Jan. 22, 1963 K. GENTNER 3,074,817

PYROLYTICALLY DECOMPOSED RESISTOR CONSISTING OF THE ELEMENTS CARBON, OXYGEN AND SILICON

Filed April 26, 1957

Fig. 1

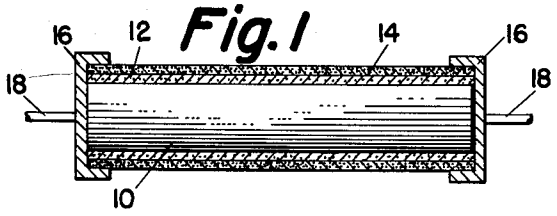


Fig. 2

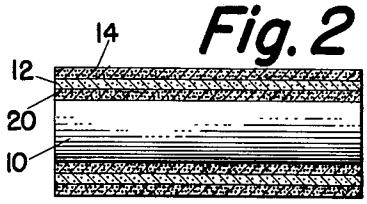


Fig. 3

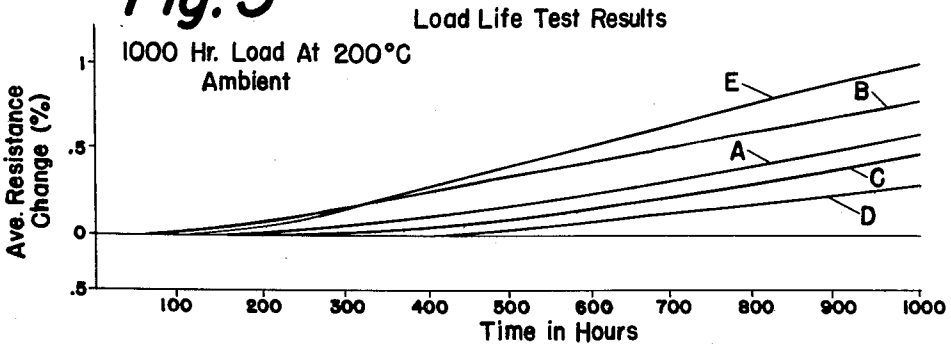


Fig. 4

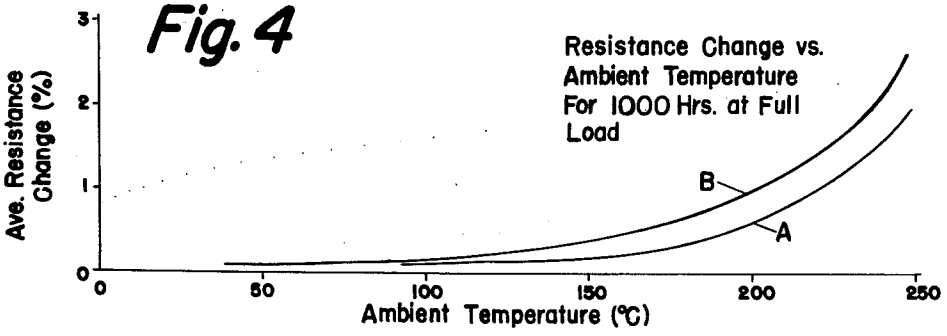
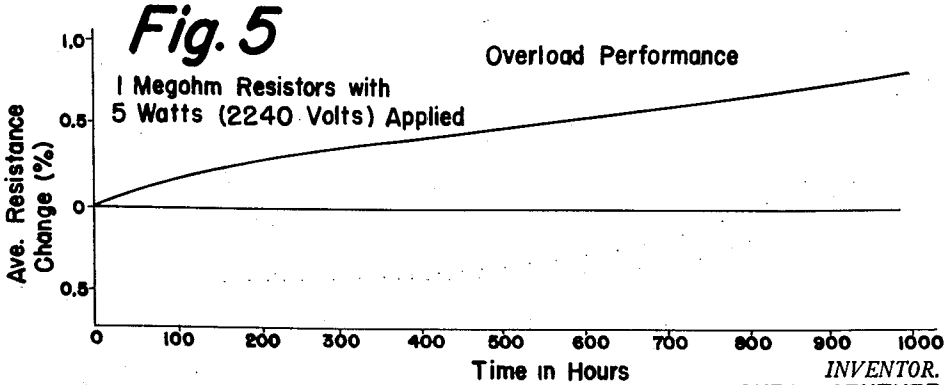


Fig. 5



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PYROLYTICALLY DECOMPOSED RESISTOR CONSISTING OF THE ELEMENTS CARBON, OXYGEN AND SILICON

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2 Claims. (Cl. 117—216)

This invention relates to a pyrolytically deposited carbon film resistor which can be made to high resistance values and having improved performance characteristics.

