United States Patent

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[54] **RESISTANCE MATERIAL AND RESISTANCE ELEMENTS MADE THEREFROM**
22 Claims, 2 Drawing Figs.

[52] **U.S. Cl.** **117/227,** 117/160, 252/514, 106/1
[51] **Int. Cl.** **H01b 1/02,** H01b 5/14
[50] **Field of Search** 117/227; 252/514; 106/1

[56] **References Cited**

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ABSTRACT: Improved material for forming resistance elements using minute amounts of noble metals in finely divided form together principally with finely divided vitreous binder material; and resistance elements made from such material.

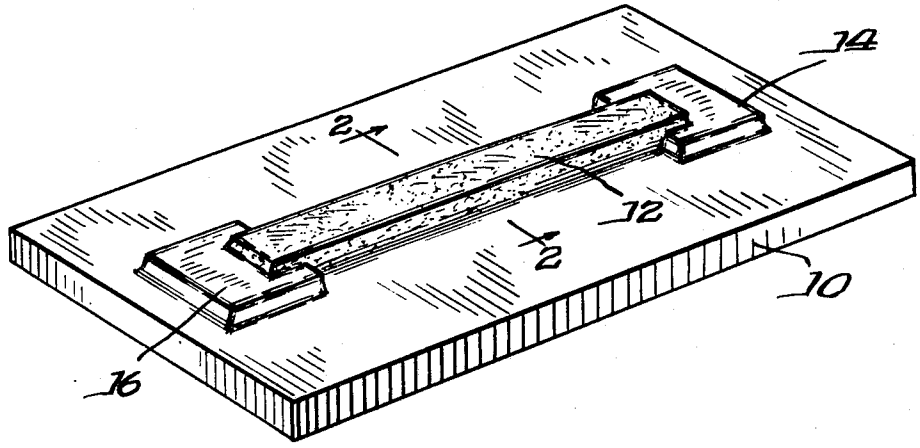


Fig. 1

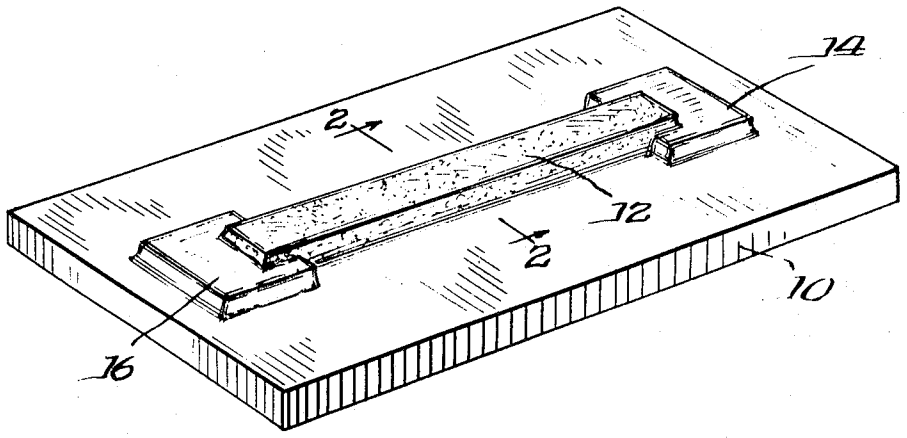
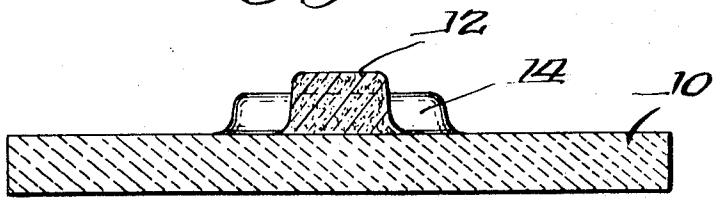


Fig. 2



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RESISTANCE MATERIAL AND RESISTANCE ELEMENTS MADE THEREFROM

BACKGROUND OF THE INVENTION

Heretofore it has generally been believed that material employed to produce stable resistors of varying resistance require large amounts of noble metals. For example, in Place and Place U.S. Pat. No. 2,950,995 it is stated that in resistance materials and in finished resistance elements the metal should be about 1 to 15 percent by weight and in Daily et al. U.S. Pat. No. 3,329,526 the noble metal, or metals, comprise 0.5 to 13 percent by weight of the resistance element. It may be noted also that in the latter patent it is stated that the film must be maintained well below 0.0005 inch in thickness to produce satisfactory results and the maximum resistance per square obtained is 400,000 ohms. In Faber et al. U.S. Pat. No. 3,304,199, which discloses the use of noble metals in the form of oxides, even higher amounts of noble metals are taught, namely 2 to 70 percent by weight of ruthenium oxide and iridium oxide with the preferred amount being 4 to 50 percent. The latter patent asserts a much higher sheet resistance in ohms per square than the inventors had previously attained, and speaks of attaining the top range of about 180,000 ohms per square.

