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[54] ELECTRICAL RESISTANT MATERIAL

[72] Inventors: **Duane Arthur Schroeder**, East Dundee; **Alvin Dennis Weiss**, Chicago; **Benedict Clare Giltner**, Bensenville, all of Ill.

[73] Assignee: **Methode Development Company**, Chicago, Ill.

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[52] **U.S. Cl.**.....**252/512**, 106/1, 117/201, 117/227, 252/513, 252/514, 252/515, 252/518, 252/519, 252/521, 338/308

[51] **Int. Cl.**.....**B44d 1/18**, H01b 1/06

[58] **Field of Search**.....252/514, 518, 512, 513, 515, 252/519, 521; 117/227, 212

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Primary Examiner—Alfred L. Leavitt
Assistant Examiner—J. R. Batten, Jr.
Attorney—Johnson, Dienner, Emrich, Verbeck & Wagner

[57] **ABSTRACT**

Electrical resistance elements are formed using minute amounts of noble metal oxide hydrate in a vitreous binder with or without the inclusion of high electrical resistance metals or their oxides to adjust the ohmic value of the elements.

8 Claims, 3 Drawing Figures

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3,673,117

Fig. 1.

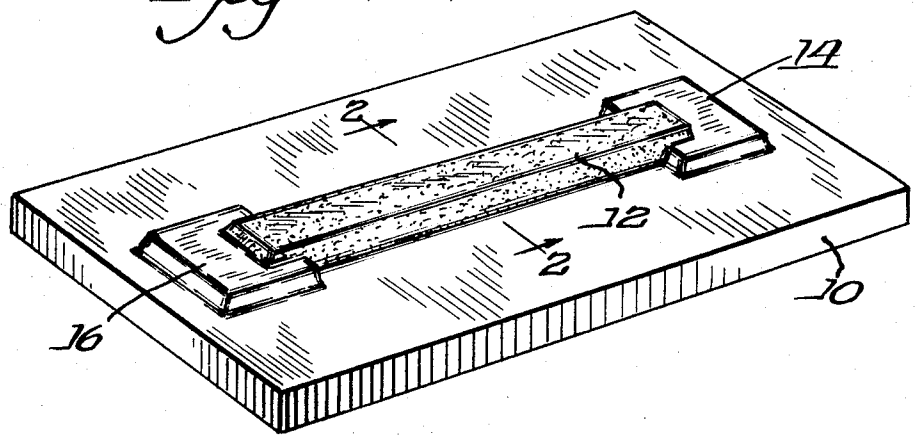


Fig. 2.

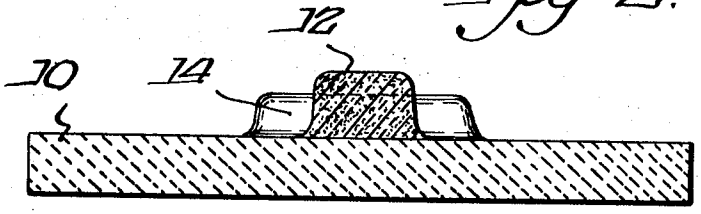
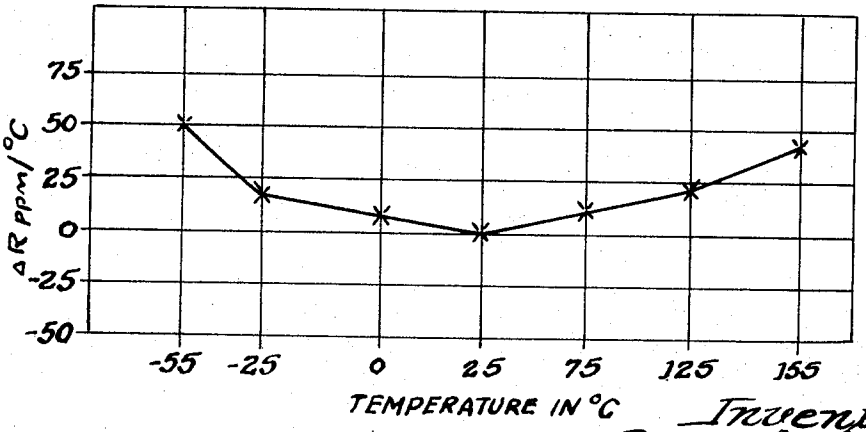


Fig. 3.



