Jan. 25, 1966 W. E. BLODGETT ETAL 3,231,522

THERMISTOR

Filed Sept. 26, 1963 4 Sheets-Sheet 1

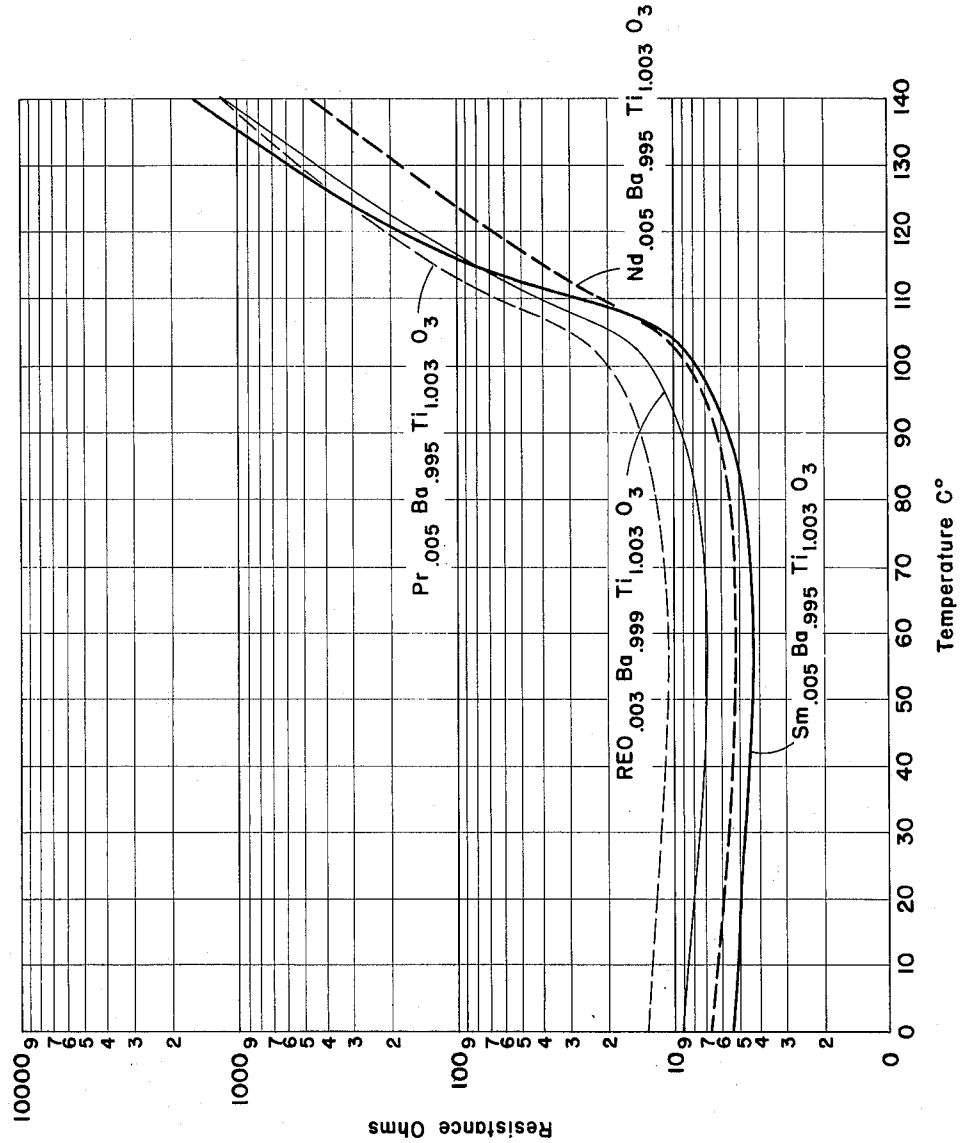
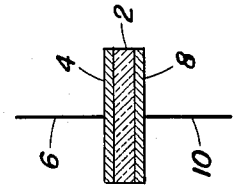


Fig. 2.

Fig. 1.



