

[54] **COMPOSITIONS FOR STABLE LOW
RESISTIVITY RESISTORS**

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[63] Continuation-in-part of Ser. No. 246,976, April 24,
1972, abandoned.

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[51] Int. Cl. **H01b 1/06**

[58] Field of Search **252/518, 520, 521;
117/229**

[56]

References Cited

UNITED STATES PATENTS

3,553,109	1/1971	Hoffman	117/227
3,630,970	12/1971	Nelson	252/518

Primary Examiner—John D. Welsh

[57]

ABSTRACT

In finely divided resistor compositions containing dielectric material and a resistive oxide which is a polynary oxide of the approximate formula $A_2B_2O_7$, improved compositions additionally comprising finely divided SiO_2 or Al_2O_3 to enhance stability of resistors made therewith. Resistors of such compositions fired on ceramic substrates.

13 Claims, No Drawings

COMPOSITIONS FOR STABLE LOW RESISTIVITY RESISTORS

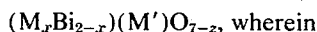
CROSS-REFERENCE TO RELATED APPLICATION

This is a continuation-in-part of my copending application Ser. No. 246,976, filed April 24, 1972 now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to resistor compositions, and, more particularly, to improved resistor compositions exhibiting reduced resistivity drift at room temperature.

Various metal oxides have been found to be useful in formulating compositions for printing on dielectric substrates and firing to form thick film resistors in electronic circuits. Such oxides are referred to herein as "resistive metal oxides" and include polynary metal oxides of the formula



M is at least one metal selected from the group consisting of yttrium, indium, cadmium, lead and the rare earth metals of atomic number 57-71, inclusive;

M' is at least one metal selected from the group consisting of platinum, titanium, tin, chromium, rhodium, iridium, ruthenium, zirconium, antimony and germanium;

x is a number in the range 0-2; and

z is a number in the range 0-1, being at least equal to about $\times/2$ when M is a divalent metal.

Compositions of these resistive metal oxides and dielectric material, and optionally noble metal and/or binary oxides, are described, for example, in Schubert U.S. Pat. No. 3,560,410; Hoffman U.S. Pat. No. 3,553,109; Popowich U.S. Pat. No. 3,630,969; and Bouchard U.S. Ser. No. 77,309, filed Oct. 1, 1970, now allowed, now U.S. Pat. No. 3,681,262.

A problem has been observed in resistors of such oxides; specifically, fired resistors made from low resistivity compositions, e.g., 100 ohms per square and lower (for 1-mil thick resistors), tend to change in absolute resistance value (drift) upon storage under room temperature no-load conditions. The degree of resistance change is strongly dependent upon the sheet resistivity of the resistor composition used and the size of the fired resistor. Under worst case conditions, e.g., sheet resistivities of 10 ohms per square or lower and resistor lengths of 0.040 inch or shorter, resistance changes after 1,000 hours at room temperature may be as high as 20 percent.

Due to the problem of room temperature resistance drift, the low resistivity oxide compositions have found commercial usage when used in conjunction with a glass-ceramic protective overcoat (e.g., Du Pont Encapsulant Composition 8185), which eliminates the room temperature drift problem. This approach of providing an overcoat, of course, involves an additional screen printing and firing step, which adds cost to the circuit.

Brady U.S. Pat. No. 3,655,440 relates to resistor compositions said to produce resistors stable at high voltages (column 1, line 40). Resistive oxides shown are those of PdO, RuO₂ and IrO₂. Alumina and barium ferrite are said to control the growth of the crystals of

PdO, RuO₂ and IrO₂, which is said to produce such resistors stable at high voltages. However, there is a need for resistor compositions of polynary metal oxides capable of producing fired resistors which combine low resistivity (about 100 ohms per square or less) with reduced low temperature drift, without requiring encapsulation.

SUMMARY OF THE INVENTION

In finely divided compositions for printing resistor materials on dielectric substrates, said compositions comprising resistive metal oxides and dielectric material, wherein the resistive oxide is a polynary oxide of the formula $(M_xBi_{2-x})(M')O_{7-z}$, wherein

M is at least one metal selected from the group consisting of yttrium, indium, cadmium, lead and the rare earth metals of atomic number 57-71, inclusive;

M' is at least one metal selected from the group consisting of platinum, titanium, tin, chromium, rhodium, iridium, ruthenium, zirconium, antimony and germanium;

x is a number in the range 0-2; and

z is a number in the range 0-1, being

at least equal to about $\times/2$ when M is a divalent metal,

this invention provides improved compositions additionally comprising a free additive oxide which is Al₂O₃ as corundum, SiO₂ or a mixture thereof, in amounts varying from an amount effective to reduce room temperature drift in fired resistors of such compositions up to about 25 percent, based on the weight of said resistive metal oxide, said additive oxide having an average particle size in the range 0.1-5 microns.

Also provided are dispersions of such improved compositions in inert vehicle and resistors of such compositions obtained by printing and firing the improved compositions on a dielectric substrate.

