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Bennett et al.

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[54] CONTROL OF RATE OF CHANGE OF RESISTANCE AS A FUNCTION OF TEMPERATURE IN MANUFACTURE OF RESISTANCE ELEMENTS

[75] Inventors: **Kenneth R. Bennett**, San Diego; **Joseph W. Crownover**, La Jolla, both of Calif.

[73] Assignee: **GTI Corporation**, Pittsburgh, Pa.

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[52] U.S. Cl. .... **29/620**, 29/612, 117/201, 219/121 LM

[51] Int. Cl. **H01c 7/00**, H01c 17/00

[58] **Field of Search** .... 29/620, 621, 613, 612; 117/201; 219/121 L, 121 LM

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Primary Examiner—Charles W. Lanham
Assistant Examiner—Victor A. DiPalma
Attorney, Agent, or Firm—Smyth, Roston & Pavitt

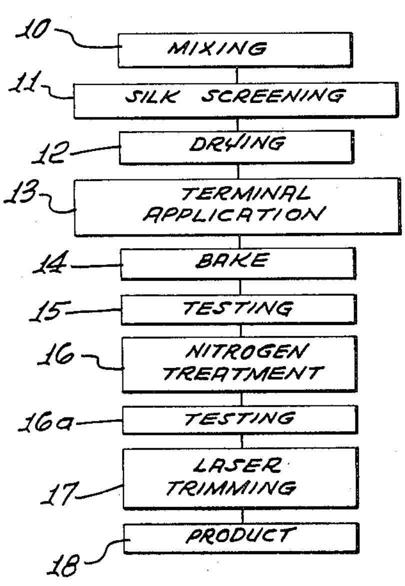
[57] **ABSTRACT**

The method of improving the properties of a film type electrical resistance element having a characteristic rate of change of resistance as a function of temperature change, within a selected temperature range, the steps that include

a. heating said element while exposed to a gaseous medium containing nitrogen in sufficient concentration to reduce said rate, and

b. thereafter impinging laser radiation on the resistance element to controllably alter the resistance level thereof, at temperatures within said selected temperature range.

12 Claims, 7 Drawing Figures



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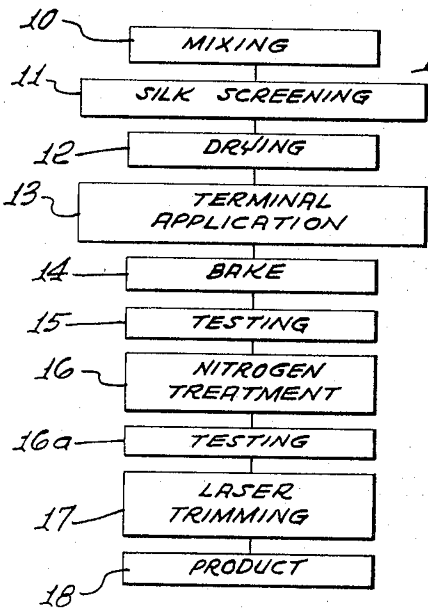


FIG. 1.

FIG. 2.

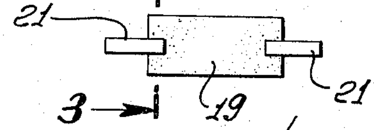


FIG. 3.

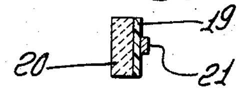
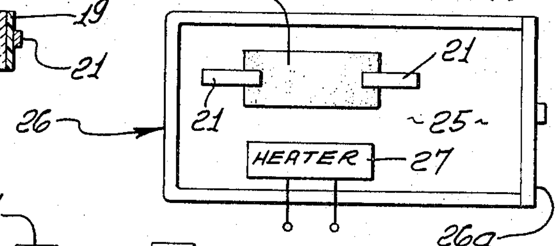


FIG. 4.



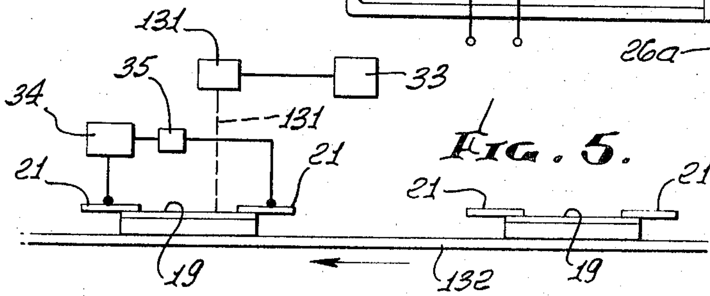


FIG. 5.

