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THERMISTOR COMPOSITIONS AND THERMISTORS MADE THEREFROM

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ABSTRACT OF THE DISCLOSURE

The invention relates to thermistor compositions which, upon being fired onto a ceramic substrate, yield glaze thermistors having resistance values of from about 500 to about 5,000 ohms/square and temperature coefficient of resistance values of from about —5,000 to —700 p.p.m./° C., consisting essentially of:

(I) 20 to 50% of a finely divided noble metal powder, and

(II) 50 to 80% of a finely divided inorganic binder powder.

The noble metal powder consists essentially of (a) 15 to 85% of a finely divided palladium or ruthenium powder or a mixture thereof, (b) 15 to 85% of a finely divided rhodium powder and (c) 0 to 12% of a finely divided silver or gold powder or a mixture thereof. The choice of metals, proportions thereof and proportions of inorganic binder are selected to provide thermistor compositions which then printed and fired will produce glaze thermistors possessing the desired resistances and temperature coefficients of resistance. Additionally, an inert vehicle may also be included to disperse the powders.

CROSS-REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part of my copending application Ser. No. 583,925, filed Oct. 3, 1966, now abandoned.

BACKGROUND OF THE INVENTION

Thermistors are electrical resistors made of materials whose resistance varies sharply in a known manner with temperature. Thermistors whose resistances decrease with an increase in temperature are said to have a negative temperature coefficient of resistance (—TCR), while thermistors whose resistances increase with an increase in temperature are said to have a positive temperature coefficient of resistance (+TCR). Many interesting commercial and industrial applications for thermistors have been developed in the last few years, and thermistors are available in a large variety of types covering a broad range of electrical characteristics. Thermistors are ideal for temperature controls and temperature sensing devices and can also be used to produce temperature compensating properties in various electrical circuits.

Resistor compositions comprising mixtures of two finely divided metals with glass are well known. More particularly, resistor compositions comprising mixtures of noble metals have been produced heretofore, for example, as shown by U.S. Pats. 2,924,540, 2,950,995, and 2,950,996. These patents also teach that by making adjustments in the metal to glass ratio, resistor compositions can be printed and fired to produce resistors having various desired resistance values.

The art is also cognizant of the fact that every noble metal has a different temperature coefficient of resistance

(TCR). Some are positive; some are negative. Therefore, it might be thought that the use of a blend of two or more metals in a resistor composition should produce a resistor having a TCR equal to the average TCR of the individual metals. However, such does not always hold true. For example, if a resistor composed of metal "A" has a TCR of +3,000 p.p.m./° C. and a resistor composed of metal "B" has a TCR of —3,000 p.p.m./° C., it would be expected that a resistor comprising a 50/50 mixture of these two metals would have a TCR equal to substantially zero. In actuality, this is not the case and the TCR of the mixture usually varies 100 to 1,000 p.p.m./° C., on the positive or negative side, from the expected or theoretical TCR. Consequently, adjustments have to be made to the ratio of the metals in order to obtain the desired TCR.

A similar, but greater, problem exists when attempts are made to obtain a desired resistance (R) from a resistor composition which contains a mixture of metals. Of course, the conventional method of attaining the desired resistance is by adjusting the overall metal to glass ratio. The resistance increases as the proportion of glass increases; and, conversely, the resistance decreases as the proportion of metal increases. This conventional method of attaining the desired resistance by adjusting the metal to glass ratio is not always successful, especially when mixtures of metals are utilized. Sometimes the proportion of glass becomes too high or too low so as to seriously affect the adhesion or bonding properties of the resistor composition. It is then that the proportions of each metal must also be varied to produce the desired resistance.

Thus, it can be seen that various adjustment have to be made to attain either a particular resistance or a particular temperature coefficient of resistance. The situation becomes much more complicated and involved when a goal is set to produce a resistor with a specific resistance and a specific temperature coefficient of resistance. For example, palladium has a positive TCR and rhodium has a negative TCR. It should be possible to obtain the desired TCR by blending palladium and rhodium. However, it is not likely that the desired temperature coefficient of resistance and the desired resistance would be obtained simultaneously from the same blend of metals with a constant metal to glass ratio.

