular orientation of adjacent packets, which are randomly oriented. However, under some circumstances, films can be produced in which the individual packets tend to be oriented with their atom planes parallel to the substrate,[13] the degree of orientation depending on film thickness and on the conditions of pyrolysis.

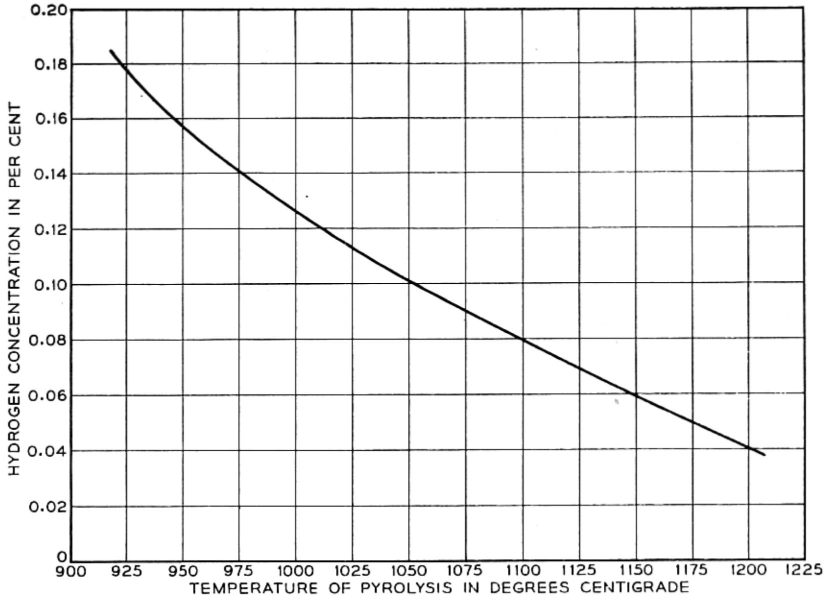


Fig. 9—Dependence of the hydrogen content of pyrolytic carbon films on the temperature of formation.

Under these circumstances, when pyrolytic carbon is produced at constant methane concentration, the degree of orientation at the surfaces of films greater than 3×10^{-5} cm in thickness passes through a maximum value as the pyrolyzing temperature increases. This maximum orientation occurs at 1025 deg C, regardless of hydrocarbon concentration. For deposition at constant temperature, the degree of orientation increases with the methane concentration.

Pyrolytic carbon can thus be pictured somewhat as in Fig. 10, which is drawn approximately to scale and which shows the orientation of the crystal axes within the packets and the orientation of the packets in the carbon films.

5. THE PHYSICAL PROPERTIES OF PYROLYTIC CARBON FILMS

The physical and chemical properties of graphite are different in its basal plane and along its *c*-axis.[17] As one common example, it is the ease with which shear occurs perpendicular to the *c*-axis which is fundamental to its value as a lubricant, even though in the base plane its hardness is great enough to warrant, in principle, its use as an abrasive. This pronounced anisotropy extends to other properties of graphite as well; and, since the crystals of pyrolytic carbon are very probably even more anisotropic because of the structural differences noted above, it is reasonable to expect that the properties of pyrolytic carbon will depend on the relative orientations of its constituent crystals. Though in some instances this expectation is confirmed, as measurements to be described show, the influence of the inter-crystal boundaries is always present and, in many cases, it is controlling.

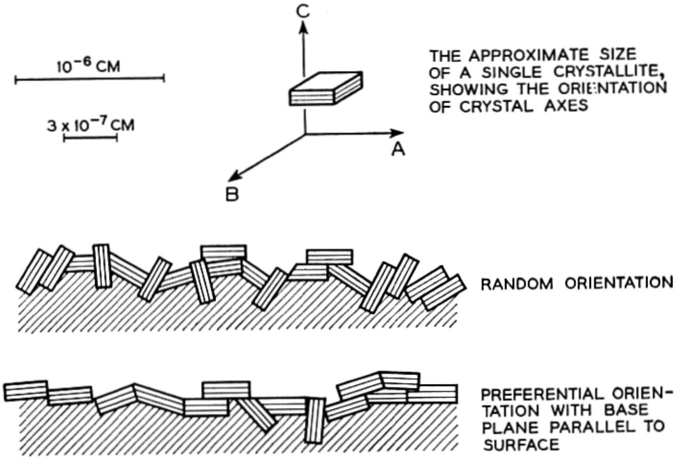


Fig. 10—Crystallite size and orientation in pyrolytic carbon.

5.1 *Density*

The density of pyrolytic carbon films composed of crystals about 25 Å in diameter was determined, by flotation in a mixture of bromoform and carbon tetrachloride, to be 2.07 ± 0.04 gm cm^{-3}. Since the interplanar spacing in the crystal packets averages 3.59 Å and the interatom distance within the base plane is 1.40 Å, the computed density, accepting that of graphite as 2.26, is 2.15 ± 0.04 gm cm^{-3}. The value 2.07 gm cm^{-3} was employed in determinations of the thicknesses and specific resistances of all carbon films, since there was no observable systematic variation of density with change in the conditions under which the carbon was prepared, despite the dependence of lattice constants on crystal size.[14,15] The difference between the measured density and that computed from lattice constants indicates that pyrolytic carbon is slightly porous, and this porosity obscures the correlation otherwise to be expected between density and crystal size.

5.2 *Hardness*

The scratch hardness or micro-hardness of carbon films deposited on fused silica plates was determined with the Bierbaum Micro-character[18]. Fused silica, with a Moh's hardness of 7, has a microhardness of 1980, while silicon carbide with a Moh's hardness of 9+ gave an average value of 7000. Repeated measurements of thick films of carbon produced at 1000 deg C and a 37 per cent methane concentration gave values for the micro-hardness ranging from 19000 to 19300, practically equivalent to diamond, or about 9.8 on Moh's scale.

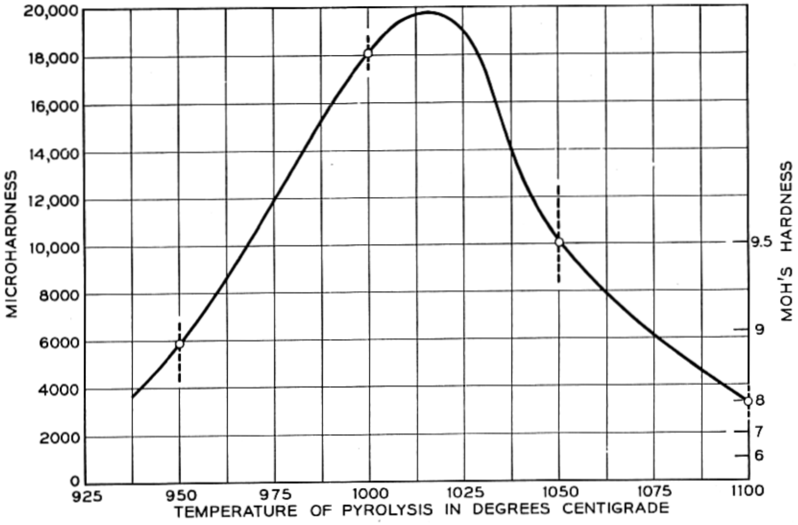


Fig. 11—Dependence of the hardness of pyrolytic carbon films on the temperature of formation.

The hardness of pyrolytic carbon is dependent on the pyrolyzing conditions. Figure 11 shows the dependence of hardness on pyrolyzing temperature for a 37 per cent methane concentration and illustrates the distinct maximum between 1000 deg C and 1025 deg C. When the temperature of the furnace is held fixed and specimens are prepared at progressively higher hydrocarbon concentrations, the micro-hardness increases monotonically. Values as high as 50,000 have been observed, and, in some instances, no perceptible mark was produced by the diamond point. The hardness was found to be independent of thickness above 6×10^{-5} cm, but for thinner films it is probable that the true hardness is greater than that observed, and the hardness shown in Fig. 11 for 950 deg C is probably low for this reason. Through this observed dependence of hardness on the conditions of pyrolysis, it appears that the hardness of pyrolytic carbon is correlated with the extent to which its crystals are preferentially oriented.

It has been shown previously that the hardness of pyrolytic carbon is a function of crystal size[19], but these measurements were made on dendritic growths of carbon, in which the crystals are randomly oriented. It is probably significant that the hardness according to these earlier measurements increased with decrease in crystal size and reached a maximum value for the crystal size at which, according to X-ray data[11,16], the lattice expansion along the *c*-axis begins to manifest itself. This may be an indication that the anisotropy in hardness of graphite crystals[17] is accentuated as the interplanar spacing increases, thus facilitating shear parallel to the basal plane. Were it not for the expansion of the lattice along the *c*-axis, it is not improbable that the hardness would increase monotonically with decrease in crystal size, since slip would be confined to progressively smaller and more perfect domains.

