

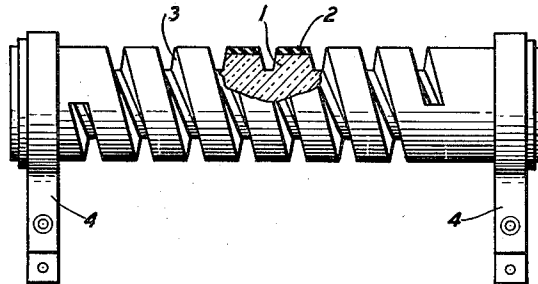
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ELECTRICAL RESISTORS AND METHODS OF MAKING THEM

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UNITED STATES PATENT OFFICE

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ELECTRICAL RESISTORS AND METHODS OF MAKING THEM

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17 Claims. (Cl. 117—46)

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This invention relates to carbon-coated electrical resistors and to methods of making them.

Electrical resistance elements are commonly formed either of a carbon coating on a non-conducting base, such as a ceramic base, or of a metallic resistance wire, usually wound helically on a non-conducting base. The carbon resistors are ordinarily considerably less expensive than the wire wound resistors, are available at much higher resistance values, and are free of the inductive properties of the wire wound resistors. The wire wound resistors, on the other hand, possess among certain other advantages a substantially lower temperature coefficient of resistance than the previously available carbon-coated resistors.

Thus, the more temperature-stable carbon-coated resistors have possessed temperature coefficients of resistance at room temperature averaging, over the range of resistance values, in the vicinity of 300 parts per million per degree centigrade (p. p. m./° C.), whereas wire wound resistors have been available, over a more limited range of resistance values, with temperature coefficients averaging in the vicinity of 100 p. p. m./° C. Therefore, in electrical circuits requiring a high stability of resistance values over a considerable temperature range, it is often necessary to employ the more expensive wire wound resistors.

With the trend toward the use of increasingly higher frequencies, the limitations of previously available resistors have become more apparent. As the frequency increases, the inductive effect of wire wound resistors coupled with their skin effect make their use less and less desirable and ultimately impossible. It is, therefore, necessary to use carbon-coated resistors in circuits designed to carry these higher frequencies. Stability of resistance values over a temperature range in such circuits can be achieved only by providing carbon-coated resistors having lower temperature coefficients of resistance than previously available.

The resistors of the present invention are coated with a layer of carbon containing a proportion of boron, both constituents being deposited simultaneously at an elevated temperature on a non-conducting base from a gas or gas mixture containing both boron and carbon. These resistors possess lower temperature coefficients of resistance than do similar carbon-coated resistors which are free of boron and which possess comparable resistance values. With proper proportioning of the boron and carbon and with proper control of the conditions of deposition,

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resistors are produced which have temperature coefficients of resistance comparable to or lower than the average values obtainable with wire wound resistors, namely, coefficients of 100 p. p. m./° C. or less. Moreover, by introducing relatively high boron contents in the carbon layer, it is possible to produce, for given dimensions, resistors having considerably higher resistance values than are obtainable with other carbon-coated resistors.

The accompanying drawing is a front elevation, partly in section, of one form of a resistor of the present invention.

The resistor shown in the drawing is made up of a non-conducting base 1, commonly formed of a ceramic, on the surface of which is a layer 2 of the deposited carbon and boron. Metal terminals 4 are fastened to each end of the resistor and provide electrical contact with the carbon layer. Good contact between the terminals and the carbon layer is usually insured by forming a metallized film on top of the carbon layer before the terminals are applied. This metallized film can be formed by means of any conventional metallizing composition, such as the common silver plates. In the form of resistor shown in the drawing, a helical groove 3 is cut in the base through the carbon layer 2 so as to lengthen the electrical path through the carbon layer and increase the resistance of the resistor.

As a base for the resistor, any non-conducting material can be used which can withstand the conditions under which the deposition of the carbon layer takes place. Ceramic materials, whether vitreous materials such as glass or fused silica, porcelain like materials such as may be formed by the firing of a mass of particles of a refractory oxide such as silica, alumina, magnesia, calcium oxide, baria, strontia, titania, zirconia, or mixtures of these or similar refractory oxides with each other or with other oxides such as lithia or sodium oxide, or crystalline bodies such as a crystal of quartz, ruby, sapphire, or zircon, are the materials most suited for forming bases for these carbon-coated resistors.