Presently, carbon film resistors are formed by either pyrolytically depositing the carbon from a gas onto a ceramic base or by coating an insulating base with a mixture of carbon particles in an insulating binder. These methods have been used for a long period of years, during which time various methods and techniques have been developed to improve the processes as well as the final product, and the advantages of each type of resistor formed thereby are well known. However, there still remains many inherent deficiencies in both types of resistors.

In the pyrolytically deposited carbon film, the resistivity of the film is constant so that for a given area of film the only way of varying the resistance is by varying the thickness of the film. However, as the film thickness is decreased to increase the resistance, the film becomes less stable, i.e. subject to greater changes in value under operating conditions. Thus, for a given area of film, the resistance value obtainable in a stable film is limited. Furthermore, this type of film is unstable at high temperatures. This is partially caused by the fact that at high temperatures the carbon oxidizes and goes off as a gas. Although in the type of resistor having a resistance film composed of a mixture of carbon particles in an insulating binder higher resistance values per unit area can be obtained than with a pyrolytically deposited carbon film, this type of resistor is also unstable at high temperatures. In fact, the normal operating characteristics of this resistor are not as good as those of the pyrolytically deposited carbon resistor.

It is therefore an object of this invention to provide a stable high resistance value pyrolytically deposited carbon type film resistor and the method of making the same. It is another object of this invention to provide a pyrolytically deposited carbon type resistor which is stable at high temperatures. It is still another object of this invention to provide a pyrolytically deposited carbon type resistor having improved performance characteristics. Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others, and the article possessing the features, properties and the relation of elements, which are exemplified in the following detailed disclosure and the scope of the invention will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawings, in which:

FIGURE 1 is a cross-sectional view of the resistor of this invention;

FIGURE 2 is a cross-sectional view of a modification of the resistor;

FIGURE 3 graphically illustrates the load life characteristics of the resistor of this invention;

FIGURE 4 graphically illustrates the stability of the resistor with respect to temperature and under a load; and

FIGURE 5 graphically illustrates the overload characteristics of the resistor.

In general, the invention resides in a resistance film composed of the elements carbon and silicon, individually and possibly in combination, and oxygen in the form of oxides of the other constituents. By varying the ratio of these elements in the film, the resistance value as well as other operating characteristics of the film can be varied. For example, by increasing the percentage of carbon in the film, the resistance value will be lowered. By decreasing the percentage of carbon or by increasing the percentage of the oxides, the resistance of the film will be increased. Therefore, the resistivity, resistance per unit area, is no longer dependent on the thickness of the film but is varied by the composition of the film so that high resistance films can be obtained with the thicker and more stable films. By increasing the percentage of the oxides in the film, not only does the resistance of the film increase but a harder film is obtained which will withstand physical abuse without affecting the resistance of the film. In addition, the film becomes much more stable with respect to high temperature, moisture and the electrical load applied to the film. By using multiple layers of this film, each having various ratios of the three elements, a resistor can be provided having one layer which provides the desired resistance value and which is covered by another layer which provides a hard durable surface which is substantially unaffected by high temperatures, moisture and high electrical loading of the resistor.

Referring to FIGURE 1 of the drawing, the resistor comprises a non-conducting base 10, commonly formed of a ceramic of the type described in United States patent to M. D. Rigterink, No. 2,386,633, issued October 9, 1945. A resistance layer 12 of the film composed of the elements carbon, silicon and oxygen is deposited on the surface of base 10 and contains a sufficient amount of carbon, percentage-wise, to provide the desired resistance value. A second layer 14 of the film composed of the elements carbon, silicon and oxygen but having a much higher percentage content of oxygen than the resistance layer 12 is deposited over resistance layer 12. Although the resistor can be terminated by any of the well-known methods, the terminals are shown to be in the form of metal caps 16 fitting over the ends of base 10 and contacting second layer 14 with lead wires 18 extending from the caps 16. This construction provides a resistor whose resistance value can be varied by varying the percentage of carbon in the resistance layer 12 so that high resistance values can be obtained with a relatively thick, stable film. In addition, the second layer 14 which has a high content of oxygen provides the resistor with a hard durable film which is very stable with respect to high temperatures and the electrical load applied to the resistor.