Prior to the present invention, no acceptable and reliably printable thermistor compositions of a noble metal mixture and glass were known to produce thermistors that exhibit resistances of 500 to 5,000 ohms/square and temperature coefficients of resistance of —5,000 to —700 p.p.m./° C. A definite need exists for these printable thermistor compositions which have both (a) the desired resistance and (b) the desired temperature coefficient of resistance set forth above, since these compositions produce glaze thermistors which are ideal for modern temperature controls and temperature sensing devices. More importantly, thermistors possessing the above properties can be extremely useful in producing temperature compensating properties in various electrical circuits.

DESCRIPTION OF THE INVENTION

This invention relates to highly useful thermistor compositions which can be printed and fired on a substrate to produce glaze thermistors having a resistance value in the range from about 500 to about 5,000 ohms/square and a temperature coefficient of resistance value of from about —5,000 to about —700 p.p.m./° C., that is to say, the glaze thermistors have a given resistance value and a given temperature coefficient of resistance value within the respective stated ranges. Briefly, this is accomplished by utilizing a mixture of certain finely divided metals and an inorganic binder in particular critical proportions.

Accordingly, the thermistor compositions of the present invention are compositions which yield, upon firing onto a ceramic substrate, glaze thermistors having a resistance value in the range of from about 500 to about 5,000 ohms/square and a temperature coefficient of resistance value in the range of from about —5,000 to about —700 p.p.m./° C., and which consist essentially of:

(I) 20 to 50% of a finely divided noble metal powder, and

(II) 50 to 80% of a finely divided inorganic binder powder.

The noble metal powder consists essentially of (a) 15 to 85% of a finely divided palladium or ruthenium powder or a mixture thereof, (b) 15 to 85% of a finely divided rhodium powder and (c) 0 to 12% of a finely divided silver or gold powder or a mixture thereof. The proportions of (a) and (b) are controlled so as to provide a predetermined temperature coefficient of resistance (TCR) for the glaze thermistor within said range of —5,000 to —700 p.p.m./° C. The effect of increasing the proportion of (a) is to increase the positivity of said TCR and the effect of increasing the proportion of (b) being to increase the negatively of said TCR. The proportions of (II) and (c) in said composition are controlled so as to provide a predetermined resistance value for the glaze thermistor within said range of 500 to 5,000 ohms/square, the effect of increasing the proportions of (II) being to increase said resistance, and the effect of increasing the proportions of (c) being to decrease said resistance.

Especially useful are thermistor compositions which yield glaze thermistors with TCR values in the range —5,000 to —1,000 p.p.m./° C.

Such thermistor compositions may be dispersed in a liquid vehicle, preferably inert, to provide a themistor paint or paste that can be applied to the surface of a ceramic dielectric and fired to form a fixed stable thermistor.

The metal and inorganic binder-containing thermistor compositions of this invention exploit a particular combination of proportions such that the compositions may be readily fired to provide easily reproducible thermistors of good stability. These thermistors have resistances in the desirable range of from 500 to 5,000 ohms/square and temperature coefficients of resistance ranging from —5,000 to —700 p.p.m./° C. By properly adjusting the proportions of the metals to each other and to the inorganic binder, printed and fired thermistors having the above-mentioned resistances and temperature coefficients of resistance can be tailor-made in accordance with the teachings described herein.

As indicated above, any of the palladium, ruthenium, rhodium, silver, gold and inorganic binder ingredients which are used should be in a finely divided or powder form, i.e., in the form of a powder sufficiently finely divided to pass through a 325 mesh (U.S. Standard Sieve Scale) stencil screen, said powder having particles no larger than about 40 microns. Generally, the powder will have an average particle size not exceeding 20 microns. Desirably, the average particle size of the metals will range from 0.1 to 5 microns while an average particle size range of 1 to 10 microns for the inorangic binder is preferred. The powders may be obtained through conventional methods. For example, the metals can be produced by chemical precipitation or by mechanical comminution.

The proportions of the various metals and inorganic binder are critical and must conform with the prescribed limits. Palladium, rhodium and ruthenium are the primary metals used in this invention. The weight ratios of these metals to each other mainly have an effect on the temperature coefficient of resistance; but, in addition, they have an effect on the resistance when considered in relation to the overall metal to inorganic binder ratio.