DETAILED DESCRIPTION

Compositions of the resistive metal oxides described above and dielectric material (e.g., glass) and optional components (e.g., noble metals and binary metal oxides such as Co₃O₄, etc.) have been found useful in printing (usually by screening or mask printing in an inert liquid vehicle) on dielectric substrates and firing to produce thick film resistors. This invention is an improvement invention regarding such compositions and fired resistors thereof. Resistive oxide synthesis, printing and firing techniques are those known in the art from, inter alia, the patents mentioned above. Selection and proportions of materials (resistive oxide, dielectric material, vehicle) will depend upon the application technique used and resistor properties desired; the present invention relates to an additive in known systems.

Known compositions exhibit significant room temperature drift in resistivity, the degree of which is dependent upon several variables, including sheet resistivity of the resistor composition, length of the fired resistor, type of termination material, and thickness of termination material.

The present invention provides improved compositions and resistors thereof, additionally comprising certain additive oxides. The additive oxide is Al₂O₃, SiO₂ or mixtures thereof. The crystalline form of the Al₂O₃ used is corundum. The SiO₂ may be either fused silica,

or crystalline silica such as quartz, tridymite or cristobalite. Fused silica is preferred among the forms of silica.

The amount of additive oxide is based upon the weight of the resistive oxide in the composition, and varies from an amount effective to reduce room temperature drift up to about 25 percent, expressed as weight percent of the weight of resistive oxide. Dependent upon the particular system employed, generally at least 2 percent additive is present to produce a significant reduction in drift.

The average particle size of the additive oxide is quite important and is in the range 0.1–5 microns, with substantially all particles less than 10 microns in diameter. The preferred additive is Al_2O_3 as corundum. Especially useful are two commercially available grades of alumina. One is a very fine grade having an average particle size in the range 0.3–1 micron and a fairly broad particle size distribution (Alcoa XA16 alumina). The other grade is coarser (average particle size in the range 3–4 microns) with a very narrow particle size distribution (Alcoa XA141).

In firing the improved resistor compositions of the present invention, it is important that the additive oxide remain substantially undissolved and appear as discrete particles in the fired resistor. Although not intended to be limiting, generally peak firing temperatures in the range 750° to 860°C., for 4–15 minutes at peak, are used.

EXAMPLES AND COMPARATIVE SHOWINGS

The following examples and comparative showings are given to illustrate the present invention and to distinguish it from the prior art. In the following and elsewhere in the specification and claims, all parts, percentages and ratios are by weight.

Resistor compositions were prepared as follows. Inorganic solids (resistive oxide, additive oxide, inorganic binder and optional noble metal) were dispersed in a liquid organic vehicle (8 percent ethyl cellulose and 92 percent β -terpineol). Resistors were prepared by first applying and firing Pd/Ag ($\frac{1}{2}$) end terminations and then screen printing (165 mesh screen) the resistor composition, on prefired dense alumina (96 percent) substrates. The firing in each run consisted of a 45-

lynary oxide $\text{Bi}_2\text{Ru}_2\text{O}_7$; the frit was a lead borosilicate frit (63 percent PbO , 26 percent SiO_2 , 10 percent B_2O_3 and 1 percent Al_2O_3). No additive oxide was employed. In Showings A and B, 51.8 g. bismuth ruthenate, 25.0 g. frit and 1.0 g. Pt were dispersed in sufficient vehicle to make 100 g.; in Showings C and D, 43.7 g. $\text{Bi}_2\text{Ru}_2\text{O}_7$ (bismuth ruthenate), 31.0 g. frit and 1.0 g. Pt were dispersed in sufficient vehicle to make 100 g. The solids/vehicle ratio was 3/1.

Table I presents typical resistance changes after 1,000 hours for 10 ohms per square and 100 ohms per square compositions. Under worst case conditions (10 ohms per square composition; 0.040 inch long resistors), changes as high as 20 percent were observed.

TABLE I

Showing	Sheet Resistivity (ohms per square)	Resistor Length (inches)	% ΔR after 1000 hrs.
A	10	0.200	+1 to 2
B	10	0.040	+9 to 20
C	100	0.200	0 to +0.4
D	100	0.040	+0.5 to 2.0

These showings illustrate the need for improved resistor compositions.

EXAMPLES 1–4; SHOWINGS E AND F

The polynary oxide and frit of Comparative Showings A–B were used and Al_2O_3 was substituted for some of the frit in Examples 1–4, as noted in Table II. The Al_2O_3 was Alcoa XA16, average particle size about 0.3–1.0 micron. The solid/vehicle ratio was 3/1. The resultant 1-mil thick resistors were 40 mils long; performance data are shown in Table II.

In Table II low-R resistors without Al_2O_3 addition are seen to drift markedly (Showing E) at various times, whereas in Examples 3 and 4, at 6 percent Al_2O_3 based on total solids in dispersion (10.7 percent Al_2O_3 based on resistive oxide), drift is minimized to a striking degree.