The hardnesses of several specially selected specimens of crystal graphite were determined by the rocking pendulum method[20], employing a 90° diamond prism. The apparatus was insensitive for measurement of hardnesses greater than 7 on Moh's scale, but the hardness of clean basal surfaces of graphite was found to lie between 6.5 and 7. The pendulum method does not eliminate purely elastic effects which may be appreciable in view of the large compressibility along the *c*-axis. For this reason the true hardness of the basal plane may considerably exceed this figure, which is, however, in agreement with published values[17]. In view of the interatomic contraction in the base plane of pyrolytic carbon crystals it is probable, also, that the hardness of their basal planes exceeds that of the basal plane of macrocrystal graphite.

With the prism edge oriented on the side of a relatively perfect graphite crystal so as to produce shear parallel to the base plane, the observed hardness was 0.5 on Moh's scale. Values of hardness on this scale from 1.0 to 1.5 were obtained for polycrystal graphite, these values being in agreement with other measurements.

In view of the pronounced anisotropy in the hardness of graphite and the probably greater anisotropy of individual crystal packets of pyrolytic carbon, the apparent relationship between scratch hardness and the degree of preferred crystal orientation is that to be expected, since preferential orientation of the type observed exposes the hardest surfaces of the crystals to the scratching tool.

5.3 *Thermal Conductivity*

A comparison method was employed to determine the thermal conductivity of the carbon films[21]. The conductivity of a carbon film deposited on a flat silica plate was compared to that of an identical silica plate to the surface of which a thin foil of lead or other metal was fastened with glycerine. One end of each of these plates was securely clamped to a heavy copper base and to the opposite ends were clamped identical copper blocks supplied with heater windings. Differential thermocouples permitted determination of temperature differences between the two heated blocks and of the temperature drops along the specimens. The temperature drop along the specimens which were about 3 cm in length, never exceeded 12 deg C, and the entire apparatus was contained in a heavy copper cylinder immersed in a constant-temperature oil bath. Calibration of the apparatus with foils of different metals and of various thicknesses showed that the relative thermal conductivities of the two specimens were accurately proportional to the powers dissipated in the two heaters when the temperatures and temperature drops were the same.

By comparison with pure lead, iron, copper, nickel, and aluminum, the thermal conductivity of carbon films about 1×10^{-4} cm thick was found to be 0.08 watt cm^{-1} deg C^{-1}. This value is in good agreement with the conductivity of black carbon determined by other methods[22], and it was independent, within the limits of accuracy of the method, of the conditions under which the carbon was deposited.

Specimens cut from samples of crystal graphite with their base planes parallel to their lengths were found by the same method to have thermal conductivities greater than that of pure copper, 4.0 watt cm^{-1} deg C^{-1}, with a temperature coefficient of about -0.0054 deg C^{-1}. According to one series of measurements, the conductivity was greater than that of pure silver, this abnormally high conductivity of graphite along the base plane being in agreement with other measurements[23].

Specimens suitable for the determination of thermal conductivity along the *c*-axis of graphite by this method could not be procured. However, specimens of like size cut from crystal graphite with their axes along the *c*-axis and the base plane, respectively, and oxidized to destroy any orientation produced at their edges by cutting, were clamped to the surface of a heated copper block with a small crystal of orthonitrophenol placed on the upper surface of each. The temperature of the block required to melt these crystals was noted and in this way it was found that the necessary temperature gradient along the *c*-axis was at least five times as great as that along the base plane, thus providing an approximate value of 0.8 watt cm^{-1} deg C^{-1} for the thermal conductivity of graphite along the *c*-axis. The conductivity of polycrystalline Acheson graphite was found to be 0.4 watt cm^{-1} deg C^{-1}, in agreement with published values[24].

The thermal conductivity of films of mesomorphic carbon is thus much smaller than those for single crystal or grossly polycrystalline graphite, and this is probably due to the definitive influence of intercrystal boundaries. As noted above, the crystals of mesomorphic carbon are more anisotropic than are those of graphite; but, despite this, the effect of the crystal boundaries is sufficient to suppress any influence of crystal orientation on the thermal conductivity.

5.4 *The Specific Resistance*

For determination of the specific resistance of pyrolytic carbon, silver electrodes were applied to the ends of films on rods or plates of fused silica and measurements were made at currents so small that there was no detectable joule heating. Comparative measurements made with and without potential probes showed no detectable contact resistance between these electrodes and the carbon film. Furthermore, the potential drop was linear along the specimens, thus indicating their uniform thicknesses.

Within the limits of experimental accuracy, the specific resistance of pyrolytic carbon films is independent of film thickness: From the measurements of the weights and film conductances of carbon films discussed in Section 2.2, and using the value 2.07 gm cm^{-3} for the density, the data of Fig. 12 relating the film resistance to its thickness were obtained. Over the measured range from about 2.5×10^{-6} cm to about 2.5×10^{-4} cm thickness there is no change in resistivity and a strictly linear dependence of film resistance on thickness is obtained. While direct measurements of the thickness of still thinner films have not been made, the actual thicknesses have been approximated on the basis of the relationship between film thickness and duration of deposition given by Fig. 3. On this basis, films having resistances in excess of 2×10^4 ohms for a square lie on an extrapolation of the curve of Fig. 12. These films are but a few Angstroms in calculated average thickness.

The specific resistance does, however, depend on the conditions under which the carbon is prepared, and it decreases with increase in the degree of preferential crystal orientation for films greater than 3×10^{-5} cm in thickness. As a probable result of the influence of crystal orientation, the specific resistance of the carbon films measured parallel to the film surface passes through a minimum value at 1025 deg C as a function of increasing furnace temperature at constant methane concentration, while, with increasing methane concentration at a constant pyrolyzing temperature, it decreases monotonically.

Single crystal graphite has a specific resistance of about 3.9×10^{-5} ohm-cm parallel to its base plane[23], with a positive temperature coefficient[23,25] of 0.009 deg C^{-1}, values confirmed by measurements made in the present study. Along the *c*-axis of the crystal, however, the specific resistance has been reported to range from 0.01 ohm-cm[26] to 1 or 2 ohm-cm[27], a value more than ten thousand times greater than that in the base plane. Measurements made in the present study show the specific resistance along the *c*-axis to be approximately 0.01 ohm-cm, with a negative temperature coefficient of about 0.04 deg C^{-1}.

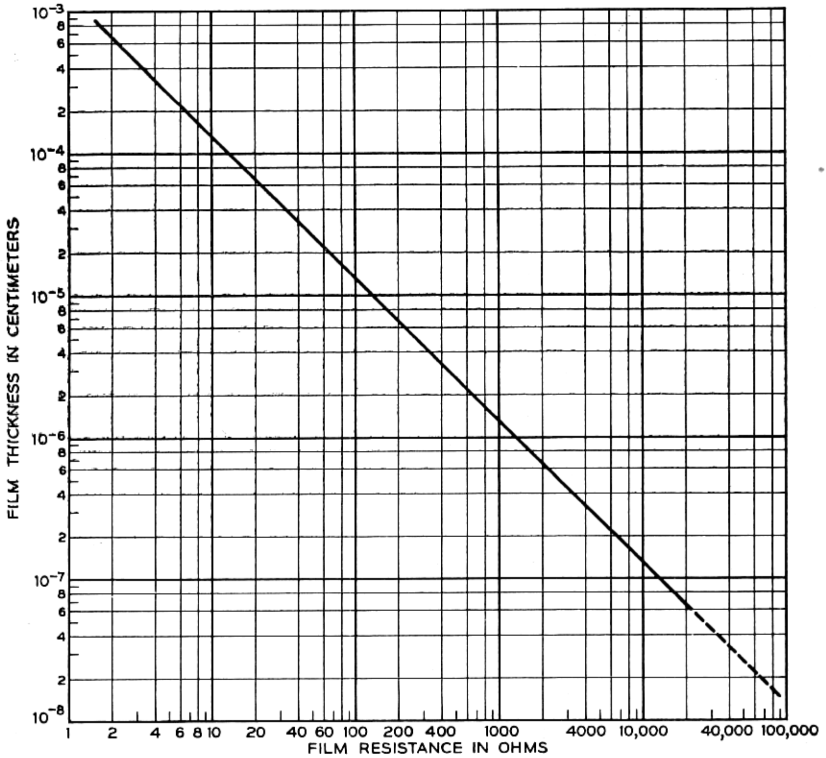


Fig. 12—Relationship between the thickness of a pyrolytic carbon film and its film resistance.