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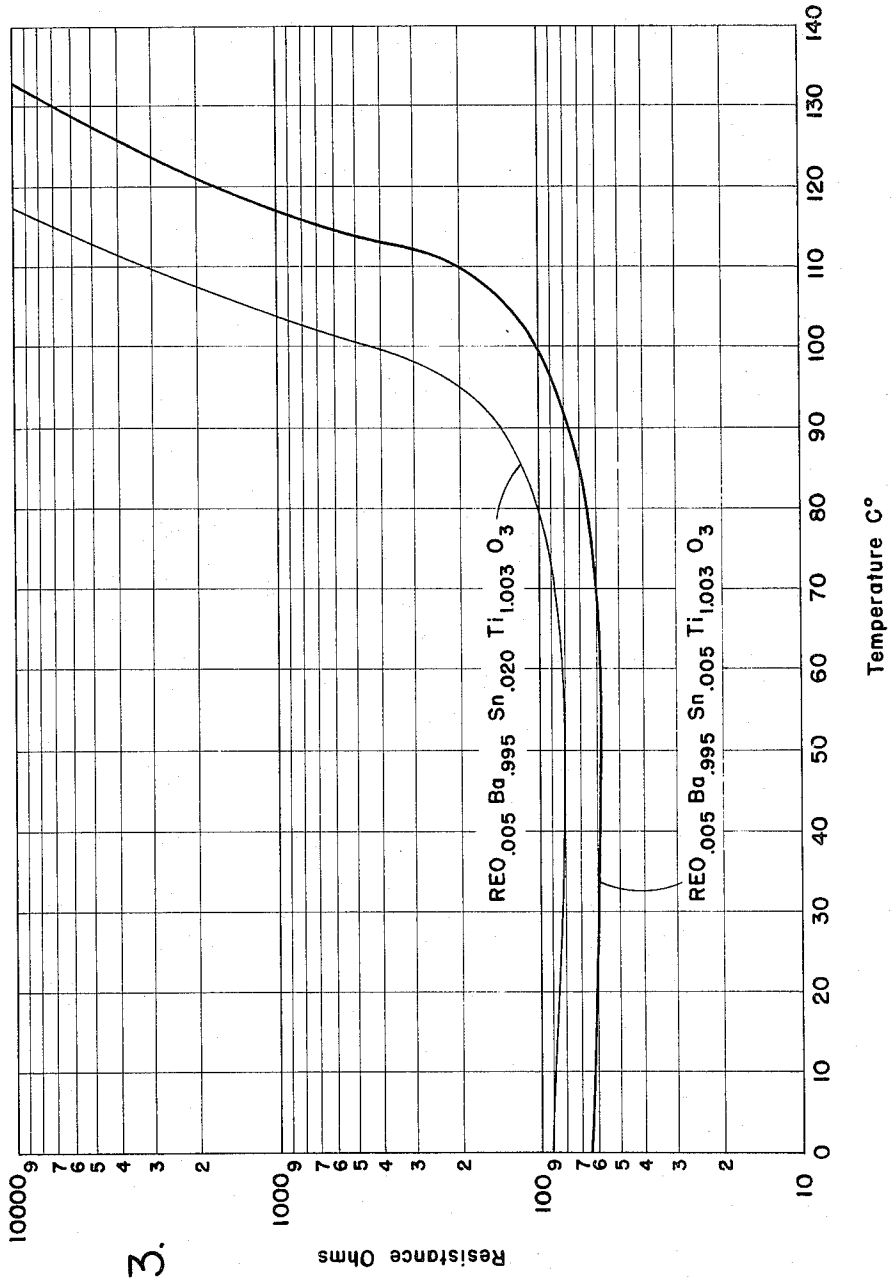


Fig. 3.

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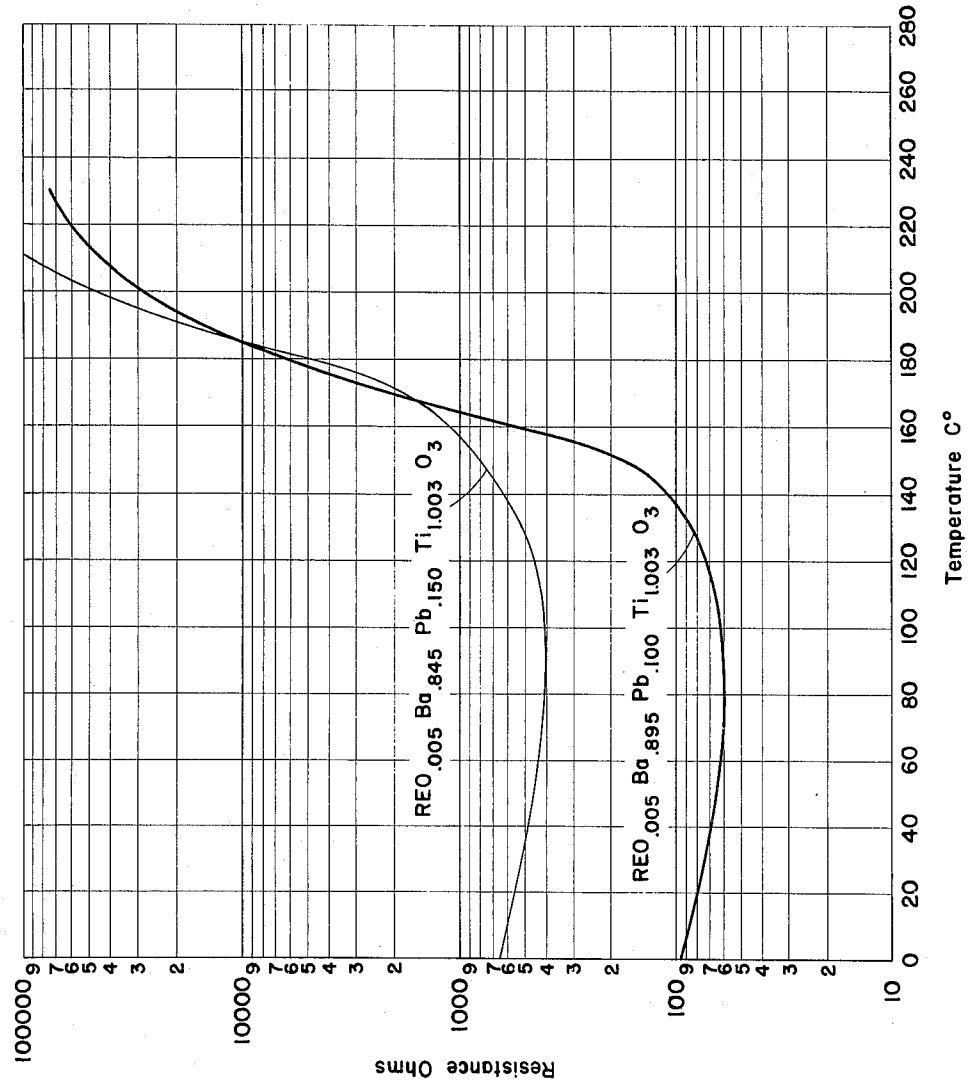


