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[54] ELECTRICAL RESISTANCE COMPOSITION

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[63] Continuation-in-part of Ser. No. 573,856, Aug. 22, 1966, abandoned.

[52] **U.S. Cl.** **252/514**

[51] **Int. Cl.** **H01b 1/02**

[58] **Field of Search** 252/512, 514, 518

[56] **References Cited**

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[57] **ABSTRACT**

An electrical resistance composition comprising finely divided metals such as the noble metals dispersed in a glass matrix and further including an additive taken from the group consisting of gallium, indium, thallium, arsenic, antimony, bismuth and combinations thereof so as to improve the electrical properties of the composition—particularly the TCR.

11 Claims, No Drawings

ELECTRICAL RESISTANCE COMPOSITION

This application is a continuation-in-part of Ser. No. 573,856, filed Aug. 22, 1966, now abandoned.

This invention pertains to an electrical resistance composition to be fired on a ceramic body.

A relatively recent development in electrical resistance compositions has been more commonly referred to as a cermet, e.g., a flux such as a vitreous enamel flux—usually a glass—including finely divided dispersed metal or metals and oxides thereof. In order that these resistance compositions can be successfully used, consideration must be given to electrical characteristics of the composition, such as current noise, change in resistance value as a function of time and temperature along with the production repeatability of similar resistance values with other characteristics.

The relation between the changing resistance as a function of temperature is defined as the temperature coefficient of resistance (TCR); which coefficient is usually described in the units: parts per million parts change per degree centigrade of temperature change (p.p.m./° C). The smaller and more uniform the TCR over a designated range of temperatures, the more commercially acceptable is the composition. The compositions of this invention provide this desired small and uniform TCR by using limited amounts of selected constituents and combinations thereof.

It is therefore an object of this invention to provide an improved electrical resistance composition.

It is a further object of this invention to provide an electrical resistance composition which exhibits relatively small and uniform TCR's.

Resistance compositions upon which the compositions of this invention are based have been known as evidenced by the article entitled "Precision Glaze Resistors" by L. C. Hoffman appearing in CERAMIC BULLETIN, Vol. 42, No. 9 (1963) at pages 490–493. This article explains the background, basic processes and characteristics of the resistance compositions basic to this invention. For purposes of brevity and clarity the following description of the invention will not include this background information supplied by the above-mentioned article.

The compositions of this invention are based upon solids comprising the several noble metals used for such compositions including palladium, gold, silver, ruthenium, rhodium, iridium and combinations thereof, along with a flux including a glass. This glass, preferably a glass frit produced from raw materials by known methods, utilizes well-known glass technology including, for example, the conventional glass building blocks: RO (e.g., PbO; ZnO; BaO; K_2O and/or Na_2O); R_2O_3(e.g., B_2O_3; Bi_2O_3 and/or Al_2O_3) and RO_2 (e.g., SiO_2; TiO_2 and/or ZrO_2). When formulating such a glass, consideration must be given to the invention's use and manufacturing process environment; which considerations suggest the following glass characteristics to most effectively implement the invention:

a. a softening point temperature ranging from 1,300° to 1,600° F.
b. a maturing in the temperatures ranging from 1,300° to 1,900° F. and
c. a coefficient of expansion which is compatible with that of the substrate upon which the glass with metals will be printed and fired.

Also, modifiers can be supplied to affect desired changes in glass characteristics in well-known fashion. It is apparent, then, that the glass to be used in the invention is not a matter of particular significance—especially to one skilled in the art.

Particularly suitable for the invention are the lead, zinc and/or barium borosilicate glass frits. While the following examples are not limiting, they do illustrate specific glass frits for use in the invention.

I		II		III	
PbO	57.4	PbO	2.0	PbO	62.2
B_2O_3	13.0	ZnO	22.3	B_2O_3	8.5
SiO_2	26.2	B_2O_3	33.9	SiO_2	21.4
Al_2O_3	3.1	SiO_2	17.0	Al_2O_3	3.0
ZrO_2	0.3	Al_2O_3	8.9	CdO	4.9
		ZrO_2	3.1		
		Na_2O	7.6		
		CaO	5.0		

These compositions are conventionally deposited upon a substrate and fired. The composition which results from this firing includes the noble metals and oxides thereof both disposed in a ceramic matrix derived from the flux. In order to be consistent with common and accepted practice and usage in the industry, the reference, herein, to solids will mean those elements and portions which makeup the fired composition and not materials which may be a part of the composition before but not after firing, e.g., organic vehicles and binders which will burn off during the firing.

