

United States Patent
Casale et al.

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[54] **RESISTOR COMPOSITION**

[72] Inventors: **Mira E. A. Casale; Owen N. Collier; Gerald S. Iles**, all of London, England

[73] Assignee: **Johnson, Matthey & Co., Limited**, London, England

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[63] Continuation-in-part of Ser. No. 675,786, , abandoned.

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[58] Field of Search**252/514, 518, 519, 521; 117/201; 106/47**

[56]

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Primary Examiner—Douglas J. Drummond

Attorney—Kimmel, Crowell & Weaver

[57]

ABSTRACT

A resistor composition in the form of an oxide containing niobium and ruthenium in which the atomic ratio of metal to oxygen is 1:2 and in which the atomic ratio of niobium to ruthenium is within the range of 1:2000 to 1:1.

8 Claims, No Drawings

RESISTOR COMPOSITION

This invention relates to electrical resistor compositions and to resistor elements made therefrom and is a continuation-in-part application of our copending application, Ser. No. 675,786, now abandoned.

It has already been proposed to produce conductive glazed contacts from a glaze containing a relatively high proportion of a noble metal such as palladium or gold in a vitreous enamel composition.

Further proposals have included the incorporation into the vitreous enamel composition of a proportion of finely divided silver or silver precursor such as silver oxide.

A later development described in the Dumesnil, U.S. Pat. No. 3,052,573 is the use of noble metal oxides (e.g., palladium oxide or rhodium oxide) with or without the addition of finely divided silver.

Disadvantages of these known compositions are that the resistivity of the "fired-on" film of material tends to vary with the firing temperature and that relatively high-firing temperatures, generally well above 600° C. are required.

An important indication of the quality of such resistance elements is the temperature coefficient of resistance. In most circumstances it is desirable that this coefficient should be relatively close to zero; that is to say, any large changes in resistivity (either positive or negative) brought about by variation in the operating temperature of the component are undesirable. For obvious reasons the electrical properties of resistor components in integrated circuits should show little or no variation under expected operating conditions.

Accordingly it is an object of this invention to provide a resistor material having temperature coefficient of resistance characteristics which can be closely controlled.

A further object of the present invention is to provide resistor compositions which may be applied and fired on to a substrate of, for example, mica or ceramic such that the resistivity of the film after firing does not vary markedly with the firing temperature.

According to the present invention a resistor composition suitable for firing on to a nonconducting substrate to form a resistor element comprises a new composition of matter consisting essentially of oxygen, niobium and ruthenium and in which the atomic ratio of metal to oxygen is 1:2 and in which the atomic ratio of niobium to ruthenium is within the range 1:2,000 to 1:1.

The invention also includes a resistor composition suitable for firing on to a nonconducting substrate to form a resistor element comprising a new composition of matter in the form of an oxide containing niobium and ruthenium in which the atomic ratio of metal to oxygen is 1:2 and in which the atomic ratio of niobium to ruthenium is within the range 1:2,000 to 1:1.

We have found that by controlling the ratio of niobium to ruthenium present within this new composition of matter, close control may be exerted over the temperature coefficient of the resulting resistor element.

As in the prior art materials, silver may be incorporated into the resistor compositions of the invention in order to provide refinement in controlling the electrical resistance of the whole element. Gold or platinum may be used in place of silver. Silver, or its above-mentioned equivalents, may be present in the resistor composition to the extent of 75 percent by weight of the whole. (That is, including the glaze components, but excluding the printing ink medium or liquid components). The glaze components may be present in an amount of 90-20 weight percent.

In the above-mentioned compositions the silver, if present, is usually added in the form of the finely divided metal, but may also be added as a metal precursor such as silver oxide or carbonate. These latter materials form the metal on firing in the enamel composition.

Many different glasses have been found to be suitable for use in resistor compositions according to the invention. Suitable glasses are those which have a melting range, the lower

limit of which is not more than 50° C. below the maximum temperature at which the composition is to be fired on to a substrate. The viscosity of the glass on melting should not become too low, however. Glasses are chosen with regard to the electrical resistance properties which it is desired the resistive element should finally have.

The oxide material of the present invention has been found to have a temperature coefficient of resistance of almost zero when the atomic ratio of niobium to ruthenium is approximately 1:320. This is a useful ratio, but is not always the preferred ratio as the temperature coefficient of resistance characteristics of the glass and other resistor components must also be taken into account.

For application to a substrate, usually ceramic and before firing, the components of the resistor composition (glass, the oxide material, finely divided silver etc.) are suspended in a liquid medium, which is preferably an organic resin in an organic solvent, to give an ink of suitable consistency for screen printing or brushing on to the substrate. A suitable organic resin is an ethyl cellulose-type material. The resistor composition may be applied to a substrate using a transfer in which a required pattern of the resistor composition forms the design layer of the transfer.