Fig. 4.

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Filed Sept. 26, 1963 4 Sheets-Sheet 4

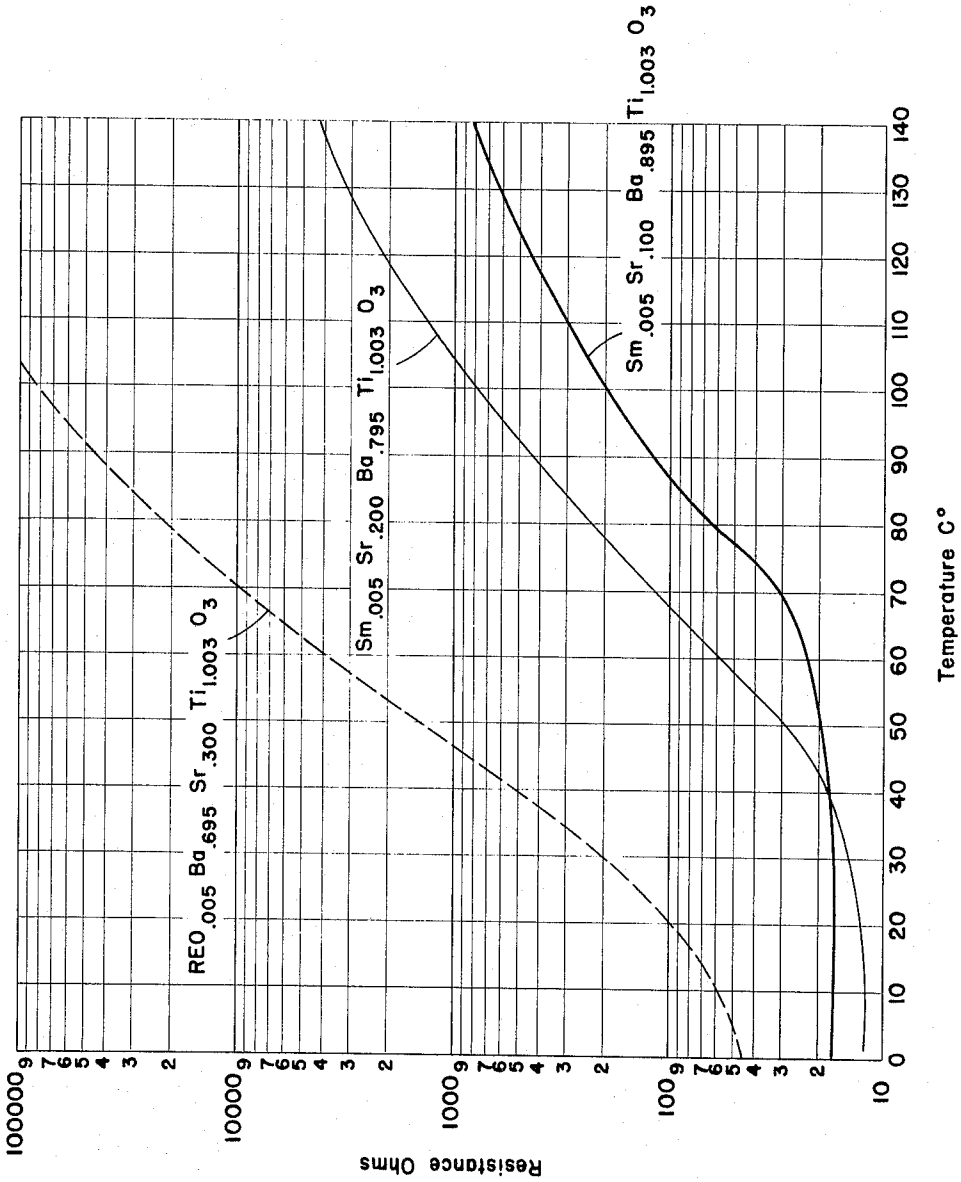


Fig. 5.

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3,231,522

THERMISTOR

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4 Claims. (Cl. 252—521)

This invention relates to thermistors having a positive temperature coefficient of electrical resistance and to processes for making such thermistors. The derivation of the word "thermistor" arises out of the contraction of the expression "thermally sensitive resistor."

Thermistors of this type find widespread applications. They may be used for highly sensitive thermostats and for automatic controls. Because of their high temperature coefficient in the temperature range of 110 to 120 degrees C. they can provide a "fail safe" protection circuit for electric motors by placing a thermistor in series with a relay. When the temperature exceeds the safe limit, the relay will open thereby cutting the power to the motor. A transistor of the present type in series with a light bulb, or an alarm, and a voltage source provides an excellent level indicator. When submerged the positive temperature coefficient thermistor, hereinafter called "PTC," cannot develop sufficient heat to cause a noticeable change in resistance but when the liquid level drops, exposing the PTC, it will heat up and extinguish the light or set off the alarm. In very small thermostats, a PTC can do double duty as a control element and as a heating element. A PTC and a negative temperature coefficient resistor in series with a light bulb and a voltage source form a thermic oscillator. Further, since current in a PTC resistor will reach a maximum value, or even decrease with increasing voltage, it can be used for current stabilization or current limiting applications.

With a view to obtaining new positive temperature coefficient thermistors having improved properties, the main object of this invention is to provide novel thermistors in which a greater degree of control can be exerted over the shape of the temperature versus resistance curve.

Another object of this invention is to provide new sintered barium titanate-based thermistors containing certain rare earth metal oxides as dopants.

An additional object of this invention is to provide sintered doped barium titanate-based thermistor compositions which have switch points at 60, 80, 120 and 180 degrees centigrade.