In Showing F, alumina alone without frit is seen to be unacceptable due to very high resistivity and rate of drift.

TABLE II

Example/Showing	Compositions (Based on Total Inorganics)		Wt. % Al_2O_3 Based on Polynary Oxide	Initial R (ohm/sq.)	% ΔR			
	% Frit	% Al_2O_3			13.5 hr.	40.5 hr.	137 hr.	8040 hr.
E	18.0	0	0	5.5	+0.59	+1.80	+4.84	+15.5
1	17.1	0.9	1.6	5.4	+0.51	+0.72	+1.44	+9.31
2	16.2	1.8	3.2	5.4	+0.04	+0.80	+1.21	+9.14
3	12.0	6.0	10.7	8.2	–0.01	–0.02	–0.01	+0.33
4	12.0	6.0	10.7	9.4	+0.01	N.D.*	0.02	+0.38
F	0	18.0	32.0	1600	+74.2	N.D.*	N.D.*	+1361

*N.D. means not determined.

minute cycle with 6–7 minutes at peak temperature (760°C.), and heating and cooling rates of about 60 40°C./minute.

The resistivity of the fired resistors was then determined after firing and after the number of hours of standing under no-load conditions, as indicated in each example.

COMPARATIVE SHOWINGS A–D

In these showings the resistive oxide used was the po-

EXAMPLE 5

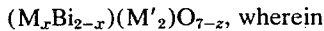
In this example silica (fused quartz) was used as the additive oxide. A composition was prepared from 49.5 parts $\text{Bi}_2\text{Ru}_2\text{O}_7$, 2.5 parts Pt, 18.5 parts of the lead borosilicate frit of Showings A–D, 0.5 parts of a cadmium borosilicate frit (78 percent CdO , 9.0 percent SiO_2 , 4.0 percent Al_2O_3 , and 9.0 percent B_2O_3), 6 parts fused quartz (–325 mesh) and 23 percent vehicle. There was 12.1 percent SiO_2 , based on $\text{Bi}_2\text{Ru}_2\text{O}_7$.

5

Resistors prepared as above had an initial resistivity of 15–16 ohms/square; percent ΔR after 21 hours was +0.23 percent, and after 42 hours +0.30 percent.

I claim:

1. Finely divided compositions for printing resistor materials on dielectric substrates, said compositions comprising resistive metal oxides and dielectric material, wherein the resistive oxide is a polynary oxide of the formula



M is at least one metal selected from the group consisting of yttrium, indium, cadmium, lead and the rare earth metals of atomic number 57–71, inclusive;

M' is at least one metal selected from the group consisting of platinum, titanium, tin, chromium, rhodium, iridium, ruthenium, zirconium, antimony and germanium;

x is a number in the range 0–2; and

z is a number in the range 0–1, being

at least equal to about $x/2$ when M is a divalent metal, said compositions additionally comprising a free additive oxide which is Al_2O_3 as corundum, SiO_2 or a mixture thereof, the additive oxide being in an amount effective to reduce room temperature resistivity drift in fired resistors of such compositions, the amount of the free additive oxide being up to about 25 percent by weight, based on the weight of said resistive metal oxide, said additive oxide having an average particle size in the range 0.1–5 microns.

2. Compositions according to claim 1 wherein the additive oxide is Al_2O_3 as corundum.

3. Compositions according to claim 1 wherein the additive oxide is SiO_2 .

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4. Compositions of claim 1 dispersed in an inert liquid vehicle.

5. Compositions of claim 2 dispersed in an inert liquid vehicle.

6. Compositions of claim 3 dispersed in an inert liquid vehicle.

7. Compositions according to claim 2 wherein the average particle size of the Al_2O_3 is in the range 0.3–4 microns.

8. Improved film resistors on dielectric substrates, useful in electronic circuits, which resistors exhibit reduced room temperature resistivity drift, said resistors comprising the resistive metal oxides of claim 1, dielectric material, and, as an additive oxide, Al_2O_3 as corundum, SiO_2 or mixtures thereof, in amounts ranging from 2 up to 25 percent, based on the weight of the resistive metal oxide, the additive oxide having an average particle size in the range 0.1–5 microns.

9. Improved resistors according to claim 8 wherein the additive oxide is Al_2O_3 as corundum.

10. Improved resistors according to claim 8 wherein the additive oxide is SiO_2 .

11. Improved film resistors on dielectric substrates, useful in electronic circuits, said resistors comprising the resistive metal oxide of claim 1, dielectric material and, as an additive oxide, Al_2O_3 as corundum, SiO_2 or mixtures thereof, the additive metal oxide being in an amount effective to reduce room temperature resistivity drift, the amount of the additive oxide being up to about 25 percent by weight, based on the weight of said resistive metal oxides, said additive oxide having an average particle size in the range 0.1–5 microns.

12. Improved resistors according to claim 11 wherein the additive oxide is Al_2O_3 as corundum.

13. Improved resistors according to claim 11 wherein the additive oxide is SiO_2 .

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