One way of preparing the resistor composition of the invention or the modified forms of it described above is to subject an aqueous suspension of the oxide material having appropriate ratios of metal: oxygen and Nb:Ru as specified and glass to ball-mill action, to filter-off and dry the resultant finely divided material and then to redisperse it in a triple roll mill in an organic medium formed by dissolving ethyl cellulose in a high-boiling point, such as butyl glycol ester, or a mixture of high boiling-point esters, alcohols and hydrocarbons, so as to form a suspension consisting of 25 weight percent organic medium and 75 weight percent of the finely divided material.

The initial ball milling should preferably be carried on until the particle size range of the resultant powder is from 0.01 to 50 microns and preferably from 0.01 to less than 5 microns.

One way of forming a resistor element from the composition prepared as described above is to apply a layer of the composition to a mica substrate by screen printing or brushing and then to heat the so-treated substrate, typically for from 2 to 10 minutes at a temperature which is preferably not more than 50° C. above the lower limit of the melting range of the glass used in the composition. Preferably, the thickness of the applied layer of resistor composition before firing is between 0.0004 and 0.0006 inch.

The oxide material according to this invention may be prepared by very strongly heating together a finely divided and intimate mixture of niobium pentoxide and ruthenium dioxide in a closed crucible for substantial periods of time.

Finely divided and intimately mixed quantities of the two constituents could be heated at, for example, 1,400° C. for 60 hours to give an oxide material according to the invention. Temperatures not less than 1,000° C. and times not less than 3 hours are normally required.

We have found that such strong treatment results in the ruthenium dioxide and the niobium pentoxide being totally consumed in the formation of the oxide material according to the invention.

Batches of material prepared in this way, however, should preferably always be checked by X-ray diffraction to ensure that a single phase of the new oxide material is formed and that no unreacted ruthenium oxide and niobium pentoxide remain as their presence is extremely harmful to the electrical properties of the resistor composition after firing. In the event of ruthenium oxide or niobium pentoxide being detected in the oxide material, the material is reheated until all traces of the oxide(s) is/are removed.

The figures given below illustrate, in part, the way in which the resistivities and temperature coefficients of resistivity of films of the resistor composition of this invention fired on to a mica substrate vary with the nature of the composition. The figures in each case relate to films of the resistor compositions

within the thickness range 0.0004 to 0.0006 inch after firing which were applied to a mica substrate by screen printing and then fired on the substrate by passing it through a continuous "lehr" type furnace.

EXAMPLES 1 and 2

The resistor composition used for examples 1 and 2 comprises powdered oxide material of niobium and ruthenium and powdered glass in the proportion of 2:1 by weight suspended in an organic medium formed by dissolving 10 g. of ethyl cellulose in 100 ml. of butyl glycol ester so as to form a suspension consisting of 25 weight percent organic medium and 75 weight percent of solids. The oxide material of niobium and ruthenium was prepared by heating together a mixture of 3.32 parts by weight of niobium pentoxide and 30.08 parts by weight of ruthenium dioxide in a closed fire clay crucible for 6 hours at 1,400° C. The resulting material was analyzed to confirm complete absence of individual starting components.

In each example, samples were passed at uniform speed through a 600° C.—650° C.—600° C. zone in a lehr furnace in 20 minutes.

The compositions of the Dupont glass used in example 1 were:

ZnO: 33.1 weight percent; SiO₂: 24.5 weight percent; B₂O₃: 25.2 weight percent;

Al₂O₃: 3.0 weight percent; Na₂O: 10.0 weight percent; and ZrO₂: 4.0 weight percent.

The Nb:Ru ratio in the oxide material according to the invention was approximately 1:10.

Example No.	Glass used	Peak firing temp. (° C.)	No. of samples tested	Resistivity range (ohms per square per mil)	Temperature coefficient of resistivity (p.p.m. per degree C.)
1.....	Dupont glass.....	650	50	60-80	-100
2.....	Lead borosilicate.....	650	50	32-42	+200

Examples of the way in which resistor compositions containing silver and resistor elements formed therefrom have been prepared, are as follows:

EXAMPLE 3

1.8 g. of oxide material was formed by heating together 4 parts by weight of ruthenium dioxide and 1 part by weight of niobium pentoxide in a closed fire clay crucible for 4 hours at 1,400° C. It was analyzed to confirm the absence of the individual starting components. It was then mixed with 11.33 g. of 1-3 micron silver oxide powder and 6.65 g. of zinc borosilicate glass and ball milled in water for 24 hours, removed from the water by filtration and dried. 18 g. of the resulting milled material was then suspended in 7 g. of a medium formed by dissolving 10 g. of ethyl cellulose in 100 ml. of butyl glycol ester and mixed thoroughly in a triple roll mill.