In view of the pronounced anisotropy in the specific resistance of crystal graphite, the relationship shown in Fig. 13 between the specific resistance of the carbon film and the degree to which its crystals are preferentially oriented with their base planes parallel to the direction of current flow is to be expected. Even in the most highly oriented specimens, however, the specific resistance is greater than 1×10^{-3} ohm-cm, and this fact emphasizes the rôle of intercrystal boundaries in determining the specific resistance of mesomorphic carbon.

This influence is also evident from the dependence of the resistance on ambient gas pressure. After a carbon specimen is heated in vacuo to about 500 deg C in order to remove adsorbed gases, it is found on subsequent exposure to air that the resistance exhibits a gradual, relatively small increase with time. If, at any later time it is reheated in vacuo, the resistance returns to its original value. These changes in resistance are completely reversible and are presumably associated with the adsorption of atmospheric constituents at intercrystal boundaries.

The influence of the intercrystal boundaries is further illustrated by the permanent decrease in film resistance by as much as 20 per cent, accompanied by a decrease in the temperature coefficient of resistance, which results from heating a pyrolytic carbon film in vacuo or in a neutral atmosphere to a temperature appreciably in excess of that at which it was deposited. These changes are presumably due to partial dehydrogenation at the boundaries with a partial intergrowth of adjoining crystals, an effect which has been confirmed by X-ray and electron diffraction examination.

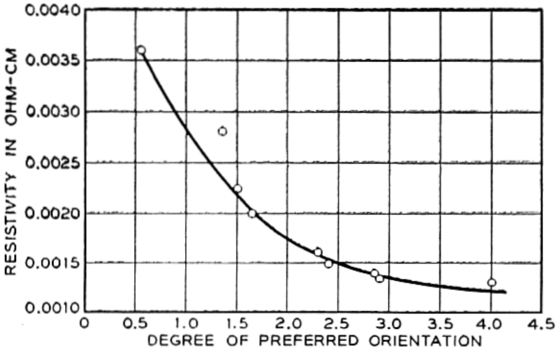


Fig. 13—Dependence of the specific resistivity of pyrolytic carbon films on the degree to which the crystallites are oriented parallel to the direction of flow of the measuring current. Scale numeral "0" represents random orientation, while "10" represents perfect orientation.

5.5 *The Temperature Coefficient of Resistance*

The temperature coefficient of resistance, α, for carbon films deposited on a suitable base depends on the thickness of the film, on the temperature of the film, and on the coefficient of thermal expansion of the base. As Fig. 14 shows, the value of α, defined as $\frac{1}{R}\,dR/dT$, where R is the resistance and T the temperature, decreases in magnitude with increasing film thickness and approaches a limiting value of about $-1.8 \cdot 10^{-4}$ deg C^{-1} which is found to be independent of the nature of the base. This value is, therefore, characteristic of the carbon film itself. The data illustrated in Fig. 14 were obtained over the temperature interval of 30 deg C to 60 deg C. Figure 15 shows the relationship between α and temperature for a typical film, the slope of which is common for all films deposited on the same base. As the coefficient of thermal expansion of the base increases, the value of α for any given film thickness less than 3×10^{-4} cm also increases, which serves to emphasize the rôle of the intercrystal boundaries in determining the properties of pyrolytic carbon, in suggesting that the resistances of these boundaries are dependent on pressure.

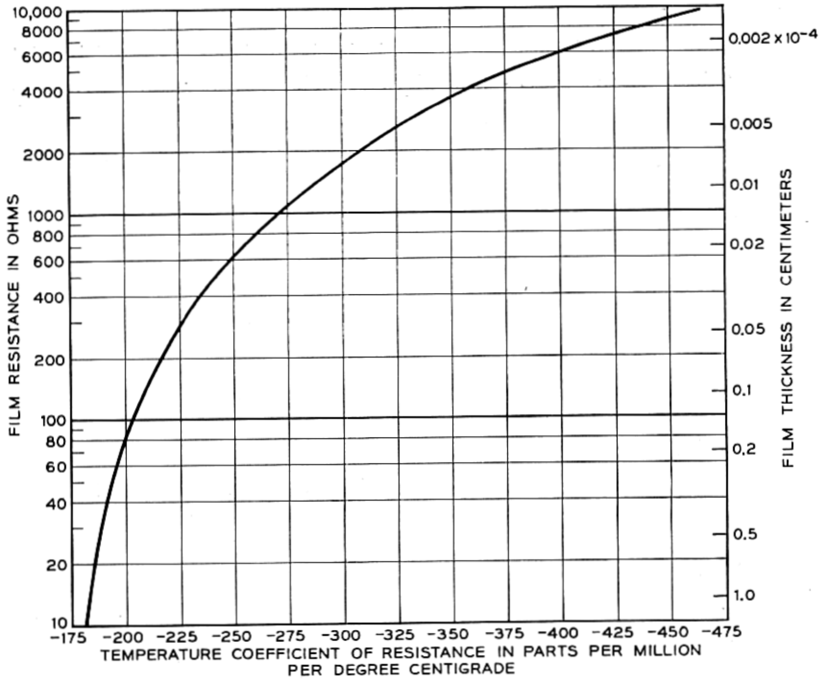


Fig. 14—Dependence of the temperature coefficient of resistance of pyrolytic carbon films on film thickness. Thickness expressed in terms of film resistance.

The thermal coefficient of expansion for graphite crystals along the *c*-axis[28] is 26×10^{-6} deg C^{-1} and parallel to the base plane[29] is 6.6×10^{-6} deg C^{-1}; that for films of pyrolytic carbon was estimated to be of the order of this latter value. Carbon films which had stripped spontaneously from smooth cylindrical fused silica bases were found to curl away from them, the radii of curvature increasing with film thickness in the manner to be expected if the surfaces of the films originally contiguous to the bases had been deformed largely in conformity with them according to the differential contractions during cooling. The thermal expansion coefficient of the pyrolytic carbon films was thus determined from measurements of their radii of curvature and of those of the bases from which they had stripped. This coefficient might be expected to depend on the nature of the intercrystal boundaries.

The anisotropy in the temperature coefficient of resistance of the constituent crystals of graphite might be expected to exist also in pyrolytic carbon, giving a dependence of α on the orientation of the crystallites. This dependence has not been observed, however, and the failure to observe it may be due to the primary influence of the intercrystal boundaries in conjunction with the usual fluctuations in the value of α for a given set of coating conditions.

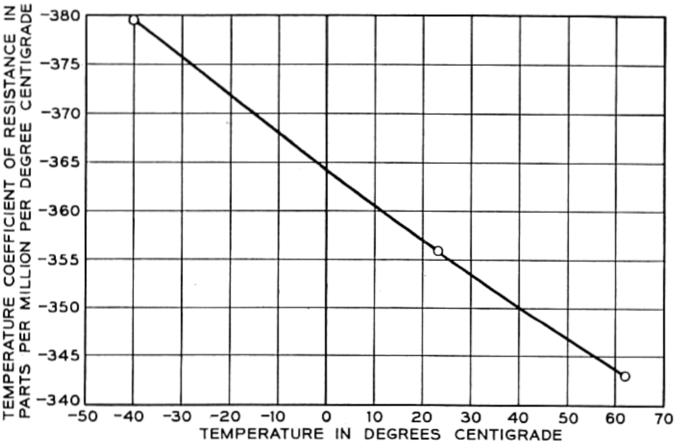


Fig. 15—Dependence of the temperature coefficient of resistance of a typical pyrolytic carbon film on temperature.

5.6 *Summary*

Pyrolytic carbon, graphitic in structure as are most black carbons, has physical properties which can be correlated in part with the size and properties of its constituent crystals and the way in which these crystals are arranged. While the lattice of these minute crystals differs in certain respects from that of graphite, it is probable that the metallic character of the layer planes is retained, that the anisotropy in properties of the crystal packets is somewhat greater than for graphite, and, hence, that conclusions as to the properties of pyrolytic carbon based on this anisotropy are valid to good approximation if the crystal packets are regarded as possessing the properties of macrocrystal graphite.

While some definite correlations are observed between structure and properties, the intercrystal boundaries in pyrolytic carbon modify its bulk properties for two reasons: First, the effects of the interruption of lattice period at them are presumably greatly accentuated by the anisotropy of the graphitic crystals; and, second, there is an actual chemical contamination at the intercrystal boundaries associated with the presence of peripheral hydrocarbon shells and of sorbed atmospheric constituents, as illustrated by the comparatively low thermal conductivity and by the changes in resistance and in temperature coefficient of resistance which heating the films in vacuo will produce.