Inventors.
Duane A. Schroeder,
Alvin D. Weiss, &
Benedict C. Giftner.

By Johnson, Dienner, Emrich, Verbeck & Wagner
Attys.

ELECTRICAL RESISTANT MATERIAL

This invention relates to improved material and method of forming electrical resistors. It particularly relates to resistance elements of the type which comprise films of vitreous materials such as glass which contain small amounts of noble metals or special types of their oxides in finely divided form dispersed therethrough, the films being customarily applied to the surface of a substrate and fired in situ.

Useful conductive materials for this purpose have included the noble metals. However, a major and important problem in the manufacture of thick resistance elements (usually of the order of 0.8 mil) is whether or not the material can be manufactured economically with a wide range of sheet resistance as well as controlled temperature coefficients of resistance. There are also the problems of ease of fabrication and the importance of being able to use only minute amounts of the noble metal and still provide resistance values which are stable in performance and also repetitive.

Heretofore, prior patents relating to electrical resistance elements and to resistance compositions, particularly those compositions for producing ceramic type elements commonly referred to today as thick film resistors, have stated that it was necessary to use large amounts of noble metals or other oxides, for example as high as 90 percent in order to obtain low resistance values. See U.S. Pat. No. 3,304,199, issued to Faber et al., wherein the prior art is discussed. This patent states that 26 percent of ruthenium dioxide is required to obtain a sheet resistance of 248 ohms per square. The cost of this quantity of noble metal is high.

However, we have found that through the selection of appropriate oxide or oxides, as hereinafter described, that chemical reactions take place which permit us to employ substantially lower percentages of the noble metal oxides, for example, ruthenium dioxide with varying proportions of waters of hydration as opposed to the prior use of anhydrous ruthenium oxide, whereby it is possible to produce resistance elements having controlled temperature coefficients of resistance and low resistivity. We can also use small amounts of other noble metal hydrates with a ruthenium dioxide hydrate to form other resistors which exhibit excellent properties. Not only is the cost reduced but we have found that we can reliably produce a wide range of resistance elements by using the appropriate noble metal hydrate $RuO_2 \cdot xH_2O$ whereby a low percentage, for example, of 4 to 6 percent, would yield resistors in the 250 ohm per square area having excellent stability and temperature coefficients of resistance through a wide range of temperature variations but still maintaining an overall resistance deviation of less than 100 ppm.

Thus it is a feature of the invention that by adding the noble metal to the glass forming constituents as a hydrate or hydrates and dispersing the mixture in an appropriate carrier vehicle, resistance elements of considerably lower resistance values can be obtained than previously thought possible, while maintaining low percentages of the costly noble metal. Furthermore, it is possible to fire relatively thick films without the problem of outgassing which hampered the prior art.

We have further found, and it is an important feature of the invention, that the low sheet resistivities obtained for such resistance films are constant, that they can be consistently obtained and are therefore predictable.

A further feature of the invention is that means and method are provided by which sheet resistivity (ohmic value per square) of such electrical resistance elements can be adjusted to provide a series of resistance elements having any desired value of sheet resistance between a low of about 200 ohms per square to a high of about 10 megohms per square while maintaining a constant content of the noble metal and film thickness. This we are able to do by adding one or more of known high electrical resistance metals such as cobalt, chromium, maganese, antimony, barium, bismuth, cadmium, cerium, calcium, lead, magnesium, silicon, strontium, tantalum, tin, tungsten, zinc, lanthanum, uranium and particularly nickel. By varying the amount of the high resistance metal added to the mixture we are able to obtain sheet resistances which are progressively greater with the increase in the weight percentage of the added high resistance material.

Thus it is a further important object and/or feature of the invention that improved resistor elements may be produced with a constant noble metal content having a predictable specific resistance within the range of approximately 200 ohms per square and 10 megohms or more per square.