However, we have discovered that, contrary to the teachings of the prior art, minute quantities of noble metals (by which we mean less than approximately 0.5 percent by weight of the resistance material) will permit a wide range of resistance values while at the same time providing a low temperature coefficient of resistance, low noise, and excellent stability, together with consistent reproducibility. Such excellent electrical characteristics growing out of the use of minute amounts of one or more noble metals totaling less than 0.5 percent by weight provides a surprising result both in performance and in cost reduction.

It is therefore an object of this invention to provide a large range of resistor elements providing resistance from a level of 5,000 ohms per square or less to 10 megohms per square or higher, utilizing minute amounts of noble metals.

It is a further object of the invention to provide a resistance material which has excellent temperature coefficients of resistance in all ranges of values including those in the megohm ranges.

It is another object of our invention to provide resistance material the resistivity of which is relatively constant over a wide range of temperatures.

It is yet another object of the invention to provide a resistance material having low noise values relative to the resistance level.

It is yet another object of our invention to provide a resistance material employing minute amounts of noble metals having stability and consistent reproducibility.

Among the further objects of our invention is to provide a resistor element of reduced cost employing minute amounts of noble metals which resistance elements have stability and low temperature coefficients of resistance and noise.

A more thorough understanding of the invention may be obtained from a consideration of the following detailed description when taken in connection with the accompanying drawings in which:

FIG. **1** is an isometric view on enlarged scale of an embodiment of the invention in the form of a resistance element; and

FIG. **2** is a sectional view taken generally on the line **2–2** of FIG. **1**, looking in the direction of the arrows.

DETAILED DESCRIPTION OF THE INVENTION

In the structure of FIGS. **1** and **2**, there is disclosed generally by the reference numeral **10** a high-temperature-resistant, electrically nonconductive base having fired on it a layer of resistance material **12** and with electrical terminals **14** and **16** being provided at opposite ends of the layer of resistance material **12** for connecting the latter to an electrical circuit. The illustrated resistor **10** is adapted for use as a fixed resistor and it will be appreciated that more than one such resistor might be formed upon the base **10** or that a resistor circuitry of complex design could be formed. A variety of materials may be employed to form the base but we have found ceramic bases formed essentially of alumina to be very satisfactory.

Although in FIGS. **1** and **2** the terminals **14** and **16** have been shown as secured to the base **10** before the resistance layer **12** has been disposed on the base, the terminals may also be formed after the resistance layer has been disposed on base **10**. Other forms of connections to the resistance layer may, of course, be substituted for those shown in the drawings.

The resistance layer **12** consists of a fused matrix of a nonconducting binder material, for example, a vitreous binder which we have found to be very suitable, and certain small amounts of other materials. The vitreous material may be a ceramic glass and among glasses considered to be suitable are borosilicate glasses and preferred among them are lead borosilicate glasses. A composition of glass which has proven to be satisfactory is set forth below in table No. I, but other glass compositions or combinations of glass compositions may be employed, if desired.

TABLE NO. I GLASS COMPOSITION

Material	Approximate Percent by Weight
H_3BO_3	14.20
Bi_2O_3	6.85
Pb O	52.60
Si O_2	17.22
Na_2O	2.82
B_2O_3	6.31

In our reference to the use of the term "noble metals" we mean to refer to such as are commonly known and for the purposes of this disclosure include gold, silver, platinum, ruthenium, rhodium, iridium and palladium. This is not to exclude other metals known to have similar properties which may be used in the practice of the invention and are intended to be included in the class of noble metals. Preferred among the noble metals is ruthenium, and a combination of ruthenium and rhodium, which when used in minute amounts, that is, totaling less than 0.5 percent by weight, provide excellent electrical characteristics in a wide range of resistance values. While various combinations of the noble metals or individual noble metals may be employed providing a range of resistance values from about 5,000 ohms per square to 10 megohms per square or higher and while small amounts of certain other materials may be employed, examples of resistance materials found to work very satisfactorily at widely different ranges of resistance are the following set out in tables II and III below:

TABLE NO. II RESISTANCE MATERIAL

Material	Approximate Percent by Weight
Glass	99.46%
Ruthenium	0.30%
Rhodium	0.18%
Copper	0.06%

(Approximately 5000 ohms per square)

TABLE NO. III RESISTANCE MATERIAL

Material	Approximate Percent by Weight
Glass	97.084%

Ruthenium	0.389%
Nickel	1.750%
Silica	0.777%

(Approximately 7megohms per square)

The noble metals, as well as the nonnoble metals, may be supplied in the form of an organo metal complex such as a resinate, for example.

It will be readily appreciated that in producing resistance values of intermediate amounts between approximately 5,000 ohms per square of the resistance material of table II and 7 megohms per square of the material shown in table III, varying percentages of the two materials may be mixed in suitable proportions.

It will be understood that it is not essential to provide small amounts of "doping agents" such as the copper in the resistance material of table II or silica of the resistance material shown in table III, but they are advantageous for favorably affecting the temperature coefficient of resistance and noise, or may provide stability in the printing step of forming a resistance element. For example, temperature coefficients of resistance found to exist when our resistance materials are employed have been the following:

Ohms/square	T.C.
5,000	±30
15,000	±30
50,000	±50
200,000	±70
500,000	±90
1,000,000	±100
5,000,000	±170

The doping agents, as noted, may be both metallic and nonmetallic. Only very small amounts are needed and the principal constituent of the resistance materials is the vitreous binder and the important minute percentages of noble metals.