Particularly suitable ceramic materials are those described and claimed in United States Patent 2,386,633, issued October 9, 1945, to M. D. Rigerink. The ceramic bodies described in that patent have an extremely non-porous surface resulting from a substantial glass content in the ceramic. They are formed from clay, silica, and a calcined mixture of at least three alkaline earth metal oxides in proportions yielding a product containing between 60 and 68 mol per cent SiO₂,

between 17 and 23 mol per cent Al_2O_3 , and the remainder the alkaline earth metal oxides, each of which is present in an amount of at least one mol per cent. A superior body of this type is formed by first forming a calcine of 60 parts kaolin by weight, 10 parts MgCO_3 , 10 parts CaCO_3 , 10 parts SrCO_3 , and 10 parts BaCO_3 , fired to 1200°C . and subsequently ground to 325 mesh. To 35 parts of this calcine are added 50 parts kaolin and 15 parts of 325 mesh flint. The resulting mixture is mixed with water, shaped, dried, and fired at 1250°C .

As indicated above, the layer of carbon and boron is deposited on the base by means of heat in the presence of a gas containing boron and carbon. As an example of the manner in which such a deposition can be carried out, carbon and boron were deposited on a ceramic base from a gaseous mixture of hydrogen, benzene vapor, and boron trichloride vapor. The apparatus used for this co-deposition comprised a resistance heated furnace with a center cylindrical core four inches in diameter and ten inches long. In the center of this core was placed a rotating fused silica bottle having an outside diameter of three inches and a length of four inches. To one end of the bottle was fused a long neck, and to the other end was fused a short, small diameter tube for the exhaust gases.

The bottle was loaded through the long neck with 30 cylindrical ceramic cores $\frac{1}{8}$ inch in diameter and $\frac{3}{4}$ inch long. These cores were formed of the ceramic referred to specifically above. In addition, 30 cc. of 60 to 80 mesh quartz particles and 20 alumina balls $\frac{1}{4}$ inch in diameter were placed in the bottle. The fine mesh particles were added to give a burnishing action to the carbon-boron deposit as it was formed, and the alumina pellets were used to provide additional agitation in order to obtain a sufficient degree of uniformity in the coated cores.

The bottle with its charge was rotated within the furnace and about the axis of the furnace core, which was horizontal, at a rate of 40 R. P. M. The gas mixture of hydrogen, benzene vapor, and boron trichloride were continuously fed into the center of the rotating bottle through a small bore fused silica tube inserted through the long neck attached to the bottle. Surrounding this small bore tube was a tube of somewhat larger diameter which extended a portion of the way into the neck and through which hydrogen was continuously introduced in order to prevent entry of air into the bottle.

It was necessary that the hydrogen used be substantially completely free of oxygen and water vapor, and for this reason, the commercial tank hydrogen which was used was first passed over palladinized alumina pellets to convert to water vapor any free oxygen present and was then dried by passage through calcium hydride. The gas mixture was formed by bubbling the purified hydrogen separately through benzene maintained at 35°C . in a controlled oil bath and through boron trichloride maintained at -78°C . in a Dry Ice acetone bath. The two gas streams, one containing benzene, the other containing boron trichloride, were combined in the proper proportions and introduced into the furnace.

The total gas flow into the furnace was maintained at 1000 cc. per minute, and a coating time of one hour was used. Batches of resistors were formed at various temperatures, with various proportions of boron trichloride and benzene, and

with various dilutions of these gases with hydrogen.

Under the different conditions of deposition, the deposited films had varying proportions of boron in the carbon deposit, were of varying thickness, and had varying resistance characteristics. The deposited film was, in each case, homogeneous, adherent, continuous, hard, and durable.

Under conditions of fixed total gas flow and fixed furnace geometry, the boron content of the deposited films increases with increasing relative proportion of boron-containing gas to carbonaceous gas and also increases with decreasing temperature of deposition. However, as will be more fully discussed below, even with fixed boron to carbon ratio in the gas and with fixed temperature of deposition, the proportion of boron in the deposited film will vary with the size, shape, and type of furnace, with the nature of the carbonaceous gas, the boron-containing gas, and the diluent gas, with the rate of gas flow, and with the nature of the gas path through the treating chamber.

It is the boron content of the deposited carbon film, together with the temperature of deposition of the film and the film thickness, which determine the resistance characteristics of the film. The effects of other conditions of deposition are less significant.

