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CARBON DEPOSITED RESISTOR AND METHOD OF MAKING THE SAME

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Fig. 1.

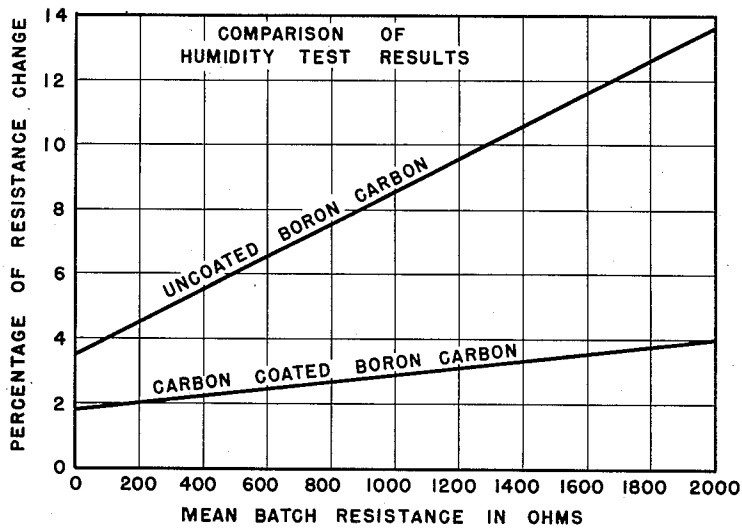
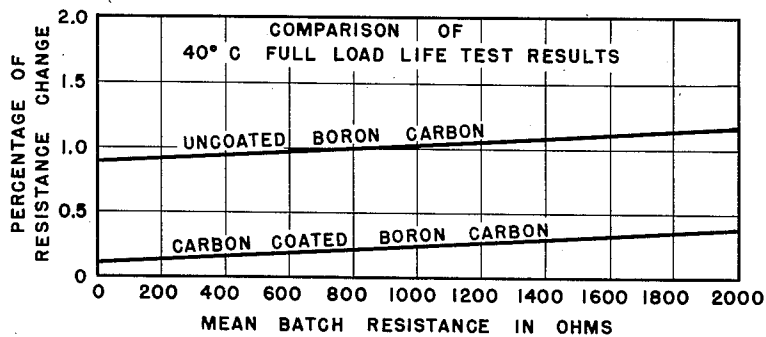


Fig. 2.



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CARBON DEPOSITED RESISTOR AND METHOD OF MAKING THE SAME

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6 Claims. (Cl. 117—216)

This invention relates to electrical resistors of the carbon deposited type and, more particularly to the boron-carbon type. A method of manufacturing such resistors is described in the pending application of George W. Ziegler, Jr., and Stuart L. Parsons, Serial No. 300,992, filed July 25, 1952, and now abandoned, hereinafter referred to as the "Ziegler et al. application." This invention relates to an improvement in such resistors and to a method of producing them.

For many years, the art of manufacturing resistances of the carbon deposited type has been well known. Generally speaking, such resistors are produced by pyrolysis of a hydrocarbon gas to deposit a carbon coating on ceramic substrates or blanks, this being accomplished by heating the blanks in a furnace to proper temperature in the presence of a hydrocarbon gas. This deposits a hard, impervious coating of carbon on the blank which thus has many desirable attributes for use as a stable electrical resistance. This process of depositing a resistance coating on a ceramic blank by pyrolysis is herein broadly referred to as "pyrolytic deposition." While carbon deposited resistors have many desirable characteristics they suffer from one basic deficiency, i. e., an unusually high temperature coefficient of resistance. The invention disclosed in the above Ziegler et al. application deals with a method of eliminating this deficiency by introducing a boron containing gas along with the hydrocarbon gas in certain proportions and by pyrolysis depositing a carbonaceous coating on the blank or substrate; the composition of such coating thus includes boron or a compound thereof with the carbon. For example, methane and boron trichloride may be heated in a furnace to deposit such a coating on substrates. The details of this process are fully explained in the above Ziegler et al. application and resistors of this type are herein referred to as "boron-carbon resistors."

Boron-carbon resistors are superior to carbon deposited resistors in that the temperature coefficient of resistance is markedly lower. However, they are inferior to carbon deposited resistors in two important respects: (a) they are not as stable in the presence of humidity, and (b) their resistance value changes excessively when a full rated load is applied thereto for long periods of time.