FIG. 6.

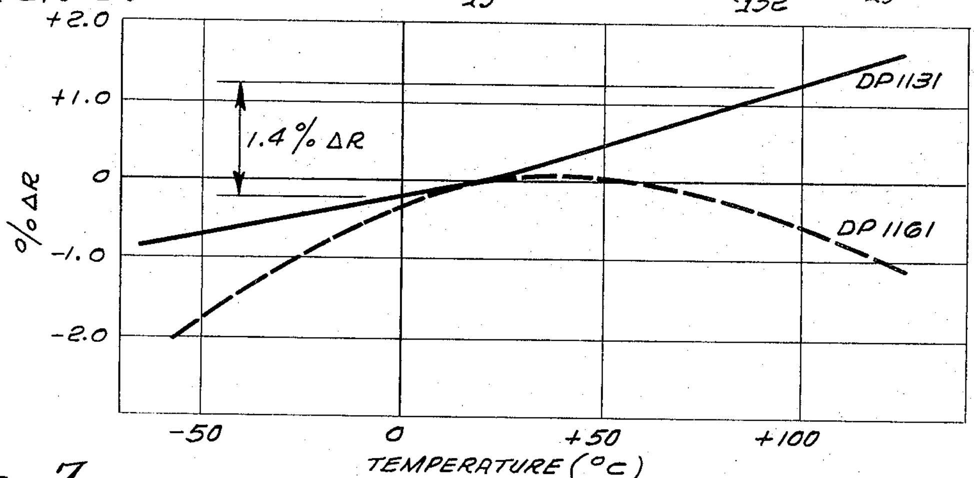
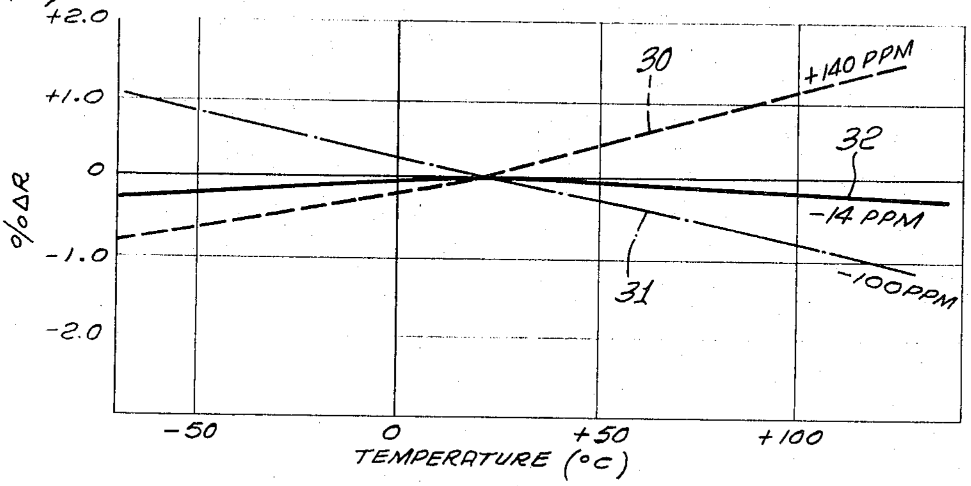


FIG. 7.



CONTROL OF RATE OF CHANGE OF RESISTANCE AS A FUNCTION OF TEMPERATURE IN MANUFACTURE OF RESISTANCE ELEMENTS

BACKGROUND OF THE INVENTION

This invention relates generally to controlling the temperature stability of resistance elements, and more particularly concerns reducing the parts per million change in resistance per degeree Centigrade change in temperature of film glaze resistor elements.

Recently, so called film glaze resistance elements have been developed for use in micro-electronics applications. These glaze resistor materials typically consist of mixtures of particular oxides of noble metals and glass frit, disbursed in a suitable resin base. The resistors are commonly formed by silk screening a paste or paint form of the resistor material onto a ceramic substrate (for example barium titanate), and thereafter baking the film material on the ceramic chip at a temperature between 400° and 800°C.

While the completed resistors compare favorably with so-called "wire-wound" resistors in certain respects, they do not exhibit the very low temperature stability found with wire-wound resistors. The latter, of course, are not generally suited to micro-electronics applications due to their undesirably large size.

SUMMARY OF THE INVENTION

It is a major object of the invention to control the temperature stability of glaze film resistor elements so as to achieve stabilities comparing favorably with those of wire-wound resistors. Such film materials typically consist of a noble metal oxide in glassy state.