Regardless of the temperature of deposition, the temperature coefficient of resistance has a minimum value when the boron content of the deposited film of carbon and boron is between about 3 per cent and 4 per cent by weight and the film thickness is such that the resistance per unit square is 200 ohms or less. With thinner films, the minimum value of temperature coefficient of resistance occurs at higher boron contents. As the boron content of the film decreases from this value, the absolute value of the temperature coefficient increases relatively rapidly, and when the boron content increases from this value, the coefficient increases less sharply. With boron contents between 1 per cent and 6 per cent, it is possible to obtain close to the minimum temperature coefficient.

With an optimum film thickness and with a deposition temperature of 1200°C ., the value of temperature coefficient of resistance at this minimum point may be of the order of -15 P. P. M./ $^\circ\text{C}$. When the boron content of a film of comparable thickness and deposited at the same temperature is decreased to about 0.25 per cent, the temperature coefficient is increased to a value of the order of -350 P. P. M./ $^\circ\text{C}$. With an increase of boron content to about 8 per cent, the temperature coefficient is increased to values of the order of -100 P. P. M./ $^\circ\text{C}$.

At lower temperatures of deposition, the minimum values of temperature coefficient which also occur at a boron content of about 3 per cent to 4 per cent in the film are somewhat higher. Thus, at a deposition temperature of 1100°C ., a minimum value of temperature coefficient of the order of -50 P. P. M./ $^\circ\text{C}$. may be obtained.

With a boron content in the deposited film between 0.35 per cent and 20 per cent and deposition temperatures between 1000°C . and 1300°C . and particularly with deposition temperatures between 1100°C . and 1250°C ., it is possible to obtain temperature coefficients below about -150 P. P. M./ $^\circ\text{C}$. By limiting the boron content to between 0.5 per cent and 10 per cent at these temperatures of deposition, it is possible to ob-

tain temperature coefficients below about 100 P. P. M./° C.

In the specific deposition procedure described above using a gaseous mixture of hydrogen, benzene vapor, and boron trichloride vapor and using deposition temperatures of 1200° C. and 1100° C., a film having a boron content of between 3 per cent and 4 per cent, corresponding to a minimum value of temperature coefficient, was obtained when the concentration of boron in the gaseous mixture was in the vicinity of 5 atomic per cent of the total boron and carbon in the gas.

However, when a similar deposition procedure was followed using methane as the carbonaceous gas in place of benzene, a boron content of between 3 per cent and 4 per cent was obtained in the deposited film when the boron concentration in the gas was between about 3 per cent and about 5 per cent for a deposition temperature of 1200° C., between about 1 per cent and about 2 per cent for a deposition temperature of 1100° C., and less than about 0.1 per cent for a deposition temperature of 1000° C. Similarly, when other variations are made in the sources of boron or carbon in the gas or in the other conditions of deposition, such as furnace geometry or rate of gas flow, the ratio of boron to carbon in the gas must be altered to furnish the required ratio of boron to carbon in the deposited film.

Although the point of minimum temperature coefficient occurs in the vicinity of 3 per cent to 4 per cent boron content in the deposited film regardless of the conditions of deposition except with relatively thin films, the value of the temperature coefficient at this minimum (as well as at other boron contents) varies somewhat with variations in the conditions of deposition. Thus, as has been indicated above, higher temperature coefficients are obtained with lower deposition temperatures. Similarly, lower temperature coefficients are obtained when the source of carbon in the gas introduced into the furnace is a normally gaseous alkane, such as methane, ethane, propane or butane, than when it is an aromatic hydrocarbon such as benzene.

The resistivity of the material of the deposited film does not appear to be substantially sensitive to the conditions of deposition and can be said to be essentially a function of the boron content of the film. The resistivity of the deposited material, like its temperature coefficient, exhibits a minimum value as the boron content of the film varies. This minimum value, as determined on a cylindrical ceramic rod of the type specifically described above, appears to be of the order of 1.25×10^{-3} ohm-cm. and occurs at a boron content in the film of about 4 per cent. The resistivity increases as the boron content is raised or lowered, reaching a value of the order of 5×10^{-3} ohm-cm. at a boron content of about 0.5 per cent and a value of the order of 0.7 ohm-cm. at a boron content of about 20 per cent. As the boron content is increased, a value of resistivity is reached, in the vicinity of 45 per cent or 50 per cent boron, beyond which it is not advantageous to go since the resistivity begins to approach that of an insulator rather than semiconductor and since, at the present time at least, such high resistivities are neither accurately measurable nor capable of useful application. Only for exceptionally high resistance values will boron contents of about 35 per cent be exceeded and, for most practical applications,

boron contents of 20 per cent or less will most commonly be used.