One method of testing the stability of a resistor with regard to temperature and the load applied to the resistor is known as the "load life" test and comprises heating the resistor to a known temperature and applying the load to the resistor which is maintained over a long period of time. The less the resistor changes in value during this test the more stable it is. FIGURE 3 shows the results of a load life test run on a group of resistors of this invention of various sizes and resistance values. The test was run on a group of resistors of this invention of various sizes and resistance values. The test was run at an ambient temperature of 200° C. for a period of 1,000 hours with the resistors for curves A and B being at their full rated load and the resistors for curves C, D and E being at their full rated voltage. As can be seen from FIGURE 3, the resistance change for these resistors was within approximately 1% of their original value after 1,000 hours. These results compare favorably with the results of "load life" tests made on pure deposited carbon resistors which are usually made at temperatures of 40° C. or 70° C. When the pure deposited carbon resistor was tested at a

higher temperature, 115° C., it was found that the resistor changed in value approximately 10%. FIGURE 4 shows the effect of temperature on the resistance value of the resistors of this invention when placed under a load. Curve A is for a group of the resistors of this invention which was placed under full rated load and curve B is for another group of resistors which was placed under full rated voltage. It can be seen from these curves that at the temperatures at which the pure deposited carbon resistor is normally tested, 40° C. and 70° C., the change in resistance was substantially negligible and even at the temperature of 250° C. the change in resistance was less than 3%. FIGURE 5 shows the effect of overloading the resistor of this invention. For this test, a resistor of a size which, for a pure deposited carbon resistor would be rated at 2 watts, was placed under a load of 5 watts. After 1,000 hours under this overload, it was found that the resistance value changed less than 1%. To test the physical durability of the film of this invention, the film was exposed to the flame of an oxygen torch until the film turned white hot and then was allowed to cool. Although the resistance value of the film changed from 10% to 20% there was no physical effect on the film. When a pure deposited carbon film was tested in the same manner, the film completely disappeared in the matter of a few seconds. Thus these tests shown that the film of this invention provides a resistor which has greater physical durability and is electrically more stable with respect to temperature and the electrical load placed on the film than other types of carbon film resistors. In addition, there is provided a resistor for use under high loads which is smaller in size than other types of carbon film resistors adapted to be used under such loads.

To form the resistor shown in FIGURE 1, the ceramic base **10** is placed in a sealed chamber having a gas inlet duct at one end and a gas outlet duct at the opposite end. The chamber is then placed under a vacuum by exhausting the chamber through the outlet duct. A gas or mixture of gases containing the elements carbon, silicon and oxygen is admitted into the chamber to flow around the base. Prior to the admission of the gas, the chamber is heated to the decomposition temperature of the gas so that, as the gas passes around the base **10**, it is decomposed to deposit a film containing the elements carbon, silicon and oxygen on the surface of the base. The gas first admitted to the chamber contains a high ratio of carbon so that the resistance film **12** is deposited on the base. When a resistance film **12** of the desired thickness has been deposited, the ratio of the elements in the gas is changed in a manner as will be explained later to provide a gas having a high percentage content of oxygen. This gas is then decomposed to provide the outer layer **14**.

The gas may be composed of a single compound containing the elements carbon, silicon and oxygen or a mixture of two or three compounds and may be obtained originally in a gaseous state or as the vapors of a liquid or solid. The carbon containing compound may be selected from various hydrocarbons, both aliphatic and aromatic, alcohols, both aliphatic and aromatic, aldehydes, ketones, organic acids, both aliphatic and aromatic, ethers, esters and nitro, sulfo and halogenated derivatives of these compounds. The silicon containing material may be selected from various halides, hydrides, alkyls and aryls of silicon, halogenated hydrides, alkyls and aryls of silicon, silicals, siloxanes, as well as amino-, oxy-, or sulfo-derivatives of these compounds. The oxygen containing material may be selected from water, alcohols, aldehydes, ketones, organic acids and mixtures of these materials. The factors for choosing the particular compound, or compounds, to be used are (1) the ease of obtaining the compound in its gaseous state, (2) that the compound can be decomposed at a reasonable temperature, and (3) that the material can be easily used without excessive danger. Some examples of various gases which can be used are as follows:

(I) Three compound systems:
Silicon tetrachloride, Mesitylene and a mixture of water and methyl alcohol.
Heptane and a mixture of propyl alcohol and water.