When used as the only metal in thermistors, palladium and ruthenium yield positive TCR's, while rhodium yields a negative TCR. Accordingly, the desired TCR can be obtained by proper adjustment of the ratios of these metals within the prescribed ranges. It has been found that palladium, ruthenium or a mixture thereof can be present in amounts ranging from 15 to 85% by weight of the total noble metal content. Also, rhodium can be present in amounts ranging from 15 to 85% by weight of the total noble metal content. A preferred range is 45 to 55%.

The inorganic binder to metal weight ratio has an effect on the resistance and on the bond strength of the printed and fired thermistor. As the proportionate amount of binder increases, the resistance and bond strength increases in the thermistor. A proper balance must be maintained between the bond strength and resistance. High bond strength is very desirable; but a very high resistance value is not preferred, although resistances up to 5,000 ohms/square are within the scope of this invention. Therefore, the amount of inorganic binder should range from 50 to 80% by weight of the total weight of the finely divided powders (metals and inorganic binder). If the glass (inorganic binder) content of the thermistor composition is below 50% by weight of the finely divided powders, the printed and fired thermistor will have poor adhesion (bond strength) to the substrate. If the glass content is above 80%, the resistivity of the thermistor will be too high for the purposes of this invention. The preferred range is 65 to 75% by weight of inorganic binder based on the combined weight of the metals and inorganic binder. Correspondingly, the metals account for 25 to 35% of the combined weight of metals and inorganic binder in the preferred range.

Additionally, silver and/or gold may be included in the thermistor composition to control the resistance value of the thermistor separate and distinct from the TCR adjustment and from the bonding adjustment. When the resistance obtainable with any thermistor composition within the scope of this invention becomes too high, a small amount of silver and/or gold can be added to lower the resistance. For example, when the inorganic binder is used in large proportionate amounts to produce high bond strength, the resistance becomes too high. Instead of adding more palladium, rhodium or ruthenium (which would affect the temperature coefficient of resistance in addition to reducing the resistance), a small amount of silver and/or gold is added. It has been found that small amounts of silver and/or gold substantially reduce the resistance without substantially altering or affecting the temperature coefficient of resistance. Thus, up to 12% by weight (based on total noble metal content of the compositions) of finely divided silver and/or gold can be utilized as desired in the thermistor compositions of this invention to independently adjust the resistance. A range of 4 to 12% is preferred.

Any inorganic material which serves to bind the metals to the substrate can be used as the inorganic binder component. The inorganic binder can be any of the glass frits employed in resistor compositions of this general type. Such frits are generally prepared by melting a glass batch composed of the desired metal oxides, or compounds which will produce the glass during melting, and pouring the melt into water. The coarse frit is then milled to a powder of the desired fineness. The patents to Larsen and Short, U.S. Pat. No. 2,822,279, and to Hoffman, U.S. Pat. No. 3,207,706, describe some frit compositions which can be employed either alone or in combination with glass wetting agents such as bismuth oxide. Typical frit compositions usable as binders in the composition of this invention include lead borate, lead silicate, lead borosilicate, cadmium borate, lead-cadmium borosilicate, zinc borosilicate and sodium-cadmium borosilicate. A preferred frit composition is a lead monosilicate glass of the formula $PbO \cdot SiO_2$, although useful lead silicates include

those wherein the ratio of lead oxide to silicon oxide varies all the way from $2PbO \cdot SiO_2$ to $PbO \cdot 2SiO_2$.

The thermistor compositions of the invention will usually, although not necessarily, be dispersed in an inert vehicle to form a paint or paste for application to various substrates. The proportion of vehicle to thermistor composition may vary considerably depending upon the manner in which the paint or paste is to be applied and the kind of vehicle used. Generally, from 1 to 20 parts by weight of thermistor composition (metals and inorganic binder) per part by weight of vehicle will be used to produce a paint or paste of the desired consistency. Preferably, 4 to 10 parts per part of vehicle will be used.