TABLE I

Property	Unit	Polycrystal Graphite	Graphite, Basal Plane	Graphite, *c*-Axis	Pyrolytic Carbon
Density	Grams/cc	2.26	—	—	2.07
Hardness	MOH's scale	0.5–1.0	>6.5	~0.5	9.8
Thermal Coefficient of Expansion	$(\text{deg C}^{-1})\cdot 10^{-6}$	7.5	6.6	26.0	6.5–7.0
Specific Resistance, ρ	Ohm-cm	8×10^{-4}	3.9×10^{-5}	$\sim 1 \times 10^{-2}$	$1\text{–}1.8 \times 10^{-3}$
Temperature Coefficient of Resistance	deg C^{-1}	-1×10^{-3}	$+9 \times 10^{-3}$	$\sim -4 \times 10^{-2}$	-1.8×10^{-4}
Thermal Conductivity, K	$\text{Watt cm}^{-1}\ \text{deg C}^{-1}$	0.4	>4.0	~0.8	0.08
Temperature Coefficient of Thermal Conductivity	deg C^{-1}	-1.1×10^{-3}	$\sim -5.0 \times 10^{-3}$	—	-7.0×10^{-3}
Wiedemann-Franz Ratio, $K\rho$	$(\text{Watt Ohm deg C}^{-1})\cdot 10^{4}$	3.2	1.6	~80.	1.1
Rate of Oxidation	Relative	—	17.	1.0	—

Some of the properties of the graphitic carbons are collected in Table I.

6. PYROLYTIC CARBON FILM RESISTORS

6.1 *The Substrate or Core*

The influences of the supporting surface or substrate on the properties of pyrolytic carbon films are both chemical and physical in nature. Mechanical perfection of the carbon films is essential to production of resistors and this perfection is determined in large part by that of the core surface. If there are cracks, pits, grooves or other mechanical imperfections in the core, these will result in corresponding imperfections in the carbon films. Various types of imperfections are shown in the schematic cross section of core and film in Fig. 16. Of the imperfections there illustrated, the thinner and thicker areas of the film are the result of the catalytic or chemical influences described earlier, and, of these, the thin areas are the more harmful. If a continuous film covering the entire cylindrical core surface is employed as a resistive element by making suitable electrical connections to its ends, the effect of the imperfections is relatively small because each individual fault is shunted by a continuous and perfect film. However, it is common practice in resistor production to cut a helical groove through the film to provide, in effect, a carbon ribbon wound around a cylindrical core and thus to increase the resistance of the element. When this is done, the imperfections may become series elements in the current path or shunt elements between turns, and their effects on resistor behavior are consequently greatly accentuated. Figure 17 shows photomicrographs of mechanical imperfections in the film both before and after the helixing operation.

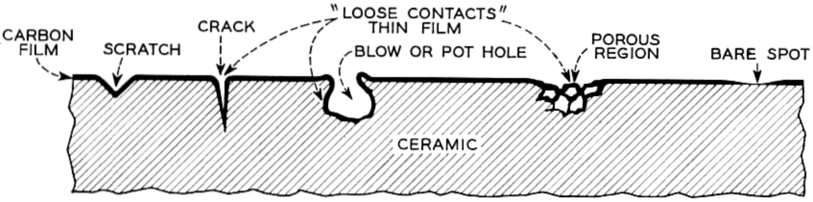
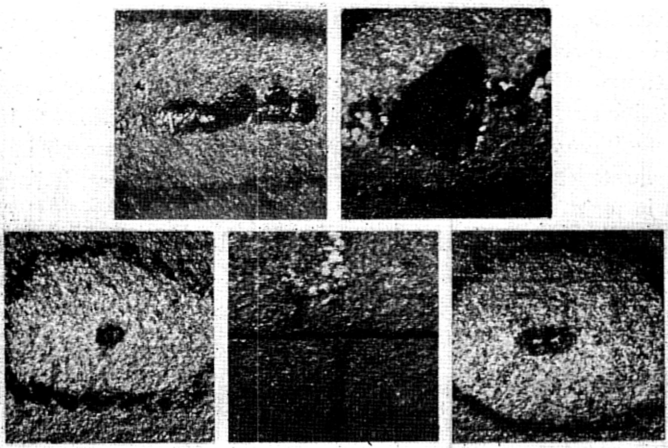


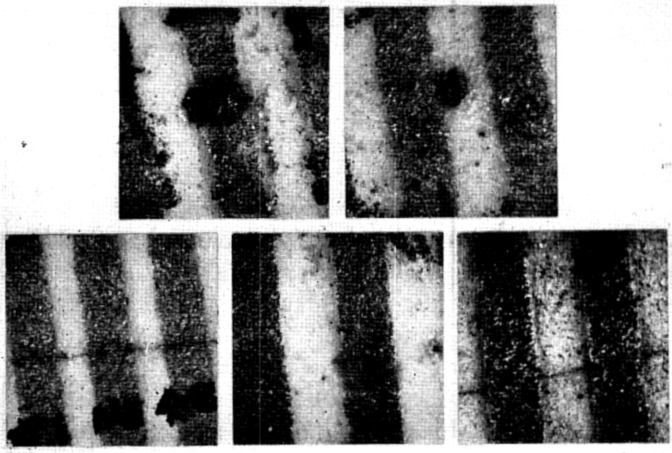
Fig. 16—Types of faults in carbon film resistors.

Carbon is deposited on the walls of cracks in the ceramic and over the surfaces of unvitrified grains in porous regions, and the contacts thus formed between carbon coated surfaces are similar to those in the carbon composition resistor or those between carbon granules in a microphone. They are unstable with time, temperature and voltage; and this instability is reflected in the behavior of the resistor. Microscopic count of such imperfections has been found to be qualitatively correlated with unfavorable effects on the temperature coefficient of resistance, the voltage coefficient of resistance, the noise level, and the stability of pyrolytic carbon resistors. While thoroughly vitrified ceramic cores are desirable, it is nevertheless possible to employ slightly porous or imperfect cores under certain conditions, particularly for thick films, since the depth of penetration of carbon into the ceramic can be controlled to some extent by proper choice of the pyrolyzing conditions.

It appears that carbon is held to the substrate by a mechanical keying action, so that the surface geometry of the core is important: The scale of roughness required for good adherence generally increases with film thickness, the films invariably being under lateral compression at normal operating temperatures. It has been found that crystalline substrates such as porcelain, zirconium silicate and alumina, which may be made nonporous, provide excellent adherence. Vitreous surfaces such as those of overfluxed



BEFORE HELIXING



AFTER HELIXING

Fig. 17—Mechanical imperfections in ceramic rods, carbon coated.

or over-vitrified porcelain, many steatites, and fused silica provide relatively inferior adherence, which can, however, be improved by chemical etching or by thermal oxidation of a previously deposited carbon film.

Even though free from mechanical imperfections resulting from corresponding faults in the substrate surface, the carbon film may still exhibit local variations in thickness as a result of catalytic influences, as described earlier. The increase in resistance of a uniformly coated core or blank due to cutting a helical groove through the film can accurately be calculated when the helix angle and groove width are known, but if there are variations in film thickness, then the observed helixing increase is greater than that calculated, because the high resistance areas become series elements in the helix. Aside from the fact that such a variation would present production problems, an increase in temperature coefficient of resistance also results since, as shown in Fig. 14, this coefficient is larger the thinner is the film. This increase is particularly undesirable if resistors with closely reproducible temperature coefficients are required.

The core of a pyrolytic carbon resistor must, obviously, be a good insulator, particularly where very high values of resistance are obtained by helixing; and when extreme stability of resistors under severe operating conditions is required, great care is necessary in the choice of the substrate material. Thus, the usual wet process electrical porcelain, when properly compounded from purified raw materials, can be made into resistor cores with very high surface perfection and good adherence for carbon films. However, it cannot be employed in resistor cores because at elevated operating temperatures the mobilities of the alkali ions in the glass matrix of this material are too great. The result of this mobility is that, under the influence of the fields between successive turns of a helixed resistor, electrochemical migration sufficient to alter the shunting resistance between turns occurs even with the resistive element sealed in a thoroughly dry and evacuated enclosure.

To obviate these electrochemical effects, which are qualitatively correlated with the analytically determined alkali concentrations, new alkali-free ceramic materials[30] have been developed for use in fabrication of cores for pyrolytic carbon resistors. These materials are essentially porcelains in which all but small residual traces of sodium and potassium have been replaced with alkaline earths such as magnesium, calcium, barium, and strontium. The ionic radii of these alkaline earth metals are sufficiently larger than those of the alkali metals that field migration is largely prevented. These alkaline earth porcelains show no evidence of electrochemical polarization when employed as resistor cores; and they have, in addition, high specific resistances and relatively low dielectric losses.