The foundation of carbon deposited and boron-carbon resistors is a substrate or blank, usually a ceramic, coated with a carbonaceous material by pyrolytic deposition. The blanks are usually cylindrical though not necessarily so and after coating a spiral path may be cut therein to increase the length of resistance path. The ends of the coated blank are then coated with silver or a like conductor, capped with terminals, and one or more outside coatings of dielectric material resistant to weather and other conditions of use is applied.

We have found that boron-carbon resistors produced by pyrolytic deposition as described above to lower materially the temperature coefficient of resistance, may be greatly improved by pyrolytic deposition of a layer or coating of carbon on the boron-carbon coating. Not

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only is the boron-carbon coating's temperature coefficient of resistance maintained in this manner, but such coefficient is often further reduced. Further, resistors so coated are more stable under adverse humidity conditions and have a much greater load life stability. In fact, these unexpected results forthcoming from this deposited carbon coating are of great importance in the art of making this type of resistance unit as will be pointed out in detail hereinafter.

The invention accordingly consists in the features of construction, combinations of elements, arrangements of parts and in the several steps and relation and order of each of the same of one or more of the others, all as will be illustratively described herein, and the scope of the application of which will be indicated in the following claims.

In the drawing,

Figure 1 graphically illustrates a comparison of the effect of certain humidity tests on the resistance values of uncoated boron-carbon resistors and carbon coated boron-carbon resistors;

Figure 2 graphically illustrates the effect of certain load life tests on the resistance values of uncoated boron-carbon resistors and carbon coated boron-carbon resistors.

The method of making boron-carbon resistors which are to be coated with deposited carbon in accordance with this invention may correspond to that of the above Ziegler et al. application. For example, ceramic substrates or blanks, preferably cylindrical in shape, are placed in a slowly rotating flask and heated while desired gases are introduced for pyrolytic deposition thereon. More particularly, air is first introduced to burn out all impurities after which the flask is flushed with an inert gas. Finally, a gaseous mixture which is preferably a large volume of nitrogen or other suitable inert gas accompanied by a hydrocarbon gas such as methane and a boron containing gas such as boron trichloride is introduced at a temperature suitable for proper pyrolysis, preferably in the range of 1850° F. and 2100° F. depending upon the type of ceramic employed and other factors. The final step of carbon deposition now takes place. A hydrocarbon such as methane with a large volume of nitrogen or other inert gas is again introduced into the flask at a temperature suitable for pyrolytically depositing a coating of pure carbon over the boron-carbon coating. The flask is next flushed with nitrogen and allowed to cool and the substrates or blanks so coated are assembled into completed resistance units in the manner described above. If desired, a layer of carbon may be pyrolytically deposited on the ceramic first and next the layer of boron-carbon deposited thereover; finally an outer layer of pure carbon is deposited on the boron-carbon coating, thus sandwiching the boron-carbon coating between two layers of carbon. We have also found that desirable results may be obtained by using a plurality of the layers of boron-carbon and pure carbon, i. e., superimposed pairs of layers with or without a base coating of carbon.

As noted above, these boron-carbon resistors coated with deposited carbon are far more stable than boron-carbon resistors without such coating under humidity tests. Such a humidity test on the two types of units was conducted and is graphically illustrated in Figure 1:

(1) Several batches of boron-carbon resistors having the resistance values indicated on the abscissa of Figure 1 were selected together with several batches of boron-carbon resistors having a deposited carbon coating but having similar resistance values. All of these resistance units were measured for resistance value under normal room temperature and humidity conditions.

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(2) All of the units were then placed in an atmosphere of $66^{\circ} \pm 3^{\circ}$ C. and 100% relative humidity for 125 hours ± 5 hours.

(3) The units were then dried for one hour at $40^{\circ} \pm 5^{\circ}$ C. and cooled to room temperature. Within thirty to sixty minutes after removal from the drying oven, resistance values of all the units were again measured.

(4) The changes in resistance were converted into percentages which percentages were graphically plotted in Figure 1.

It can be seen from a study of Figure 1 that the uncoated boron-carbon resistors changed in resistance value much more markedly than was the case with the units having the deposited carbon coating.

As previously noted, boron-carbon resistors coated with deposited carbon remain more stable throughout their load life than is the case with uncoated resistors. This is indicated by full load life tests such as graphically illustrated in Figure 2 where,

(1) Several batches of boron-carbon resistors having the resistance values indicated on the abscissa of Figure 2 were selected together with several batches of boron-carbon resistors having a deposited carbon coating but having similar resistance values. All of these resistance units were measured for resistance value under normal room temperature and humidity conditions.