As is true of all deposited carbon resistors, the temperature coefficient of resistance of the boron-containing carbon films increases markedly as the thickness of the deposited film decreases. It is, however, an advantage of the boron-carbon resistors of the present invention that, regardless of how high a resistance is required, it is possible to form the film with a thickness as great as is desired for mechanical or other reasons. Therefore the increase of temperature coefficient with decreasing film thickness need offer no disadvantages. In contrast, the resistance of the common deposited carbon films can be varied only by varying the thickness of the deposited film since the resistivity of the deposited material is relatively fixed. This means that, for high values of resistance, thin carbon films must be used, resulting not only in higher temperature coefficients but also in increased difficulty of obtaining stable and continuous films. It also follows that, since a minimum film thickness exists below which, for mechanical reasons, a continuous carbon deposit cannot be formed, there is a limit to the resistance values which can be obtained with an ordinary carbon deposit.

With the resistors of the present invention, on the other hand, the resistance of the deposited film can be increased, substantially without limit, by increasing the boron content and with it the resistivity of the film. Therefore the optimum thickness of deposited film, from the standpoint of mechanical properties and temperature coefficient, can be employed. It is obvious, however, that if there is any desirability for doing so, thinner films may be used. Even with the thinner films, lower temperature coefficients are obtained than with ordinary deposited carbon films of comparable resistance values. Moreover, it is possible to obtain temperature coefficients not substantially in excess of 100 p. p. m./°C. if the resistance of the deposited film is maintained, by control of film thickness or boron content or both, at a value not in excess of 500 ohms per unit square.

With ordinary deposited carbon resistors, it is not ordinarily feasible to form carbon films having a resistance per unit square greater than 10,000 ohms. With the carbon-boron resistors of the present invention, resistances greater than this value can be obtained, with films of optimum thickness from a mechanical standpoint, with boron contents of about 18 per cent and greater, corresponding to resistivities of the order of 10^{-2} ohm-cm. or greater.

The film thickness on the resistors of the present invention, as calculated from the total weight of the deposit, the area of deposition and the estimated density of the material, is preferably of the order of 10^{-4} to 10^{-5} cm. since at these thicknesses the best mechanical properties are obtained. As the film thickness is increased beyond these values it becomes increasingly difficult to form a mechanically stable film which will not split off from the base. With the best type of ceramic bases, it is possible in some instances to obtain film thicknesses of the order of 5×10^{-3} cm. without undue sacrifice of mechanical properties. Ordinarily, however, film thicknesses between 10^{-4} and 10^{-6} cm. will be used. The lower limit of film thickness which will form suitable films is of the order of 5×10^{-7} cm. although this will also depend upon the nature of the surface upon which the deposit is made.

A specific method of deposition of the carbon and boron film has been described above. There may be considerable variation in this procedure so long as the film is deposited on a non-conductor at elevated temperatures from a boron-containing and carbonaceous gas.

As the source of carbon in the gas, any carbon compound capable of being introduced as a gas or vapor into the furnace and capable of being decomposed within the furnace to deposit carbon may be used. The most suitable of such carbon sources are the hydrocarbons, both paraffinic and aromatic, such as methane, ethane, propane, butane, benzene, toluene and xylene, and the halogenated hydrocarbons such as the chlorinated methanes, CCl_4 , CHCl_3 , CH_2Cl_2 , CH_3Cl , and the corresponding brominated and iodinated methanes. Fluorine and its compounds are ordinarily to be avoided because of their attack on ceramic resistor bases and on common furnace materials. However, if the bases and the furnace materials were of such nature as to resist attack by fluorine, this substance would not be objectionable from the standpoint of either the process operation or the quality of the product.

Any boron compound capable of being introduced into the furnace as a gas or vapor can be used as a boron source. This includes borane, $(\text{BH}_3)_2$, as well as the partially or completely halogenated boranes or borines, BH_2Cl , BH_2Br , BH_2I , BHCl_2 , BHBBr_2 , BHI_2 , BCl_3 , BBr_3 and BI_3 . Again a restriction is placed on the use of the corresponding fluorine compounds only because of the presence of materials susceptible to attack by fluorine.

Both the carbon and the boron may be introduced as components of a single compound as in borines substituted with hydrocarbon radicals, namely compounds of the structure



wherein R_1 , R_2 and R_3 are either hydrogen or a monovalent hydrocarbon radical. Examples of suitable compounds of this type are propyl allyl borine and tripropyl borine. The borine may also be partially substituted with hydrocarbon radicals and partially substituted with halogens, as in phenyl dichloro borine. Where the boron to carbon ratio in the substituted borine is not the proper one for the desired boron content of the deposited film, the proper ratio in the gas may be obtained by adding the required amount of either a carbon-free boron compound or a boron-free carbon compound.