Basically, the method of the invention involves heating the film form resistance element at relatively high temperature and while exposed to a gaseous environment containing nitrogen in greater percentage concentration than is found in air, and continuing such heating for a time interval to significantly reduce the rate of change of resistance of the element as a function of temperature change. Typically, the gas, which may consist of a mixture of air and nitrogen, is maintained at a temperature of between 650°C and 750°C and in contact with the resistor film during the heating interval. The percentage of nitrogen in the mixture may be selected to produce a parts per million change in resistance per degree Centigrade change in temperature of about 10, as will be seen.

Additional objects include the encapsulation and laser trimming of the treated resistance element, in the manner to be described, so as to provide the container with an extremely accurate resistor exhibiting a high degree of temperature stability, for use in micro-electronic circuitry.

These and other objects and advantages of the invention, as well as the details of an illustrative embodiment, will be more fully understood from the following description and drawings, in which:

DRAWING DESCRIPTION

FIG. **1** is a flow chart;

FIG. **2** is a plan view of a resistor element;

FIG. **3** is a section on lines **3—3** of FIG. **2**;

FIG. **4** is an elevation showing heating of the resistance film, in a nitrogen environment;

FIG. **5** is an elevation showing laser trimming of the FIG. **2** resistance element after encapsulation;

FIG. **6** is a graph; and

FIG. **7** is a graph.

DETAILED DESCRIPTION

Temperature stability of resistors, generally expressed as the number of parts per million change in resistance per degree Centigrade change in temperature, can be mathematically expressed as follows:

$$PPM = \Delta R \times 10^6 / R\Delta C \tag{1}$$

where:

R = resistance

ΔR = change in resistance

ΔC = change in temperature expressed in degrees Centigrade.

Heretofore, the temperature stability of glaze film resistors exhibited rather wide tolerance levels, as for example is represented in FIG. **6.** Thus, the material DP **1131** exhibits a PPM slope of:

$$(14) \times 10^6/1{,}000\ (100) = +140$$

Characteristically, such resistors are produced by mixing between 20 and 60 weight parts of noble metal oxide particulate with between 4 and 20 weight parts of glass frit, adding between 50 and 60 weight parts of a liquid resin (as for example acryloid) and silk screening the mixture onto a ceramic substrate or chip. Suitable noble metals and oxides include Ruthenium, Ruthenium silver, and Palladium silver paste of a particle size 0.3μ; the glass frit may consist of lead borosilicate glass of a particle size 5μ; and the chip may consist of barium titanate ceramic material. Commercial pastes and inks of this variety include Du Pont "Berox," Sel-Rex "Resonate," and Electro-Materials Corp. of America "Firon."

After mixing, silk screening and drying as appear at **10–12** in FIG. **1,** metal terminals (for example platinum gold) are applied to the opposite ends of the film (as represented by step **13** in FIG. **1**) and the assembly is baked in air at betewen 400° and 800°C for approximately ½ hour, (as represented by step **14** in FIG. **1**). The resultant dry film is glassy or glazed, and has a thickness between 0.5 and 1.5 mil, after firing. FIGS. **2** and **3** show the film **19** on the ceramic substrate **20,** with end terminals **21** fused in position.

Dp **1131** consists of a glazed film of noble metal oxide (50 percent Ruthenium, 25 percent Ruthenium oxide and 25 percent lead borosilicate frit) having a thickness of about 1 mil after firing, and DP **1161** consists of a glassy film of noble metal oxide (35 percent Ruthenium, 40 percent Ruthenium oxide and 25 percent lead borosilicate frit) having the same thickness. These may be considered as "Cermet" type resistors. Reference to FIG. **6** shows that DP **1131** exhibits a 1.4 percent change in electrical resistance over the temperature range 0° to 100°C, which corresponds to the **140PPM** previously referred to, and which is considered as lacking in desired temperature stability.

In accordance with the invention, the glazed film is heated at a relatively high temperature and while exposed to a gaseous environment containing nitrogen in greater percentage consentration than found in air, such heating being continued for a time interval characterized in that the rate of change of resistance as a function of temperature change is significantly reduced; for example, the parts per million change in electrical resistance of the film per degree Centigrade change in temperature is substantially reduced. For best results, the nitrogen containing gaseous environment should be at a temperature of between 650°C and 750°C (and preferably about 700°C) and in contact with the resistor element during the heating interval, the gas being at about atmospheric pressure; and the heating interval should be less than 1 minute, and preferably between 20 and 40 seconds (about 30 seconds for optimum results). FIG. **4** shows the resistance element **19** in a nitrogen gas environment **25** within a container **26,** a heater **27** being operated to maintain the gas at the described temperature or temperatures. A door for the container appears at **26*a*.** Steps **15, 16** and **16** *a* in FIG. **1** respectively indicate initial PPM testing of the resistance film, nitrogen treatment, and subsequent PPM testing of the resistance film.