6.2 *Terminating and Adjusting to Value*

Transformation of a carbon coated ceramic rod into a completed resistor requires the application of low resistance contacts to the carbon film. Such electrodes may be applied directly to the carbon film by use of a water suspension of colloidal graphite (Aquadag) or of suitable metallic paints, or by other means. Except for resistors of low resistances, colloidal graphite, burnished and baked, provides an excellent termination. It is, however, susceptible to moisture; to provide greater stability and to facilitate subsequent manufacturing operations, metallic paints are generally preferred.

To obtain resistors within given tolerances, it is necessary to adjust the resistances of the terminated units, since the statistical variation which the resistances would otherwise exhibit generally exceeds the allowable tolerance. There are two reasons for this variation: First, there is, despite the most precise control of coating conditions in either the batch or the continuous process, a statistical variation in film thickness; and, second, there are variations in the core surfaces and in the dimensions of the cores.

Primary control of resistance tolerance is accomplished through control of the conditions of pyrolysis. The close control which is necessary in view of the great sensitivity of film thickness to the conditions of pyrolysis, as shown in Fig. 3, Fig. 4 and Fig. 5, requires careful attention to furnace design. The furnaces illustrated in Fig. 1 and Fig. 2 have proved satisfactory for resistor production: Either of them will furnish carbon films reproducible in film resistance to within about 7 per cent.

The adjustment by means of which resistors with resistance tolerances as small as ±0.5 per cent or less are produced from coated blanks may be accomplished in two stages: if helixing is employed, by choice of the helix pitch and width; and by removal of a small amount of the carbon film by abrasion.

The helix is ground through the carbon film by use of a water-cooled metal-bonded diamond cutting wheel. It is essential that the helical groove be smoothly ground in order to prevent the occurrence of cracks or fractures extending into the carbon ribbon, which lead to high noise levels and instability. The machines employed are so constructed that the carbon-coated blank "floats" against the abrasive wheel, thus providing a groove of essentially uniform depth and width regardless of any slight ellipticity in the cross-section of the core. Provision is made in the machines for continuously varying the helix pitch; and, over the range of pitch normally employed, the resistance of the coated blank can be increased by any desired factor from about 10 to about 8000. With uniformly coated blanks the helixing operation does not increase the spread of resistance values nor the value of the temperature coefficient of resistance. A typical helixing machine is shown in Fig. 18.

Choice of film resistance and helix pitch is made to yield a resistor blank slightly lower in resistance than is ultimately desired, in order to permit final adjustment to tolerance. This final adjustment is ordinarily accomplished by light and uniform abrasion over the entire surface of the resistor, through application of a cotton pad, moistened with an organic solvent, to the surface of the rotating resistor while the resistance is being measured continuously. Measurement has shown that the resistance stability of helixed resistors is slightly increased by this adjustment, probably in part because minute fractures of the film at the groove edges are partially eliminated.

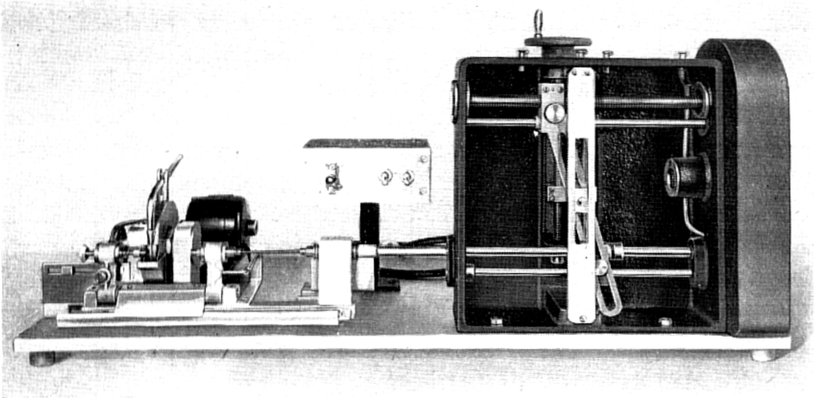


Fig. 18—A typical variable pitch helixing machine with cover removed to show pitch-changing mechanism.

Since the surface irregularities of the core are large relative to the carbon film thickness, abrasion does not remove carbon uniformly from the surface and large increases brought about in this way are often undesirable because of the resulting non-uniformity in film thickness. This non-uniformity results in non-uniform potential gradients over the film surface and thus increases the distributed capacity of the film, which is undesirable in resistors to be used at very high frequencies. Non-uniformity in film thickness is also particularly undesirable in resistors designed to dissipate large amounts of power, which may be as great as 30 watts per square inch for hermetically enclosed types or 1000 watts per square inch for liquid-cooled types. In such resistors, a small high resistance area may result in such pronounced local heating as to fuse the ceramic core locally with resultant progressive failure of a region across the entire conducting path if the power input is maintained.

6.3 *Protection of the Carbon Film*

The conducting film of pyrolytic carbon is extremely thin and, unprotected, it is subject to change or damage from several causes. Principal among these are increases in resistance due to gas adsorption, oxidation, and physical damage as a result of unintentional abrasion or other rough handling. To lessen or eliminate these causes of change, protection is given the film in various ways.

The simplest and most generally accepted method of providing this protection consists in the application of one or more coats of baking varnish over the carbon film. The application of the varnish causes an increase in resistance of the film which must be compensated for in adjusting the resistance to tolerance. This increase, which is generally less than one per cent, corresponds roughly to that observed over long periods of time in free air and is probably due to satisfaction by the varnish or its solvent of the adsorptive forces previously discussed.

While an organic protective film over the carbon surface inhibits time aging of the resistance, it also introduces a complexity in resistor behavior. The varnish film is strongly adherent to the carbon and it has a thermal coefficient of expansion greater than either the carbon or the ceramic core. Further, thermal expansion of the varnish is subject to a form of hysteresis in that stresses introduced by a large temperature change relax only slowly with time after return to the original temperature. These properties have an important bearing on the change of resistance, with time and temperature, of varnish-protected resistors, particularly when the carbon films are thin.

As noted earlier, stresses set up in the carbon films due to the greater thermal expansion of the core produce changes in the resistance of the films. The stresses set up in the films by expansion or contraction of the protective layer do likewise. Figure 19 illustrates the fact that the stresses set up during curing of the varnish change subsequently with time in such a way that the resistance decreases, approaching an asymptotic limiting value. If the resistors are cycled in temperature, the immediate result is an increase in resistance followed by a slow decrease towards the initial value. Cycling of unvarnished resistor units sealed in vacuo or in helium, however, produces no change in resistance nor does shelf aging, thus leaving little doubt that the observed changes are due to the protective varnish finish.

The carbon films are most stable and reproducible in properties when no solid material is in contact with their exposed surfaces. However, as discussed earlier, the resistance of a carbon film in free air increases with time, due to adsorption of atmospheric constituents. When resistor blanks are hermetically sealed in suitable enclosures filled with air at atmospheric pressure, the magnitude of the resistance increase with time due to the sorption of atmospheric constituents is proportional to the enclosed volume of air. Hence, where high temperature operation is not necessary, hermetical sealing in air provides resistor units of relatively high stability free from any hysteresis in their resistance-temperature characteristics. When the carbon film is thick and the enclosed volume of air is small, such resistors can also be operated at higher temperatures if the permanent increase in resistance due to partial oxidation of the film and consumption of the enclosed oxygen can be tolerated.

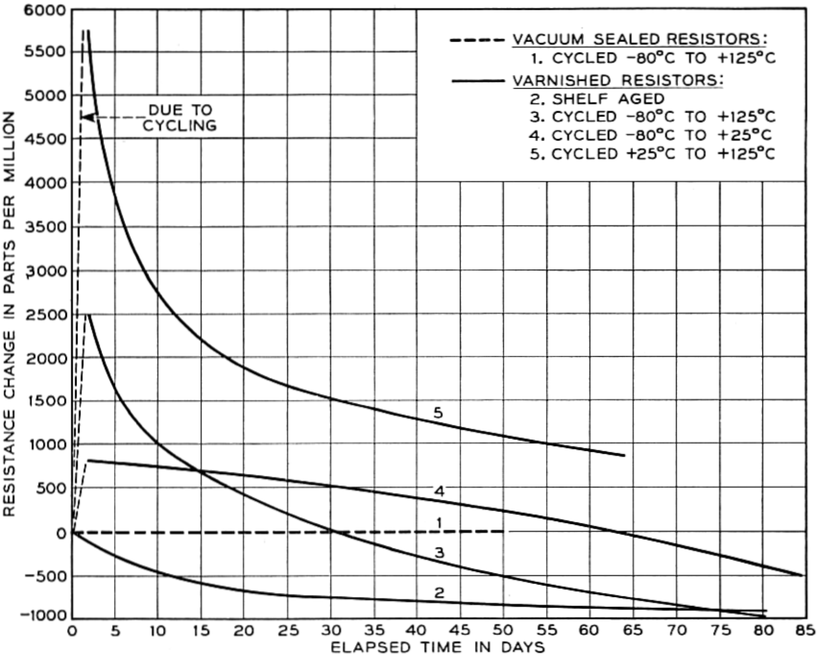


Fig. 19—Resistance aging of varnished and hermetically enclosed pyrolytic carbon resistors as influenced by thermal cycling and time.