(II) Two compound systems:
Trimethylchlorosilane and acetone.
Silicon tetrachloride and a mixture of propyl alcohol and water.

(III) Single compound system:
Hexamethyldisiloxane.
Methyltriethoxysilane.

The starting gas or gaseous mixture, should be selected to provide the desired resistance layer **12**. The particular starting gas may be changed to provide the outer layer **14** by adding or increasing the amount of water vapor or in the case of the two or three compound systems, by decreasing the amount of the carbon containing compound.

The temperature to which the chamber is heated depends on the decomposition temperature of the particular gas or gaseous mixture being used and can be easily obtained by one skilled in the art from the literature or experimentally. However, it has been found that the temperature will range between 1400° F. and 2000° F. for most gases, particularly those previously described. The chamber is maintained under a vacuum during the deposition process to remove undesirable reaction products so as to obtain an uncontaminated film as well as to control the rate of flow of the gas into the chamber. Preferably, the vacuum is between .01 and 10 millimeters of mercury, depending on the desired rate of flow of the gas into the chamber.

FIGURE 2 shows a modification of the resistor in which, in addition to the resistance layer **12** and the outer layer **14**, an under layer **20** is deposited on the surface of the body **10** beneath the resistance layer **12**. The under layer **20** is also composed of the elements carbon, silicon and oxygen and, like the outer layer **14**, has a higher percentage content of oxygen. It is well known in the art of pyrolytic deposition from a gas that the material upon which the deposition is made may have a catalytic affect on the rate of deposition and different materials affect the reaction differently. The ceramic materials usually used as the body **10** for making resistors are composed of a mixture of materials which are exposed non-uniformly along the surface of the body. Since certain of these materials have a greater affect on the rate of deposition than the others, the film deposited on the surface of the body is thicker at the points where these materials are exposed so that the film is not of uniform thickness over the entire surface of the body. By first depositing the layer **20** on the surface of the base **10**, there is provided a layer of more uniform composition on which the resistance layer **12** is deposited. Thus the resistance layer **12** will be of more uniform thickness to provide a resistance unit having improved operating characteristics. This resistor is made in the same manner as previously described except that the gas first admitted to the chamber has a high percentage content of oxygen. Once the under layer **14** is deposited, the gas is changed to contain the proper amount of carbon to provide the resistance layer **12** and then changed again to contain a high percentage of oxygen to deposit the outer layer **14**.

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained and, since certain changes may be made in carrying out the above method (process) and in the article set forth without departing from the scope of the invention, it is intended that all matter contained in the above description or shown in the accompanying drawing, shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims

are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

Having described my invention, what I claim as new and desire to secure by Letters Patent is:

1. An electrical resistor formed by pyrolytically decomposing over a non-conductive base an atmosphere containing the elements carbon, silicon and oxygen, and depositing on the base a resistance film consisting essentially of the elements carbon, silicon and oxygen with the content of carbon in said resistance film being sufficient to provide a desired resistance value, and then pyrolytically decomposing over said resistance film a second atmosphere containing the elements carbon, silicon and oxygen with the percentage content of the oxygen in said second atmosphere being greater than that in said first atmosphere, and depositing on said resistance film a second film consisting essentially of the elements carbon, silicon and oxygen with the percentage content of oxides in said second film being greater than that in said first resistance film.

2. An electrical resistor formed in accordance with claim 1 in which prior to pyrolytically decomposing the first atmosphere to deposit the first resistance film a third atmosphere containing the elements carbon, silicon and oxygen with the percentage content of oxygen in said third atmosphere being greater than that in the first atmosphere is pyrolytically decomposed over the base and a third film consisting essentially of the elements carbon, silicon and oxygen is deposited on said base with the percentage content of oxides in the third film being greater than that in the first resistance film.

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