A further feature of the invention is that such resistance elements have a resistivity which is relatively constant over a wide range of temperatures in which the resistance element may be operated.

Still another feature of the invention is that such resistance elements employ only minute amounts of the costly noble metal so that the invention provides an economic advantage.

Still another feature of the invention is that the resistance elements produced are nevertheless stable and predictable in their sheet resistivities while providing satisfactory temperature coefficients of resistance and reduced noise levels.

Further objects, advantages and features, as well as 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 an enlarged scale of an embodiment of the invention in the form of a resistance element;

FIG. 2 is a sectional view taken along line 2—2 of FIG. 1, looking in the direction of the arrows; and

FIG. 3 is a graph on which are plotted a curve depicting resistance changes in a resistor according to the invention which is subjected to temperatures through a range of −55° to +150° C.

In the structure of FIGS. 1 and 2 there is disclosed generally by the reference numeral **10** a high-temperature-resistant, electrically non-conductive base or substrate having a layer of resistance material **12** fired on one surface thereof and with electrical terminals **14** and **16** at opposite ends of the layer of resistant 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 substrate **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 terminals **14** and **16** are shown as secured to the base **10** before the resistance layer **12** has been disposed on the substrate **10**, the terminals may also be formed after the resistance layer has been disposed on the base **10**. Other forms and 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 non-conducting binding material, for example, a vitreous binder through which is uniformly dispersed minute amounts of a conductive material or materials as will now be particularly described. The vitreous binder material may be a ceramic glass and among glasses considered to be suitable are borosilicate glasses and preferred among them are bismuth lead borosilicate glasses. A particularly suitable composition of glass forming constituents for the purposes of this invention is set forth below in Table No. I, although it will be understood that other glass compositions or combinations of glass compositions may be employed, if desired.

TABLE No. I

GLASS COMPOSITION

Constituents	Weight %
K_2O	.85
Na_2O	.18
CaO	.06
PbO	65.11
Al_2O_3	1.4
SiO_2	20.7
B_2O3	7.9
Bi_2O_3	3.8

Total	100.00

In accordance with the invention, our novel resistance material is produced by adding minute amounts of a noble metal hydrate, and specifically ruthenium hydrate $RuO_2 \cdot x(H_2O)$, in finely divided form to the glass forming constituents to comprise between 0.1 and 25 percent by weight of Ru. By the term "noble metals" we mean to refer to such as are commonly known and for the purposes of this disclosure the noble metals include gold, silver, platinum, ruthenium, rhodium, iridium and palladium. Their hydrates usually exist as complexes of the oxides of one of these noble metals combined with water of crystallization, $x(H_2O)$ where x represents the number of moles. This is not to exclude other metals and their hydrates 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 and hydrates thereof.

Hydrated ruthenium oxide, $RuO_2 \cdot x(H_2O)$ is available as the precipitate obtained when an alcohol is added to a solution of ruthenium tetra-oxide and a dilute solution of sodium hydroxide and then boiling. The hydrate can also be formed by reducing RuO_4 at 50° C. with hydrogen at 60 lb/inch^2 pressure. Anhydrous RuO_2 is formed from ruthenium by heating the metal in air to a temperature of 800° C.

The noble metal hydrate and glass forming constituents are worked with a carrier vehicle such as pine oil, dipentene, oil of lavender or the like, into a cermet paste which can be applied in a conventional manner as by screening, dipping or spraying onto one surface of the base 10 to form a film of required shape and thickness which is subsequently fired at a temperature sufficiently high to melt the glass mixture, but below the temperature at which the substrate 10 melts.

The resultant lower sheet resistances which are obtained through the addition of the noble metal to hydrate form, as opposed to its addition of pure metal form or as the anhydrous metal oxide, are apparent in the following examples which are summarized below in Table II with their test results. As indicated, each of the eight batches comprises 40 gram batches of identical glass forming constituents according to Table I to which 1.0 gram (Batches A B C D) and 1.47 gram (Batches A–1 B–1 C–1 D–1) measures of ruthenium materials were added in the form designated. The mixture was combined with the carrier vehicle as indicated above, applied to a substrate to the same film thickness, size and shape and similarly fired. The resistance values and temperature coefficient of resistance of the eight resistor elements were then measured and the results were as indicated in Table II below. No attempt was made to adjust temperature coefficient of resistance so we would have a true comparison of various ruthenium materials.