The resulting composition was then screen printed on to about 100 mica sheets so as to form coatings approximately 0.0005 inch thick following which the coated sheets were fired by passing them at uniform speed through the 600° C.—650° C.—600° C. zone of a lehr furnace in 20 minutes.

The electrical characteristics of at least 25 of the resulting resistive coatings were measured and it was found that the mean resistivity was 80,000 ohms per square per 0.001 inch thickness of coating. The mean temperature coefficient of resistivity was +100 p.p.m. per °C. The Nb:Ru ratio in the oxide material of the invention used in the example was approximately 1:4.

EXAMPLE 4

Example 3 was repeated but with the 11.33 g. of silver oxide powder of the initial composition replaced by 10.55 g. of 1-3 micron silver powder. In this case the resulting resistive coatings had a mean resistivity of 2,000 ohms per square per 0.001 inch thickness whilst the mean temperature coefficient of resistivity was +42 p.p.m. per °C.

EXAMPLE 5

Example 4 was repeated except that in this case the composition of the initial mixture was:

5 g. of oxide material

7.5 g. of 1-3 micron silver powder

6.72 g. of zinc borosilicate glass.

The resulting resistive coatings had a mean resistivity of 30 ohms per square per 0.001 inch thickness, and a mean temperature coefficient of resistivity of +100 p.p.m. per °C.

EXAMPLES 6-16

The following examples show resistance characteristics obtained from varying ratios of Nb:Ru in resistive elements made from an oxide material according to the invention.

Example No.	Resistance (ohm per sq./mil.)	% w/w Glass component present	Temperature coefficient of resistivity (+250°-+125° C.)	Ratio Nb:Ru
6	50	27.5	+250	1:4
7	100	30.0	+150	1:4
8	200	32.0	-50	1:4
9	1000	36.5	-100	1:11
10	2000	38.5	-200	1:11
11	10000	43.0	-300	1:55
12	20000	47.5	-350	1:55
13	100000	49.0	-450	1:1110
14	200000	51.0	-550	1:1110
15	1000000	56.0	-600	1:1110
16	2000000	57.5	-800	1:1110

In these examples the glass was zinc oxide-silica-boric acid based but also contained small quantities of alumina and zirconia.

EXAMPLE 17

40.7 g. of the oxide material used in example 6 was replaced by 47.7 g. 1-3 micron finely divided silver powder.

The resistance obtained from the resistor prepared was 50 ohms per square per 0.001 inch thickness with a temperature coefficient of resistivity of 100 p.p.m.°C. (Range: -55° C. to +125° C.). Use of silver therefore gave a lower positive temperature coefficient.

EXAMPLE 18

37.7 g. of the oxide material used in example 10 was replaced by 35.4 g. 1-3 micron finely divided silver powder.

The resistance obtained from the resistor prepared was 2,000 ohms per square per 0.001 inch thickness with a temperature coefficient of resistivity of zero p.p.m. per °C. for the range -55° C. to +125° C.

The invention also includes a resistor or resistor element embodying a film including the oxide material of the invention fired on to a suitable substrate.

What is claimed is:

1. A resistor composition suitable for firing on to a nonconducting substrate to form a resistor element comprises a new composition of matter in the form of an oxide containing niobium and ruthenium in which the atomic ratio of metal to oxygen is 1:2 and in which the atomic ratio of niobium to ruthenium is within the range 1:2,000 to 1:1.

2. A resistor composition suitable for firing on to a nonconducting substrate to form a resistor element, the composition consisting essentially of oxygen, niobium and ruthenium in which the atomic ratio of metal to oxygen is 1:2 and in which the atomic ratio of niobium to ruthenium is within the range 1:2,000 to 1:1.

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3. A resistor composition according to claim 2 wherein the atomic ratio of niobium to ruthenium is within the range 1:1,110 to 1:4.

4. A resistor composition according to claim 3 wherein the atomic ratio of niobium to ruthenium is within the range 1:320.

5. A resistor composition according to claim 1 including from 90-20 weight percent of glass.

6. A resistor composition according to claim 1 including a metal precursor which decomposes on heating to produce a

metal selected from the group consisting of silver, gold and platinum and thereby assists in controlling the electrical characteristics of a resistor element made from the said composition.

7. A resistor composition according to claim 6 wherein the metal precursor is a silver oxide or a silver carbonate.

8. A resistor composition according to claim 6 wherein the said metal is present in an amount up to 75 weight percent of the total composition.

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