Any liquid, preferably inert, may be employed as the vehicle. Water or any one of various organic liquids, with or without thickening and/or stabilizing agents, and/or other common additives, may be utilized as the vehicle. Examples of organic liquids that can be used are the higher alcohols; esters of such alcohols, for example, the acetates and propionates; the terpenes such as pine oil, alpha- and beta-terpineol and the like; and solutions of resins such as the polymethacrylates of lower alcohols, or solutions of ethyl cellulose, in solvents such as pine oil and the monobutyl ether of ethylene glycol monoacetate (butyl—O—CH_2CH_2—$OOCH_3$). The vehicle may contain or be composed of volatile liquids to promote fast setting after application; or it may contain waxes, thermoplastic resins or the like materials which are thermofluid so that the vehicle-containing composition may be applied at an elevated temperature to a relatively cold ceramic body upon which the composition sets immediately.

The thermistor compositions are made by admixing the metals and inorganic binder solids in the proportions of 20 to 50% and 50 to 80%, respectively, based on their total combined weights. Additionally, one part of an inert vehicle for every 1 to 20 parts of solids mentioned above may be admixed. Then the thermistor composition is applied to a ceramic body and fired to form a stable thermistor.

Application of the thermistor composition in paint or paste form to the substrate may be effected in any desired manner. It will generally be desired, however, to effect the application in precise pattern form, which can be readily done empolying well-known screen stencil techniques or methods. The resulting print or pattern will then be fired in the usual manner at a temperature from about 650 to 820° C. (1200 to 1500° F.) in an air atmosphere employing the usual firing lehr.

The invention is illustrated by the following examples. In the examples and elsewhere in the specification, all parts, ratios and percentages of materials or components are by weight.

Various thermistor compositions were prepared employing finely divided metals and inorganic binder in varying proportions. The particle sizes of the metals and inorganic binder ranged from 0.1 to 20 microns, which are sufficiently finely divided to pass through a 325 mesh (U.S. Standard Sieve Scale) stencil screen. All were suspended in an inert vehicle consisting of 8% ethyl cellulose and 92% beta-terpineol. In Examples 1 to 6 the weight ratio of solid thermistor composition to vehicle was 1 to 1, while in Example 7 to 14 the ratio was 4 to 1 to insure paints having a preferred consistency. The paints were printed onto alumina substrates and fired to 760° C. (1400° F.) for 45 minutes. The resistance (R) and temperature coefficient of resistance (TCR) were determined for each example. TCR values were based upon determinations in the range −40° C. to +120° C.

TABLE I

Ex. No.	Inorganic binder [1]	Pd	Rh	Ru	Ag	R (ohms/square)	TCR (p.p.m./° C.)
1	50	50	0	0	0	2,000	+2,000
2	50	25	25	0	0	1,800	−3,500
3	50	10	40	0	0	4,000	−4,700
4	50	0	50	0	0	9,000	−6,000
5	50	0	0	50	0	2,000	+4,000
6	68	15	15	0	2	1,360	−3,000

[1] A lead monosilicate glass frit ($PbO \cdot SiO_2$) was utilized.

It should be pointed out that Examples 1, 4 and 5 are not part of this invention since only one metal is used in each of those examples while the present invention requires the use of at least two metals. Examples 1, 4 and 5 are set forth merely to show some starting base resistance values and temperature coefficients of resistance for palladium, rhodium and ruthenium in a metal to glass binder ratio of 50 to 50. With the latter values in mind, a skilled artisan can begin to use mixtures of the metals to produce the desired R and TCR.

In Examples 1 to 5, it can be seen that the overall glass to metal ratio remained constant. The resistances and temperature coefficients of resistance were controlled by using different metals in varying proportions. This is in contrast to Example 6 where the proportionate amount of glass was increased to increase the bond strength of the thermistor. Correspondingly, the proportionate amounts of metals were decreased. However, the resistance was controlled by adding a small amount of silver. For instance, compare Examples 2 and 6. The amount of glass used in Example 6 was 18% more than in Example 2. While the bond strength would be increased, the resistance would also be increased due to the higher glass content. However, to control the resistance a small amount of silver was added. Note that the resistances in Examples 2 and 6 are similar in spite of the substantial difference in glass to metal ratio. The TCR values are also similar, but this is due to the constant palladium to rhodium ratio. Thus, it is readily apparent that the resistance and temperature coefficients of resistance can be adjusted to the desired needs while also obtaining proper bond strength.