The most stable pyrolytic carbon resistors are those in which the resistive unit is sealed in an hermetical enclosure which is baked and evacuated or filled with an inert gas. During the pumping and baking the resistance of such a unit decreases due to removal of previously adsorbed gases and residual low-molecular-weight hydrocarbons from the carbon film. Hence in contrast to the varnish-coated units, which are adjusted below tolerance before application of the finish, hermetically sealed units are adjusted to values somewhat above tolerance prior to sealing.

To increase thermal dissipation over that which obtains with the evacuated unit, and to achieve rapid response of the resistor temperature to that of the ambient, the hermetical enclosure is filled with an inert gas, oxygen-free nitrogen or helium normally being employed. Hydrogen is not used because it is not wholly "inert": Carbon films sealed in this gas increase in resistance with time, as if there were a tendency for them to revert to the hydrocarbons from which they were produced.

Resistors sealed in vacuo or helium exhibit a small initial aging, of the order of 100 parts per million (PPM) in resistance value, which can be completely eliminated by cycling them between -80 deg and 120 deg C. After this thermal cycling, the resistors do not change in resistance with time or further cycling. Measurements over more than seven years show the resistance to be stable to at least ± 50 PPM and the temperature coefficient of resistance to about 0.2 PPM deg C^{-1}, within the limits of measuring accuracy[5]. For resistance values ranging from 100,000 ohms to tens of megohms, these stabilities are far greater than can be obtained in any other type of present-day resistor.

Certain applications of these precision hermetically enclosed units have required that all resistors in a given network possess temperature coefficients alike to within 1.0 PPM deg C^{-1}. As illustrated in Fig. 14, the temperature coefficient of resistance of the film, α, depends on the film thickness, and hence all such "tracking" resistors are produced from a constant film thickness, different resistance values being obtained by the techniques of adjustment which have been described. The value of α for the films employed is 300 ± 35 PPM deg C^{-1}. While this value is from 3 to 6 times larger in absolute magnitude than that for wirewound units, its statistical variation for these resistors is no greater. This statistical variation in α, however, makes it necessary to measure each resistor, if groups with values of α differing by no more than 1.0 PPM deg C^{-1} are required.

Precision hermetically sealed resistors are very sensitive to faulty seals; and failure to reproduce resistance values at a constant reference temperature after temperature change is a criterion of the effectiveness of the seal, resistance changes greater than 15 PPM in absolute value being sufficiently large to be significant in this respect, if this change occurs in a relatively short time. The resistance of the film attains a stable value in a given gaseous environment, but if this environment changes only very slightly in composition or pressure it is necessary to restabilize once more by thermal cycling. If the composition changes with time, as in the case of a leaking envelope, stabilization to these accuracies is impossible.

The sensitivity of resistance value of carbon films to their gaseous environments would seem to be associated with adsorption equilibria, and there are data to show that adsorption of certain materials is more deleterious than that of others. There is evidence, moreover, that adsorption may not only change the number or mobility of the electrons in carbon, but that it may give rise to conduction by positive holes, which in the extreme case yields a positive Hall constant, rather than the negative Hall constant, indicating conduction by electrons, which carbon normally possesses.

6.4 *Characteristics*

Figure 20 shows some types of pyrolytic carbon resistors produced, while Table II summarizes the essential characteristics of some of the more widely used varieties. Pyrolytic carbon resistors are compared in Table III with representative carbon composition and wire-wound resistors.

These tables show that for many uses pyrolytic carbon resistors are superior to other available varieties. Thus, for high frequency applications, particularly when high values of resistance or large power dissipations are required, they are almost unique.[3] Similarly, regardless of frequency or of resistance, they exhibit greater stability in all respects than do carbon composition types. The stabilities and the tolerances to which they can be held are such that they could well serve as replacements for wire-wound types in many applications if it were not for the numerically large values of their temperature coefficients of resistance.

It has, however, been found possible to decrease the temperature coefficients of resistance of resistors in all other respects equivalent to the pyrolytic carbon type to values smaller than are, on the average, available in wire-wound varieties. These are produced by modification of the pyrolytic carbon film by the addition of boron and are known as "borocarbon resistors"[31]. The comparatively small temperature coefficients of these borocarbon resistors are, of course, of considerable interest. Besides being increasingly requisite for applications in which appreciable amounts of high frequency power must be dissipated, they greatly simplify production of closely matched units for computer network and other applications, are of particular advantage for electronic equipment which is subject to extremes of temperature, and can be employed as replacements for wire-wound types in many applications.

7. BOROCARBON RESISTORS

Investigations of the properties of carbon shortly after the turn of the century indicated that they could be greatly modified by the addition of boron.[32] So far as can be ascertained, however, the implications of this early work for the pyrolytic carbon resistor went unnoticed until, during the recent war, an investigation of the pyrolytic codeposition of carbon and boron was undertaken in these Laboratories. Results of this preliminary study indicated a good probability that composite pyrolytic films of boron and carbon would have appreciably smaller temperature coefficients of resistance than films of carbon, as has been confirmed by subsequent development.

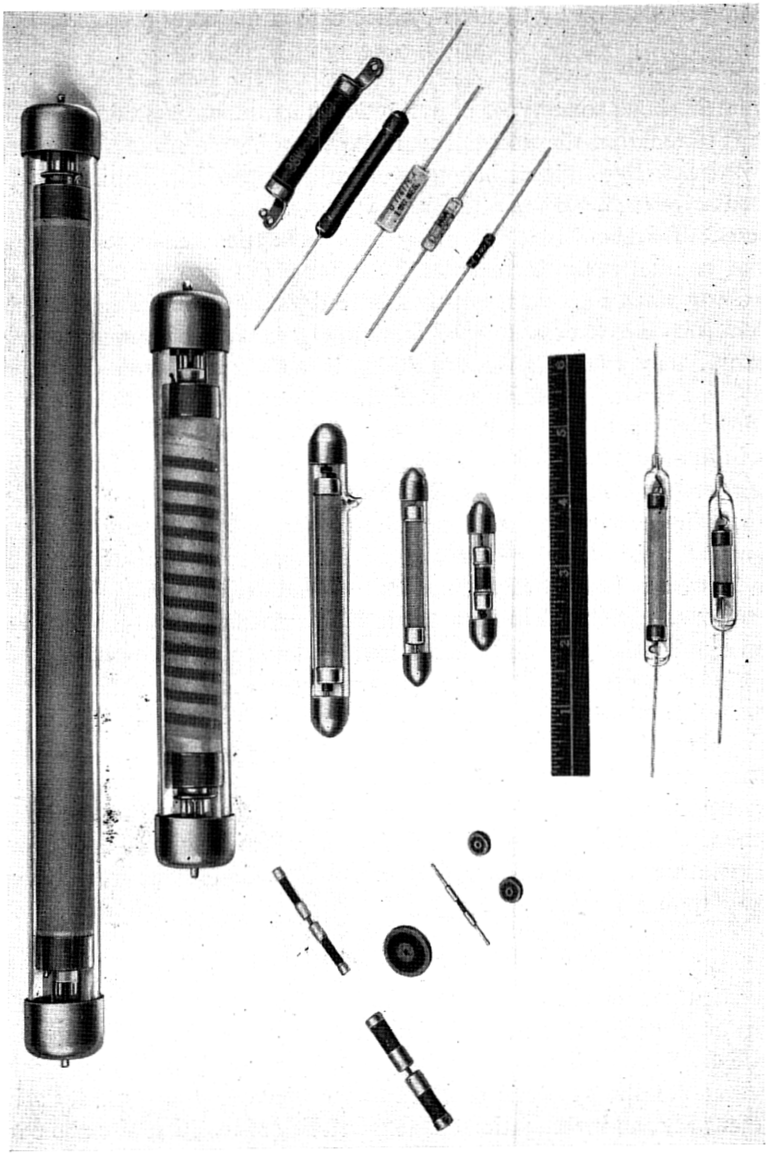


Fig. 20—Types of pyrolytic film resistors: Carbon and Borocarbon.