TABLE II

Batch No.	% Ru	Ru & form added	Wt. % Ru in product added	Sheet resistivity in ohms/sq.	T.C.R. ppm/ 125°C.	Formula
A	1.37	RuO_2 Hydrate	56.25	900	+1720	$RuO_2 \cdot 3H_2O$
B	1.25	RuO_2 Hydrate	51.2	26K	+476	$RuO_2 \cdot 4H_2O$
C	1.86	RuO_2 Anhydrous	76.08	>500 M	—	RuO_2
D	2.41	Ru powdered	99+	>500 M	—	Ru
A–1	1.98	RuO_2 Hydrate	56.25	290	+1750	$RuO_2 \cdot 3H_2O$
B–1	1.77	RuO_2 Hydrate	51.2	3.6K	+1000	$RuO_2 \cdot 4H_2O$
C–1	2.63	RuO_2 Anhydrous	76.08	115K	+265	RuO_2
D–1	3.42	Ru powdered	99+	>500 M	—	Ru

From Table II it will be seen that hydrated RuO_2 allows resistance values to be obtained which are not possible at comparable levels of Ru with either anhydrous RuO_2 or the powdered Ru metal. The test data further indicates that when the batches employing anhydrous ruthenium oxide or powdered metal ruthenium were fired in the same manner, the resultant resistance elements had sheet resistances so high as to be not measurable using a standard laboratory ohmeter. The examples also indicate that not only does the addition of Ru in the form of ruthenium oxide hydrate permit the manufacture of resistance elements having consistently lower sheet resistances, but also that the ohmic values of the resistance elements can be varied in accordance with the specific hydrate used.

Thus, whereas Faber et al U.S. Pat. No. 3,304,199 suggests the need to add approximately 20 percent by weight of ruthenium in order to produce a resistance element having a sheet resistance as low as 250 ohms per square, we have been able to obtain substantially the same resistance value by using an amount of ruthenium oxide hydrate which introduces less than 2.0 percent by weight of Ru to the fired resistance element.

In the past it has been the practice to increase sheet resistance by either gradually reducing the weight percentage of the noble metal in the cermet paste or adding an increasing amount of organic carrier material which when fired in the subsequent glass melting operation would decompose into gaseous vapors, thus substantially reducing the fired film thickness and so to obtain thinner film deposits and therefore greater sheet resistances because of the reduced cross-sectional area of the conducting material. However, both of these methods introduce inherent inconsistencies in maintaining narrow ranges of resistances. By constantly increasing or decreasing the conductive metal or metal oxide content, the uniformity of dispersion and the particle to particle content of the conductive materials becomes increasingly critical as higher resistance values are obtained through reduced conductive element concentrations.

We, however, have found that these disadvantages and problems can be conveniently overcome while maintaining the concentration of the ruthenium or the noble metal at a fixed value or percentage and without varying the resultant fired film thickness. Rather, the sheet resistance is increased by appropriate selection of a doping agent which may be either a noble metal within the range of 0.1 to 10 percent by weight or a non-noble metal within the range of 0.01 to 25 percent by weight. Instead of changing the kind of doping agent, we are also able to progressively increase the sheet resistance by increasing the weight percentage of the added high resistance material. Examples of such high resistance materials include cobalt, chromium, manganese, antimony, barium, bismuth, cadmium, cerium, calcium, lead, magnesium, silicon, strontium, tantalum, tin, tungsten, zinc, lanthanum, uranium, and preferably nickel. The form of the nickel or other metal added as doping agent may be as resinates or organo metallic complexes, metallic salts or metal oxides and in all cases are finely divided to approach particle sizes of 325 mesh or smaller.