Additionally, the above examples demonstrate the unexpected results of this invention. In particular, it is shown that silver may be added to the thermistor composition to control the resistance of the printed thermistor without materially affecting the temperature coefficient of resistance.

In the following examples various combinations of metal to metal and metal to glass ratios are utilized to further demonstrate the versatility and usefulness of this invention.

It can be seen from the tabulated data in Tables I and II that a proper balance must be maintained among the various metals and between the total metals and inorganic binder so as to obtain the desired resistance and temperature coefficient of resistance. Particular significance is attached to the fact that small amounts of silver or gold may be added to adjust the resistance when desired without significantly affecting the temperature coefficient of resistance.

TABLE II

Example number	Inorganic binder [1]	Pd	Rh	Ru	Ag	Au	R (ohms/square)	TCR (p.p.m./° C.)
7	70	15	15	0	0	0	700	−900
8	70	20	10	0	0	0	1,100	−850
9	70	25	5	0	0	0	1,100	−650
10	75	12.5	12.5	0	0	0	2,200	−1,700
11	80	10	10	0	0	0	4,500	−1,800
12	75	12	12	0	1	0	1,200	−1,700
13	75	11.5	11.5	0	2	0	800	−1,600
14	75	11	11	0	3	0	500	−1,600

[1] A lead monosilicate glass frit ($PbO \cdot SiO_2$) was utilized.

By using the teachings of this invention, thermistor compositions which can be printed and fired to yield thermistors having various resistances, temperature coefficients of resistance and bonding strengths can be tailor-made through proper adjustment of the proportions of metals and inorganic binder as taught herein.

Since it is obvious that many changes and modifications can be made in the above-described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited to said details except as set forth in the appended claims.

What is claimed is:

1. A thermistor composition which yields, upon firing onto a ceramic substrate, a glaze thermistor having a resistance value in the range of from about 500 to about 5,000 ohms/square and a temperature coefficient of resistance value in the range of from about —5,000 to about —700 p.p.m./° C., consisting essentially of:

(I) 20 to 50% by weight of a finely divided noble metal powder, and

(II) 50 to 80% by weight of a finely divided inorganic binder powder;

said noble metal powder consisting essentially of (a) 15 to 85% by weight of a finely divided palladium or ruthenium powder or a mixture thereof, (b) 15 to 85% by weight of a finely divided rhodium powder and (c) 0 to 12% by weight of a finely divided silver or gold powder or a mixture thereof.

2. The composition of claim **1** which is dispersed in an inert vehicle, said composition being present in an amount of from 1 to 20 parts by weight per part of inert vehicle.

3. The composition of claim **1** wherein the average particle size of said finely divided components (I) and (II) does not exceed 20 microns.

4. The composition of claim **1** wherein the inorganic binder is a lead silicate glass.

5. The composition of claim **1** wherein the proportions by weight of (I) and (II) are 45–55% and 45–55%, respectively, and (II) is composed of 45 to 55% of (a) and 45 to 55% of (b).

6. The composition of claim **1** wherein the proportions by weight of (I) and (II) are 25–35% and 65–75%, respectively, and the amount of (c) in (I) is 4–12% by weight.

7. The composition of claim **6** which is dispersed in an inert vehicle, said composition being present in an amount of from 1 to 20 parts by weight per part by weight of inert vehicle.

8. The composition of claim **7** wherein the average particle size of said finely divided components (I) and (II) does not exceed 20 microns.

9. The composition of claim **6** wherein the inorganic binder is a lead silicate glass.

10. A glaze thermistor comprising a ceramic dielectric substrate having fired thereon a thermistor material of the composition of claim **1**.

11. A glaze thermistor comprising a ceramic dielectric substrate having fired thereon a thermistor material of the composition of claim **5**.

12. A glaze thermistor comprising a ceramic dielectric substrate having fired thereon a thermistor material of the composition of claim **6**.

References Cited

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DOUGLAS J. DRUMMOND, Primary Examiner