By including selected constituents in the metal and glass compositions set forth above, and in accordance with this invention, it is possible to produce an electrical resistance composition which has substantially improved characteristics—especially the TCR. These particular constituents are gallium, indium, thallium, arsenic, antimony, bismuth and combinations thereof. Experiments have shown that these constituents must be present in proportion measuring up to 5.0 percent by weight of the solids in the fired composition in order to provide the desired improved characteristics. It was further revealed that the more desirable results, with bismuth, for example, were achieved when this constituent was present in the range of 1.8 percent to 5 percent by weight of the solids while for indium the better results were achieved with a range of 0.05 percent to 1 percent by weight of the solids.

The particular theory by which the constituents produce these improved electrical characteristics remains in doubt; although it has been suggested that these constituents act as doping agents at the junctions between the dispersed metals, metal oxides and a matrix. These junctions occur after the metals and flux are fired. The doping here is used in the same context as solid state junction doping. Regardless of the particular theory, it is well established that these constituents when incorporated into the electrical resistance composition provide substantially improved electrical characteristics—especially TCR.

The constituent is preferably included in the composition, before firing, as a part of the flux where it may take the form of a free metal or an oxide with the form being either a part of or separate from the glass frit. Also, the constituent may be included in a vehicle such as a resinate. However, these constituents can be mixed with the noble metals before firing; but this mixture, by definition herein, would comprise the conducting metals, such as the noble metals, plus the remaining portions defined as the flux and including the indium resinate, for example.

EXAMPLE I

A resistance composition was prepared by mixing finely divided metals comprising palladium and silver, in the weight ratio of 50 percent palladium to 50 percent silver, with a flux comprising a glass frit and with sufficient organic vehicle and binder to make the composition printable. The finely divided metals represented 46.5 percent of the solids in the fired composition. A constituent, bismuth, was added in the form of Bi_2O_3 to the flux—part of this Bi_2O_3 being integral to the glass frit so that the bismuth oxide content was 4.6 percent of the fired solids (i.e. the Bismuth content was 4.2 percent of the fired solids). This composition was printed by silk screen methods on a ceramic body and fired to peak temperatures ranging from 1,350° to 1,575° F. using an 18–35 minute cycle above 1,000° F. to produce a resistance element with an average resistance of 5,000 ohms. The TCR's were less than 100 p.p.m./° C. and TCR's of 50 p.p.m./° C. were readily obtainable based upon temperatures from −50°to +° C.

EXAMPLE II

A resistance composition was prepared by mixing finely divided metals comprising palladium and silver, in the weight ratio of 70 percent palladium to 30 percent silver, with a flux comprising a glass frit and with sufficient organic vehicle and binder to make the composition printable. The finely divided metals represented 26.3 percent of the solids in the fired composition. The constituent indium was added via the flux with a resinate vehicle to provide an indium content of 0.9 percent of the fired solids. Printing and firing were accomplished as in example I to produce a resistance element with an average resistance of 120,000 ohms. The TCR's were less than 200 p.p.m./° C. and TCR's of 100 p.p.m./° C. were readily obtainable based upon temperatures from −50° to +150° C.

EXAMPLE III

A resistance composition was prepared by mixing finely divided metals comprising palladium and silver, in the weight ratio of 50 percent palladium to 50 percent silver with a glass flux and with sufficient organic vehicle and binder to make the composition printable. The finely divided metals represented 31 percent of the solids in the fired composition. Bismuth and indium constituents were incorporated through the flux with indium resinate as in example II (the indium being 0.53 percent of the fired solids) and with bismuth oxide as in example I (the bismuth being 3 percent of the fired solids). Printing and firing were accomplished as in example I, but with the time cycle running up to 45 minutes, to produce a resistance element with an average resistance of 100,000 ohms. The TCR's were less than 200 p.p.m./° C. and TCR's of 50 p.p.m./° C. were readily obtainable based upon temperatures from −50° to +150° C.