As examples thereof, four batches of resistance materials are identified in Table No. III below, each of which contains a constant amount of ruthenium oxide hydrate and glass forming constituents to which have been added different amounts of rhodium oxide hydrate and nickel resinate. Rhodium and nickel in other forms can also be used to obtain equal advantageous effect. The resultant batches were worked into a cermet paste with a carrier vehicle. Comparable films of the same thickness were applied to substrates, commonly fired and the resistance values and the $\Delta R/°C.$ of each element determined. The typical resistance values obtained by this kind of "doping" using a constant glass formulation in all cases are indicated in the chart below.

TABLE III

Element	Weight %			
Ru	1.6	1.6	1.6	1.6
Ni	1.3	1.0	.61	.32
Rh	.11	.20	.36	.45
Rs in K ohm/sq.	200	100	15	5
ΔR/°C. in ppm	+70	+55	+80	+60

In FIG. 3 we have illustrated the comparably flat parabolic curve of ΔR which is formed by taking resistances of the above ruthenium nickel rhodium glass resistance elements while subjecting the finished resistor to temperatures from −55° C. to +155° C. Readings were taken at the indicated temperatures, ΔR in ppm/°C. being determined by $(R_2-R_1/R_{25}(t_2-t_1)) \times 10^6$.

A method for preparing the resistance elements of the invention will now be described with the constituents being a finely divided vitreous binder in the form of glass forming constituents such as set forth, for example in Table I, to which have been added a noble oxide hydrate and in some instances either a second noble metal or its oxide and/or one or more of the mentioned "doping" agents. The glass forming constituents are weighed out and the noble metal hydrate and other noble metal or non-metal "doping" agents are weighed and blended in with the glass forming constituents. This may be done by a blender. After being weighed and blended, the material is ground as by a mortar and pestle or other suitable means. The carrier vehicle is then added to achieve a suitable viscosity. The mixture is then thoroughly stirred and roller milled. Thereafter the material is screened, fired, 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, stencilling, 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, preferably a tunnel kiln, but not necessarily.

In the kiln, the temperature is increased to approximately 775° C. at a rate of approximately 35° C. per minute, and held at this temperature for approximately 7 minutes. During this time all of the volatiles and organic materials are driven off, the glass fuses, and the resistor is formed. The fired resistance element is then 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, within the scope of the following claims, may be suggested readily to one skilled in the art, having our disclosures before him.

We claim:

1. A resistance forming material consisting essentially of powdered bismuth lead borosilicate glass forming constituents containing ruthenium dioxide hydrate uniformly dispersed therethrough in a carrier vehicle, said ruthenium dioxide hydrate containing an amount of ruthenium equal to 0.1 to 25.0 percent by weight of the amount of glass forming constituents and hydrate after firing.

2. The resistance forming material of claim **1** further containing between 0.01 and 25 percent by weight of at least one high resistance metal selected from the group consisting of cobalt, chromium, manganese, antimony, barium, bismuth, cadmium, cerium, calcium, lead, magnesium, silicon, strontium, tantalum, tin, tungsten, zinc, lanthanum, uranium and nickel.

3. The resistance forming material of claim **1** which further contains from 0.01 to 25 percent by weight of nickel in finely divided form.

4. The resistance forming material of claim **3** wherein the nickel is added as the metal itself, an organo-metallic complex, an oxide or a salt thereof.

5. A resistance forming material consisting essentially of from about 0.1 to 25 percent by weight of Ru as ruthenium dioxide hydrate and from about 75–99.9 percent by weight of bismuth lead borosilicate glass forming constituents.

6. The resistance forming material of claim **5** further containing from 0.1 to 10 percent by weight of rhodium.

7. The resistance forming material of claim **6** wherein the rhodium exists as the elemental metal, as an anhydrous metal oxide or salt, as an organo-metallic complex or a hydrated oxide.

8. A resistance composition with which a base may be coated in a desired pattern and when fired produce stable resistor films having a sheet resistivity in the area of 250 ohms per square, said composition consisting essentially of powdered bismuth lead borosilicate glass forming constituents containing from about 4 to 6 percent by weight of finely divided ruthenium dioxide hydrate.

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