(2) The units were placed in an oven at 40° C. and current passed therethrough to produce full rated load. The units here tested were rated at $\frac{1}{2}$ watt. Such full load was applied for 1.5 hours followed by .5 hour of no load, the cycle being repeated for 500 hours.

(3) After cooling to room temperature, the resistances of the units were again measured.

(4) The changes in resistance were converted into percentages which percentages were graphically plotted in Figure 2.

An analysis of Figure 2 indicates that the carbon coated boron-carbon resistors are much more stable throughout a substantial resistance range than is the case with the uncoated boron-carbon resistors. This test is of particular significance because resistances in many modern electronic circuits are required to operate for substantial periods of time and variation of resistance value is increasingly harmful to over-all efficiency as such circuits become increasingly complex.

We have also discovered that a given resistance value may be reached more quickly, i. e., with less pyrolytic deposition time, by first coating the substrate with boron-carbon and then depositing a coating of carbon thereon rather than depositing boron-carbon alone until the desired resistance value is achieved. Obviously, deposition time is an important factor in achieving economies in manufacture.

We have thus provided a new resistance unit of the deposited carbon type which is markedly superior to the old units made by pyrolytic deposition of pure carbon, and superior in important respects to the boron-carbon type of unit. Yet, the particular advantage of the boron-carbon type (a low temperature coefficient of resistance) is maintained, and deposition time is greatly reduced.

As many possible embodiments may be made of the above invention and as the art herein described might be varied without departing from the scope of the inven-

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tion, it is to be understood that all matter hereinabove set forth or shown in the accompanying drawings is to be interpreted as illustrative and not in a limiting sense.

I claim:

1. In a resistor construction the combination of a ceramic substrate, a coating of boron-carbon pyrolytically deposited thereon, and a coating of pure carbon pyrolytically deposited on said boron-carbon coating.

2. In a resistor construction the combination of a ceramic substrate, a coating of pure carbon pyrolytically deposited thereon, a coating of boron-carbon pyrolytically deposited on said pure carbon coating, and a coating of carbon pyrolytically deposited on said boron-carbon coating.

3. In a process for the production of resistors by pyrolytic deposition in which blanks are heated in the presence of a gaseous atmosphere, the steps of heating the blanks in the presence of hydrocarbon and boron gases to deposit by pyrolysis a coating of boron-carbon thereon, and thereafter heating the blanks in the presence of a hydrocarbon gas to deposit by pyrolysis a coating of pure carbon on said boron-carbon coating.

4. In a process for the production of resistors by pyrolytic deposition in which blanks are heated in a furnace in the presence of a gaseous atmosphere, the steps of introducing methane and boron trichloride into said furnace while heating the same at or above the temperature required to deposit by pyrolysis a boron-carbon coating on said blanks and stopping the boron trichloride so that methane is introduced at or above the temperature required to deposit by pyrolysis a pure carbon coating overlying said boron-carbon coating.

5. In a process for the production of resistors by pyrolytic deposition in which blanks are heated in a furnace in the presence of a gaseous atmosphere, the steps of heating the blanks in the presence of hydrocarbon and boron-containing gases mixed with an inert gas to deposit a coating of boron-carbon thereon by pyrolysis, and thereafter heating the blanks in the presence of a hydrocarbon gas mixed with an inert gas to deposit a coating of pure carbon on said boron-carbon coating by pyrolysis.

6. In a process for the production of resistors by pyrolytic deposition in which blanks are heated in the presence of a gaseous atmosphere, the steps of heating the blanks in the presence of a hydrocarbon gas to deposit a coating of pure carbon by pyrolysis on the blanks, heating the blanks in the presence of hydrocarbon and boron gases to deposit by pyrolysis a coating of boron-carbon on said carbon coating, and thereafter heating the blanks in the presence of a hydrocarbon gas to deposit by pyrolysis a coating of pure carbon on said boron-carbon coating.

References Cited in the file of this patent

UNITED STATES PATENTS

1,019,391	Weintraub	Mar. 5, 1912
2,671,735	Grisdale et al.	Mar. 9, 1954

OTHER REFERENCES

Ginsdale et al.: Bell System Tech. Jour., vol. 30, April 1951, pages 271-314.