EXAMPLE IV

A resistance composition was prepared by mixing finely divided metals comprising palladium and silver, in a weight ration of 70 percent palladium to 30 percent silver, with a glass flux comprising a glass frit and with sufficient organic vehicle and binder to make the composition printable. The finely divided metals represented 27 percent of the solids in the fired composition. The constituent gallium was added as a free metal in the flux so as to represent 0.53 percent of the total solids fired by weight. Printing and firing were accomplished as in example I but with peak temperatures ranging from 1,525° to 1,675° F., to produce a resistance element with an average resistance of 160,000 ohms. The TCR's were less than 250 p.p.m./° C. based upon temperatures from −50° to +150° C.

It should be noted in each of the examples that vehicles such as pine oil and binders such as ethyl-cellulose can be used.

As previously mentioned, it is within the scope of this invention to substitute other noble metals and combinations such as gold, ruthenium, iridium and rhodium for the palladium, silver including combinations thereof.

The TCR's shown in the examples demonstrate the significant contribution of this invention in view of the very low and readily reproducible values made possible. Without the constituents of this invention, comparable components were shown to have TCR's from 225 p.p.m./° C. and higher with the lower TCR values being difficult to reproduce.

A preferred composition which has demonstrated exceptionally good electrical characteristics utilizes the metals palladium and silver in a combined percentage weight between 8 and 55 percent by weight of the fired solids. Among the metals, the palladium ranges between 30 and 75 percent leaving the silver a corresponding range between 25 and 70 percent. The constituents represent up to 5 percent by weight of the fired solids; the constituents being those mentioned above, i.e., taken from the group consisting of gallium, iridium, thallium, arsenic, antimony, bismuth and combinations thereof.

We claim:

1. An electrical resistance composition adapted to be applied to and fired on a ceramic body comprising:
   a. finely divided metals taken from the group consisting of the noble metals palladium, gold, silver, rhodium, ruthenium, iridium and combinations thereof which metals comprise 8–55 percent by weight of the fired solids,
   b. a flux comprising:
      1 a constituent dopant to improve the temperature Coefficient of Resistance of the composition and taken from the group consisting of gallium, indium, thallium, arsenic, bismuth and combinations thereof which constituent comprises greater than 0.05 but less than 5 percent by weight of the fired solids, and
      2. a glass comprising 40–91.95 percent by weight of the fired solids.

2. The electrical resistance composition of claim 1 wherein said constituent is bismuth in the proportion greater than 1.8 but less than 5 percent by weight of the fired solids.

3. The electrical resistance composition of claim 1 wherein said constituent is indium in the proportion 0.05 percent to 1 percent by weight of the fired solids.

4. The electrical composition of claim 1 wherein:
   a. said finely divided metals are taken from the group consisting of palladium, gold, silver, rhodium and combinations thereof, and
   b. said glass is taken from the group consisting of lead borosilicate glass frit, zinc borosilicate glass frit, barium borosilicate glass frit and combinations thereof.

5. A resistor composition adapted to be applied to and fired on a ceramic body comprising:
   a. the metals palladium and silver between 8 and 55 percent by weight of the fired solids having,
      1. 30–75 percent palladium and
      2. 25–70 percent silver, and
   b. a flux comprising up to about 5.0 percent by weight of the fired solids of a constituent taken from the group consisting of gallium, iridium, thallium, arsenic, and bismuth and combinations thereof.

6. The electrical resistance composition of claim 5 in which said constituent is bismuth.

7. The electrical resistance of claim 6 in which said bismuth constituent is in the form of bismuth oxide.

8. The electrical resistance composition of claim 5 in which said constituent is indium.

9. The electrical resistance composition of claim 5 in which said constituent is bismuth and indium.

10. A fired electrical resistance composition of a substrate comprising:
   a. metals taken from the group consisting of the noble metals palladium, gold, silver, rhodium, ruthenium, iridium and combinations thereof, which metals comprise 8–55 percent by weight of the composition solids,
   b. a constituent to improve the Temperature Coefficient of Resistance of said composition and comprising greater than 0.05 but less than 5 percent by weight of the composition solids and taken from the group consisting of gallium, indium, thallium, arsenic, bismuth and combinations thereof, and a ceramic matrix which comprises 40–91.95 percent by weight of the composition solids.

11. The electrical resistance composition of claim 10 wherein:
   a. said metals are taken from the group consisting of palladium, gold, silver, rhodium and combinations thereof, and
   b. said ceramic matrix is taken from the group consisting of solidified lead borosilicate glass, zinc borosilicate glass, barium borosilicate glass and combinations thereof.

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