A method for preparing the resistance material of the invention will now be described with the constituents being finely divided vitreous binder in the form of glass frit such as that set forth, for example, in table I, noble metals in the form of resinates, and doping agents. The glass frit is weighed out and the noble metals and doping agents (if the latter are used) are weighed and blended in with the glass frit, which may be done by a spatula but preferably by a blender having uniform operation. After being weighed and blended, the material is ground as by a mortar and pestle or other suitable means. Thereafter the total mixture is subjected to approximately 3 hours of heating at about 200° C. during which time most of the volatiles are removed from the resinate. The mixture is then once again ground and blended to make a very fine powder in dry form. Screening media such as common oily organic material is then added in varying quantities depending upon the preferred viscosity and that mixture is then thoroughly stirred and roller milled. Thereafter the material is screened and tested.

In the preparation of resistance elements from the resistance material of our invention, the mixture as just described above is applied to the base **10** to form the layer **12** by any suitable means such as brushing, stenciling, spraying or, preferably, silk screening with the resistance pattern desired. The base with such layer on it may, but need not, be permitted to dry for a short period of time. Thereafter the base with its layer is fired in a kiln, such as a tunnel kiln, for purposes of removing all volatile and organic materials from the mixture and providing uniform distribution of heat through the base **10** and the layer **12**, ultimately fusing the glass but not raising the base and layer to a temperature at which the metal will be melted.

It may be desirable to provide a preheat chamber for the base onto which the layer has been screened, with the preheat "chamber" being a bank of infra red heaters, for example, disposed prior to a tunnel kiln, in which chamber heating for 10 minutes at about 100° C. may be carried on. In the kiln the temperature is increased to approximately 760° C. at a rate of approximately 40° C. per minute. During this time all of the volatiles and organic materials are driven off, and the glass fuses. The temperature is then reduced to approximately 300° C. at a rate of approximately 65° C. per minute and the baked resistance element is then removed from the tunnel and permitted to cool.

Exemplary embodiments of the invention have been disclosed but it will be appreciated that other embodiments of the resistance element and variations or modifications of the resistance material may, within the scope of the following claims, be suggested readily to one skilled in the art, having our disclosures before him.

We claim:

1. A resistance material consisting essentially of finely divided nonconductive vitreous binder material and at least one noble metal totaling less than 0.5 percent by weight and in finely divided form.

2. The material of claim **1** wherein the vitreous binder material comprises a combination of borosilicate glasses.

3. The material of claim **1** wherein at least one of the noble metals is provided by an organometal complex.

4. The material of claim **1** wherein the noble metal comprises ruthenium.

5. The material of claim **1** wherein the noble metals comprise ruthenium and rhodium.

6. The material of claim **1** wherein there is included a small amount of at least one doping agent.

7. The material of claim **6** wherein the doping agent comprises a metal.

8. The material of claim **7** wherein the doping agent comprises copper.

9. The material of claim **7** wherein the doping agent comprises nickel.

10. The material of claim **7** wherein the doping agent comprises copper and the noble metals comprise ruthenium and rhodium.

11. The material of claim **7** wherein the doping agent comprises nickel and the noble metal comprises ruthenium.

12. The material of claim **6** wherein the doping agent includes a nonmetal.

13. The material of claim **12** wherein the doping agent comprises silica.

14. The material of claim **12** wherein the doping agents comprise silica and nickel and the noble metal comprises ruthenium.

15. A resistance element comprising a high-temperature-resistance, electrically nonconductive base having fired on it a layer of resistance material consisting essentially of solidified nonconductive vitreous material and at least one noble metal totaling less than 0.5 percent by weight dispersed through the solidified vitreous material in a manner to provide controlled flow of electrical current.

16. The resistance element of claim **15** wherein the noble metals comprise ruthenium and rhodium.

17. The resistance element of claim **15** together with at least one nonnoble metal in small amounts.

18. The resistance element of claim **17** wherein the nonnoble metal comprises copper and the noble metals comprise ruthenium and rhodium.

19. The resistance element of claim **17** together with a nonmetal in small amounts.

20. The resistance element of claim **19** wherein the nonmetal comprises silica, the nonnoble metal comprises nickel and the noble metal comprises ruthenium.

21. A resistance composition with which a base may be coated in desired pattern and when fired produce stable resistor films having a controlled ohmic value per square

between 5K ohms and 10 megohms and characterized by low temperature coefficients of resistance and low noise values relative to their resistance levels, said composition consisting essentially of finely divided nonconducting glass frit containing a minute quantity of one or more finely divided noble metals including ruthenium, the total quantity of noble metal being less than 0.5 by weight of the composition.

22. The resistance composition of Claim 21 wherein the minute quantity of noble metals comprises rhodium in addition to the ruthenium.

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