In the process described above, hydrogen was used as a diluent for the boron-containing and carbon-containing gases. This diluent gas serves as a medium for controlling the relative proportions of the boron and carbon in the gas since it can be bubbled through the source compounds of these elements while they are at a temperature at which they are in a liquid state and have a definite vapor pressure. The rate of deposition of the film, and hence the film thickness, can also be controlled by controlling the degree of dilution of the boron and carbon gases.

Hydrogen is preferred as the diluent gas since its presence tends to suppress formation of carbon in the gas before it contacts the surface on which the deposit is to be formed and since it

can readily be freed of traces of oxygen which would interfere with the operation of the process. Any other gas which is inert to the reaction occurring during deposition and which can be rendered sufficiently free of oxygen and water vapor can be employed, such as helium and carbon monoxide.

It is theoretically possible to use a gas for deposition which contains no diluent. However, as a practical matter, in order to reduce the rate of deposition to a practical value, it is not ordinarily desirable to use a gas for deposition more than 50 per cent of which is made up of the carbon-containing gas, the remainder being the diluent and boron-containing gas. Similarly, it is not ordinarily desirable that the carbon-containing gas constitute less than 5 per cent of the total gas and it is preferable that it constitute at least 10 per cent of the total gas.

Deposition proceeds more readily in the presence of halogens, free or chemically combined, and it is therefore desirable, but not necessary, that chlorine, bromine or iodine be present in the depositing gas. The halogen may be present in the boron-containing gas, as when boron trichloride or phenyl dichloro borine is used, or in the carbon-containing gas, as when carbontetrachloride is used, or it may be present as a part of the diluent gas.

As indicated above, to obtain temperature coefficients below 100 P. P. M./° C., the deposition temperature should not be below 1000° C. and preferably not below 1100° C. The most suitable temperature of deposition is 1200° C. Higher temperatures may be used but it is not ordinarily feasible to operate at temperatures substantially above 1250° C. or 1300° C. since at these higher temperatures most of the available suitable resistor bases become chemically or physically unstable and since the design of furnaces to operate at these higher temperatures becomes increasingly difficult. However, with resistor bases and furnaces capable of withstanding the higher temperatures, these temperatures up to perhaps 1400° C. can be employed and will yield resistors of low temperature coefficients.

Where resistors of high resistance values are desired and low temperature coefficients are not so important, lower deposition temperatures may be used. It is necessary only that this temperature be sufficient to cause a deposit to be formed. The boron compound has a catalytic effect on the deposition and it is possible to obtain a deposit at even lower temperatures than in ordinary carbon deposition. Ordinarily temperatures lower than 900° C. or 950° C. will not be used but it is possible with proper choice of carbonaceous gas to obtain deposits at temperatures as low as 650° C.

The invention has been described in terms of its specific embodiments and, since certain modifications and equivalents may be apparent to those skilled in the art, this description is intended to be illustrative of and not necessarily to constitute a limitation upon the scope of the invention.

What is claimed is:

1. An electrical resistor having a temperature coefficient of resistance not greater than 150 parts per million per degree centigrade comprising a ceramic core having on its surface an adherent, continuous, homogeneous film of carbon containing between 0.35 per cent and 20 per cent by weight of boron, deposited at a temperature between 1000° C. and 1300° C. from a gas

containing boron in the form of a compound selected from the group consisting of boron hydrides, boron halides and boron hydrohalides and carbon in the form of a compound selected from the group consisting of hydrocarbons and halogenated hydrocarbons.

2. An electrical resistor having a temperature coefficient of resistance not greater than 100 parts per million per degree centigrade comprising a ceramic core having on its surface an adherent, continuous, homogeneous film of carbon containing between 0.5 per cent and 10 per cent by weight of boron, deposited at a temperature between 1000° C. and 1300° C. from a gas containing carbon in the form of methane and boron in the form of boron trichloride.

3. A resistor as described in claim 2 wherein the resistance of the film per unit square is not greater than 500 ohms.

4. A resistor as described in claim 2 wherein the boron content is between 1 per cent and 6 per cent and the temperature of deposition is between 1100° C. and 1300° C.

5. A resistor as described in claim 2 wherein the boron content is between 3 per cent and 4 per cent and the temperature of deposition is about 1200° C.