TABLE II

Western Electric Type Number	Protective Enclosure	Overall Dimensions (ins.)		Resistance Range		Power Rating in Air (Watts)	
		Dia.	Length	Min. (ohms)	Max. (meg.)	Free Convection (Normal)	Forced Convection (200 ft/min)
145	Plastic Shell	0.219	0.781	1	5	0.5	3.0
144	Varnish	0.281	0.938	50	5	1.0	8.0
147	Varnish	0.281	2.063	200	50	2.0	20.0
D-170000	Glass	0.438	3.25	200	15	10.	75.
152	Glass	0.615	4.63	20	10	60	500
153	Glass	1.25	8.75	10	1	300	2000
154	Glass	1.25	14.75	40	10	600	4000

TABLE III

	Pyrolytic Carbon (144 Type)	Carbon Composition (RC-30)	Wire Wound (107 Type)
Nominal Power Rating	1 Watt	1 Watt	¼ Watt to 1 Watt
Resistance Range	50 ohms to 5 megohms	10 ohms to 22 megohms	0.4 ohms to 0.25 megohms
Tolerance	±1, ±2, ±5%	±5, ±10, ±20%	±0.1, ±0.25, ±1.0%
% Resistance Change at Rated Load	−3.5	±7.5	±0.25[1] ±1.0[2]
Temp. Rise (°C) at Rated Load	75	52	56
Max. Cont. Voltage	1000	500	500
% Resistance Change per year (Shelf aging)	±0.1	±2	Negligible
Temperature Coeff. (ppm per °C)	−250 to −540	−1200 to +2400	±40[1] +30 to +130[2]
Approx. Ind. (μH) for 0.1 Megohm	0.26	<.02	125
1.0 Megohn	0.48	<.02	—
Approx. Cap. ($\mu\mu$f)			
for 0.02 Megohm	<1	<5	1.0
0.1 Megohm	<.1	<2	1.5
Approx. Ratio of high frequency Res. (Re) to d-c Res. (Ro) for fR_0 (megacycles x Megohms) of			
1	0.95	0.5 to 0.8	Not suitable for High Frequency Use
10	0.60	0.2 to 0.6	

[1] For resistances of 0.4 ohms to 90,000 ohms
[2] For resistances of 90,000 ohms to 0.25 megohms

It is possible now to produce pyrolytic film type resistors with temperature coefficients as small as −20 PPM deg C^{-1}, roughly one tenth the minimum value for pyrolytic carbon, and, indeed, lower than for many wire-wound types.

Boron is incorporated in the carbon by the simultaneous pyrolytic deposition of carbon and boron from gaseous compounds of these elements.

It can be accomplished, for example, by pyrolysis of a single compound such as tripropylborane, or by use of a mixture of a boron hydride and a hydrocarbon such as methane or benzene. Usually, however, boron trichloride is employed as the source of boron and a suitable hydrocarbon as the source of carbon. The films produced by codeposition of carbon and boron are, in many respects, indistinguishable from carbon films of like thickness.

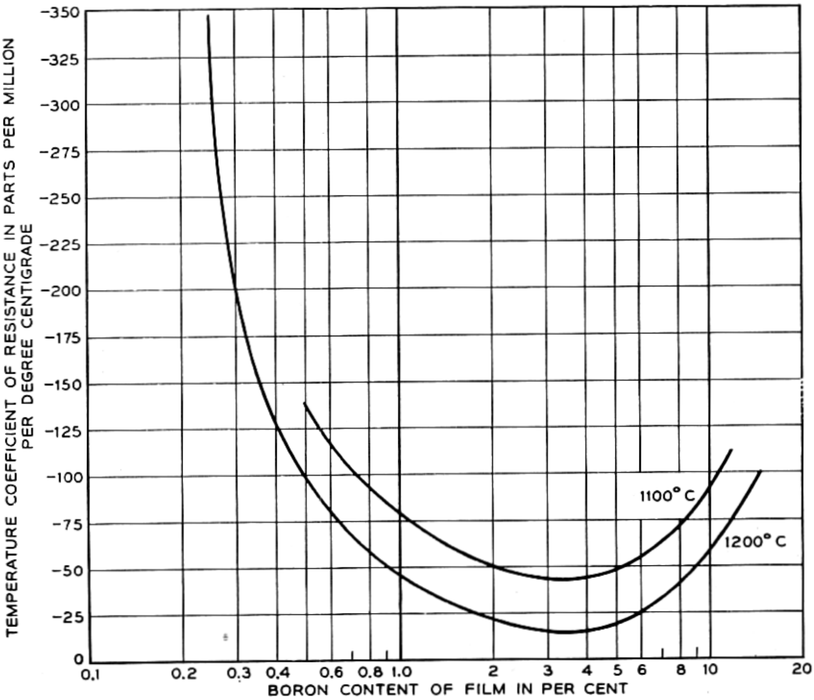


Fig. 21—Dependence of the temperature coefficients of resistance of borocarbon films on boron content and temperature of formation

As the boron content of thick films increases from zero in films of like thickness, however, the temperature coefficient of resistance, α, decreases through a minimum value and then increases, as shown in Fig. 21. The position of the minimum value of α is essentially independent of the pyrolyzing temperature, but the magnitude of α at the minimum decreases, as shown, with increase in furnace temperature. It will be noted that, at its minimum, the magnitude of α is less than 20 PPM deg C^{-1} when comparatively high pyrolyzing temperatures are employed.

The specific resistance of carbon films, except for the relatively small variations shown previously in Fig. 13, is independent of the pyrolyzing conditions and of the nature of the parent hydrocarbon. The specific resistance of borocarbon films, however, is a function of boron content, and it can be varied over a wide range, as shown in Fig. 22. Associated with this dependence of specific resistance on boron content there is a corresponding dependence of α, the relationship between α and specific resistance being shown in Fig. 23.

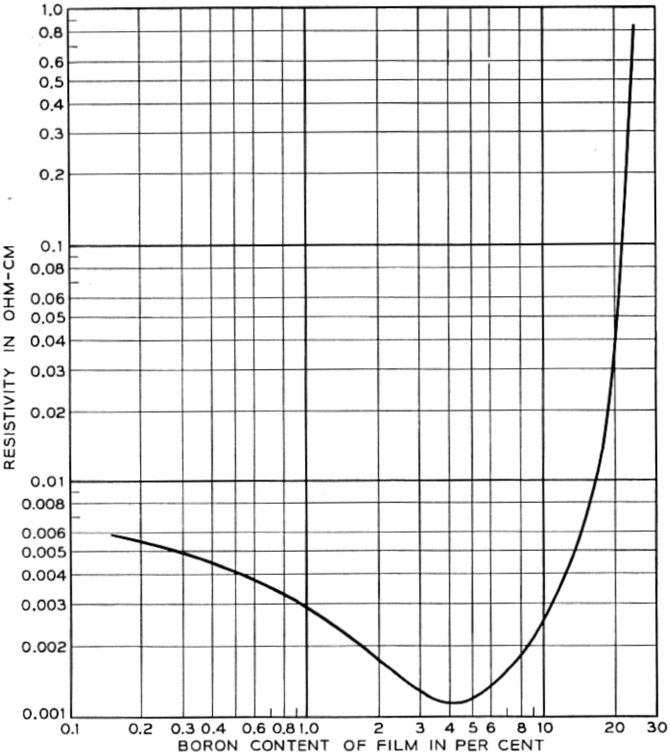


Fig. 22—Dependence of the specific resistivity of borocarbon films on boron content.

As for pyrolytic carbon films, the value of α for pyrolytic borocarbon films of constant composition depends on the film thickness. However, the nature of this relationship is dependent on the boron content of the film, as illustrated by Fig. 24 for three different boron contents and hence three different specific resistances. Film thickness is given in terms of film resistance and hence to each of these curves there corresponds a separate scale of geometrical film thickness. The greater is the specific resistance of the film, the greater, of course, is the actual thickness at any given film resistance. It will be noted that at, for example, a film resistance of 2000 ohms the value of α is smaller the higher is the specific resistance, a behavior just opposite to that for thick films with film resistances of 100 ohms. Associated with this "crossing over" of the curves is the circumstance that, to obtain the lowest values of α over a range of film resistances, the boron content of the film must increase with increase in film resistance. The envelope of the curve family of Fig. 24 gives, as shown, the relationship between minimum α and film resistance.