The graph in FIG. **7** contains three curves **30, 31** and **32.** Positive slope curve **30** corresponds to the 140 PPM curve for **DP 1131** in FIG. **6**; negative slope curve **31** shows that -**100** PPM is obtained for **DP 1131** upon heat treatment at 700°C for **30** seconds in a 100 percent nitrogen environment **25** in FIG. **4**; and curve **32** shows that -**14** PPM is obtained for **DP 1131** (for temperature changes in the range about about 25°C) upon heat treatment at about 700°C for 30 seconds. in a gaseous environment consisting of 80 percent air and 20 percent nitrogen. Accordingly, the nitrogen concentration in the gaseous environment **25** should be above that of air, but less than 100 percent nitrogen, for minimizing the PPM results. If that environment consists of 86 percent air and 14 percent nitrogen, a PPM level of about **10** is obtained, for **DP 1131** fired at about 700°C for 30 seconds.

Turning to FIG. **5,** it shows the use of a laser beam **130** emanating from source or generator **131** and directed to impinge on the resistance element **19,** thereby to effect a change in the electrical resistance of the precision resistor to a desired value at a temperature or temperatures within the range of interest. For this purpose, the beam may be caused to impinge on successively different portions of each of several resistors supported and displaced on a belt **132.** Also, the beam may be controlled, as by control means **33** connected with the generator, to interrupt the beam when the measured resistance of the resistor **19** arrives at the precise desired value, and for that purpose a source of voltage **34** and a precision ohmmeter **35** may be temporarily connected in series with the leads **21** projecting form the opposite ends of the film **19.** Typically, beam impingement on the relatively moving resistance element is continued for a time interval of between 0.10 and 60 seconds, depending on the amount of resistance increase desired, and the intensity of the beam.

The laser beam may be of low frequency with wave length the order of one thousandth of a millimeter or longer. It is found that the resistance element can be tuned, in this manner, over a relatively wide range, i.e., up to around three times its original resistance value, and to a resolution or tolerance of 0.01 percent of a given or desired resistance value, at a selected temperature. As an example, a raw, randomly selected resistor exhibiting a resistance of 21,850 ohms, after nitrogen treatment as described above, may be tuned in this manner to a value of 62,000 ± 6 ohms.

The invention is also applicable to film type resistors where the resistance film is applied to a substrate by sputtering techniques, the metal of the element consisting for example of chronium, and alloys therewith, an example being Nichrome.

We claim:

1. The method of improving the temperature stability of an electrical resistance element in film form and which has been fired at relatively high temperature in air, the element including a component selected from the group consisting of noble metals and oxides thereof, that includes:

a. heating said element at relatively high temperature between about 650°C and 750°C and while the element is exposed to a gaseous environment containing nitrogen in greater percentage than found in air, and

b. continuing said heating for a time interval characterized in that the rate of change of resistance of the element as a function of temperature change is substantially reduced.

2. The method of claim **1** wherein said metals include ruthenium, palladium and silver.

3. The method of claim **1** wherein said gas is at a temperature of about 700°C and in contact with the resistor element during said interval.

4. The method of claim **1** wherein said time interval is less than 1 minute.

5. The method of claim **3** wherein said time interval is between about 20 and 40 seconds.

6. The method of claim **1** wherein the resistance element film is in glassy state.

7. The method of claim **5** wherein the resistance element film is in glassy state.

8. The method of claim **7** wherein the percentage of nitrogen, by weight, in the gaseous mixture is selected to produce a parts per million change in resistance per °C change in temperature of about 10.

9. The method of claim **1** including the step of directing a laser beam to impinge on said element and thereby effect a change in the electrical resistance of said element to a desired value.

10. The method of claim **9** wherein the laser beam exhibits a wave length of at least about one thousandth of a millimeter.

11. The method of claim **9** including the step of effecting relative movement of the beam and element to impinge the beam on different portions of the element.

12. The method of improving the properties of a film type electrical resistance element having a characteristic rate of change of resistance as a function of temperature change, within a selected temperature range between about 0°C to 100°C, the element including a component selected from the group consisting of metals and metal oxides, the steps that include

a. heating said element while exposed to a gaseous medium containing nitrogen in greater percentage than found in air to reduce said rate, and

b. thereafter impinging laser radiation on the resistance element to controllably alter the resistance level thereof, at temperature within said selected temperature range.

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