6. An electrical resistor comprising a non-conducting base having thereon a film having a resistance greater than 10,000 ohms per unit square and formed of carbon containing between 18 per cent and 50 per cent boron, said film having been deposited at a temperature between 650° C. and 1300° C. from a gas containing boron in the form of a compound selected from the group consisting of boron hydrides, boron halides and boron hydrohalides and carbon in the form of a compound selected from the group consisting of hydrocarbons and halogenated hydrocarbons.

7. A process of forming electrical resistors comprising heating a plurality of ceramic bodies in a closed rotatable container partially filled with granules of a hard inert material, continuously passing therethrough a dry, oxygen-free gas containing carbon in the form of a hydrocarbon and boron in the form of a halogenated borine, maintaining the temperature within said container at between 1000° C. and 1300° C. and continuously rotating said container, the boron and carbon in said gas being so proportioned that a deposit of carbon is formed on said ceramic bodies which contains between 0.5 per cent and 10 per cent boron by weight.

8. The process of forming an electrical resistor comprising passing a dry, oxygen-free gas consisting of hydrogen, hydrocarbon and boron halide over the surface of a non-conductive refractory base maintained at a temperature between 1100° C. and 1250° C. until a deposit of carbon and boron is formed on said surface, the hydrocarbon constituting between 5 per cent and 50 per cent of said gas, the boron halide being present in a proportion relative to said hydrocarbon such that the said deposit contains between .35 per cent and 20 per cent boron by weight.

9. An electrical resistor having a temperature coefficient of resistance not greater than 100 parts per million per degree centigrade comprising a ceramic core having on its surface an adherent, continuous, homogeneous film of carbon containing between .5 per cent and 10 per cent by weight of boron deposited from the gaseous mixture of a hydrocarbon and a boron

halide at a temperature between 1000° C. and 1300° C.

10. The process of forming an electrical resistor comprising passing a dry, oxygen-free gas containing carbon in the form of methane and boron in the form of boron trichloride over the surface of a ceramic base maintained at a temperature between 1000° C. and 1300° C. until a deposit of carbon and boron is formed on said surface, the boron trichloride being present in a proportion relative to the methane such that the said deposit contains between 1 per cent and 6 per cent boron by weight.

11. A process as defined in claim 10 wherein the methane and boron trichloride are so proportioned that the boron content of the deposited film is between 3 per cent and 4 per cent.

12. The process of forming electrical resistors comprising heating a body of non-conducting, refractory material in a furnace, continuously passing through the furnace a dry, oxygen-free gas containing carbon in the form of a compound selected from the group consisting of hydrocarbons and halogenated hydrocarbons and containing boron in the form of a compound selected from the group consisting of boron hydrides, boron halides and boron hydrohalides and maintaining the temperature in said furnace between 900° C. and 1300° C., the boron-containing and carbon-containing constituents of said gas being so proportioned that the deposit contains between .35 per cent and 50 per cent boron by weight.

13. The process as defined in claim 12 wherein the chemically-combined carbon in the gas is present in the form of a hydrocarbon and the chemically-combined boron in the gas is present in the form of boron trichloride.

14. The process as defined in claim 13 wherein the hydrocarbon is methane.

15. An electrical resistor comprising a refractory, non-conducting base having on its surface an adherent, continuous film of carbon containing between 0.35 per cent and 50 per cent by weight of boron deposited from a gas containing chemically-combined carbon and chemically-combined boron, the chemically-combined carbon being present in said gas in the form of a hydrocarbon and the chemically-combined boron being present in said gas in the form of boron trichloride.

16. The process of forming electrical resistors comprising heating a body of non-conducting, refractory material in a furnace, continuously passing through the furnace a dry, oxygen-free gas containing chemically-combined carbon and chemically-combined boron in the form of a borine partially substituted with hydrocarbon radicals and partially substituted with a halogen, and maintaining the temperature in said furnace between 650° C. and 1300° C., said boron and carbon being so proportioned in said gas that a deposit of carbon is formed on said body which contains between 0.35 per cent and 50 per cent boron by weight.

17. The process of forming electrical resistors comprising heating a body of non-conducting, refractory material in a furnace, continuously passing through the furnace a dry, oxygen-free gas containing chemically-combined carbon and chemically-combined boron in the form of a borine substituted with hydrocarbon radicals, and maintaining the temperature in said furnace between 650° C. and 1300° C., said boron and carbon being so proportioned in said gas

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that a deposit of carbon is formed on said body which contains between 0.35 per cent and 50 per cent boron by weight.

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