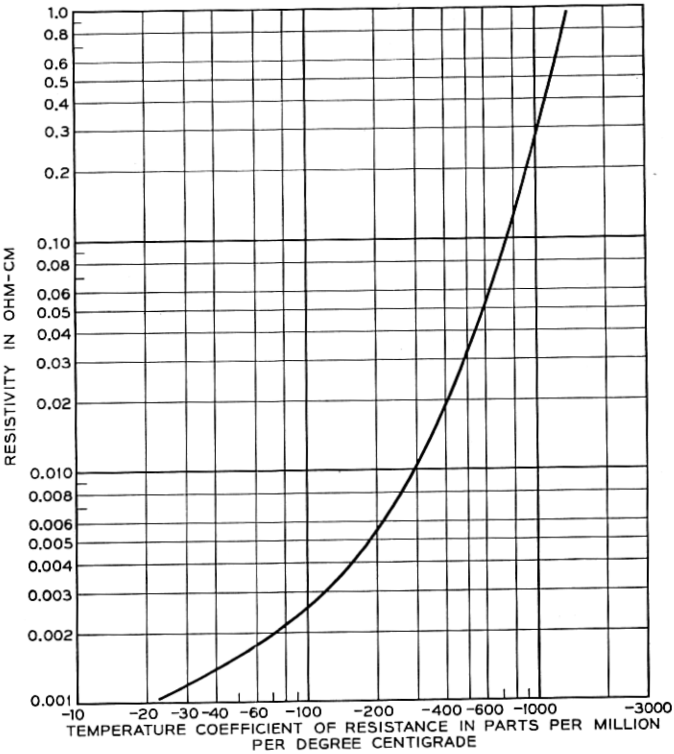


Fig. 23—Relationship between the resistivities of thick borocarbon films and their temperature coefficients of resistance.

This envelope is reproduced in Fig. 25 and is there compared with the curve of Fig. 14 for carbon films. For films of low resistance, the temperature coefficient, α, for borocarbon films is about one tenth of that for carbon films. This difference decreases with increasing film resistance until, between 10^4 and 10^5 ohms for a square, it becomes negligible and the curves appear to coincide, the addition of boron to carbon then appearing to offer little advantage. However, with attainable helixing factors, small (as well as large) borocarbon resistors of about 10 megohms resistance can be produced with temperature coefficients of resistance not exceeding 100 PPM deg C^{-1}, a representative value for high-resistance wire-wound types.

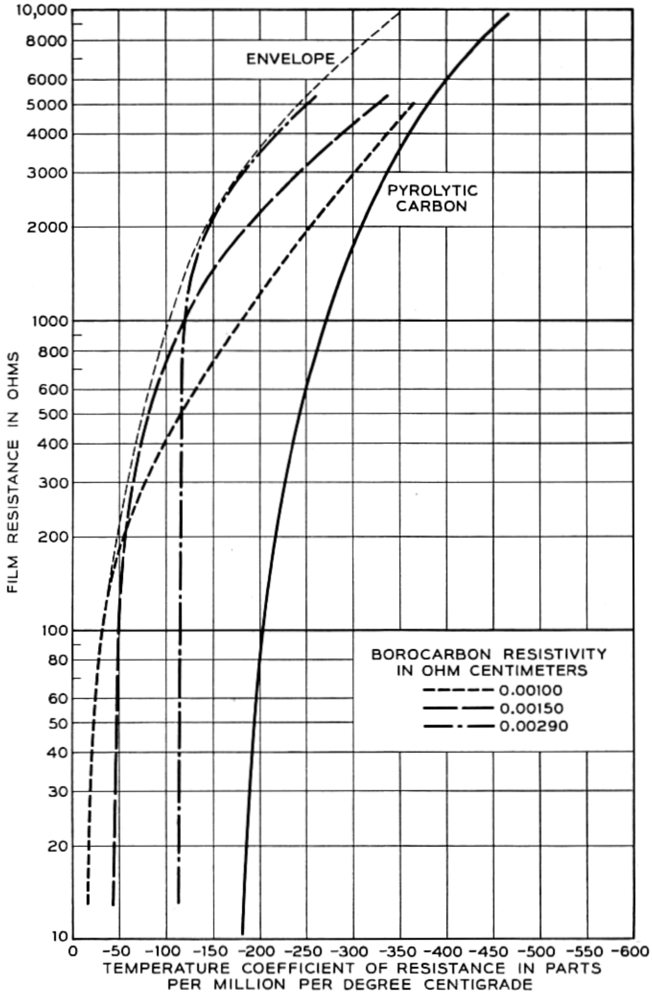


Fig. 24—Dependence of the temperature coefficients of resistance for borocarbon films of different resistivities on film resistance.

The maximum film resistance normally used in production of carbon film resistors is between 10^4 and 10^5 ohms, but much higher resistances can be employed with borocarbon films. Thus, in Fig. 25, data for film resistances of about $8 \cdot 10^5$ ohms are given, and films of 10^9 ohms have been successfully produced. The temperature coefficients of resistance for such films are, of course, larger than for lower resistance films; but in the very high resistance range made accessible through use of borocarbon films, the temperature coefficient of resistance is relatively less important.

The data of Fig. 24 and Fig. 25 suggest that the maximum usable film resistance for a given material of constant specific resistance may be determined by purely geometrical factors. Films which are thinner than a given limiting value become increasingly less coherent, or less continuous and uniform in thickness. The result of this may be that contacts between "patches" of the conducting material become increasingly important, the spreading resistance at these contacts being more temperature sensitive and giving rise to the observed increase in temperature coefficient of re-

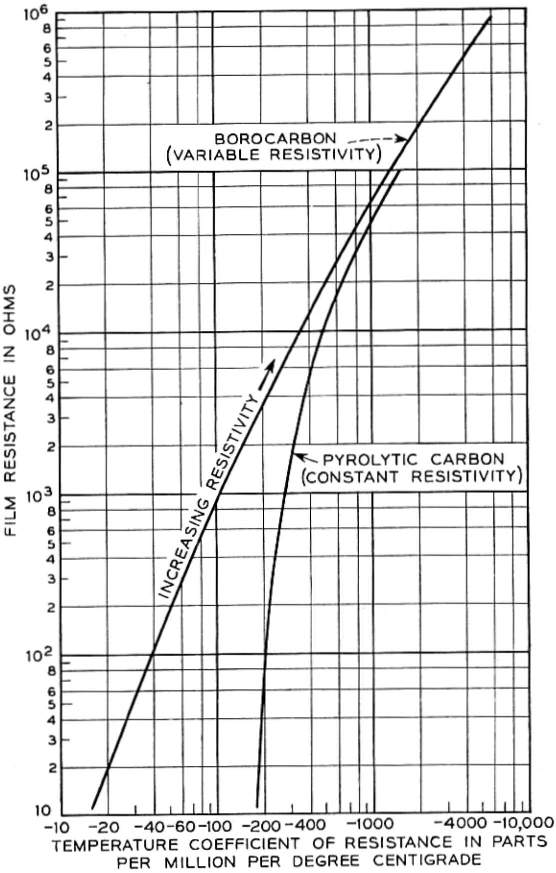


Fig. 25—Dependence of the temperature coefficients of pyrolytic films of carbon and borocarbon on film resistance.

sistance. Thicker films of materials with higher specific resistances but with the same resistance for a square might, therefore, have lower temperature coefficients of resistance.

While such considerations may be generally applicable to thin films, the low temperature coefficients of thick borocarbon films are probably due to another cause. It appears that boron decreases the temperature coefficient of resistance of carbon films because it acts as a dehydrogenating or "graphitizing" agent. As noted earlier, the crystal packets of which pyrolytic carbon is composed are surrounded by complex hydrocarbons which have a profound influence on the resistivity of the films. Boron is believed to act primarily to decrease the thickness and total volume of these peripheral layers, since it is known that the average diameter of the packets in borocarbon films is at least twice as great as in carbon films and that boron strongly catalyzes the pyrolysis of hydrocarbons.

Although the principal result of adding boron to the carbon films is thus believed to be a type of graphitization, it is possible that its effect may be due to other causes: Boron may act to produce "cross links" between the atom layers in adjacent packets; or, in view of its favorable atomic diameter, boron may enter substitutionally into the graphite lattice itself.

It will be recalled that the resistance stability of the pyrolytic carbon resistor is largely dependent on the characteristics of the boundaries between crystal packets, and that adsorption of contaminants at these boundaries produces changes in resistance. With the relatively decreased importance of interpacket boundaries in borocarbon films it is reasonable to expect that the films might also be more stable with time. While data as extensive as those for pyrolytic carbon films are not yet available, it now appears that this expectation is fully confirmed.

Borocarbon films thus make possible the production of film type resistors of improved stability with temperature coefficients of resistance as low as and in many cases lower than can be obtained in the wire-wound type. Further, borocarbon films make accessible the very high resistance ranges hitherto inaccessible to stable film type resistors.

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