A still further object of this invention is to provide a process for preparing a barium titanate-based body which will exhibit the switch points noted in the preceding object.

These and other related objects, features and advantages of the present invention will be more readily understood as the description thereof proceeds, particularly when taken together with the accompanying drawing wherein:

FIGURE 1 is an elevational view of a thermistor in accord with the invention:

FIGURES 2 to 5 are graphs of the temperature versus the resistance for various compositions of the invention.

The thermistors of the present invention consist of ceramic materials composed essentially of, in mole per cents, 0.4 to 0.998 of barium oxide; 0.997 to 1.003 of titanium oxide, 0 to 0.300 of strontium oxide; 0 to 0.150 of lead oxide, 0.005 to 0.020 of tin oxide and from 0.001 to 0.006 of an oxide of a rare earth metal selected from the group consisting of praseodymium, neodymium, samarium and a mixture of rare earth metal oxides made up of cerium, lanthanum, neodymium, praseodymium, samarium, gadolinium, and yttrium. These components are intimately mixed in rubber lined balls mills with some distilled water, and then dried, calcined, reground, remilled, formed into pellets and fired.

In accordance with the invention there are provided members having a diameter of 9.52 mm. and 2.17 mm. in thickness. In the practice of this invention, titanium is provided in the form of titanium dioxide in electronic grade. Barium or strontium is provided in the form of carbonates in SL or reagent grades. Tin is provided in the tin oxide form, the reagent grade being preferred. Lead oxide may be introduced in that form, the analytical grade being preferred. The rare earth metal oxides are provided in that form while the mixture thereof is added in the form of a product sold commercially under the name "REO" mixture. The desired proportions of the constituents are weighed to the nearest 0.001 gm. and placed in rubber-lined balls mills with 1250 gm. of "Burundum" balls which previously are rinsed out with distilled water. Two mole equivalents of material and 500 cc. of distilled water are used per mill. Milling for about 8 hours at 75 r.p.m. gives a suitably homogeneous mixture which is oven dried at 100 degrees C. The dried powder next is placed in a refractory crucible, such as one of zirconia, and calcined at 1090° C. The sintered material plus 250 cc. of distilled water are placed in the mill and reground for 7 hours. One percent of a 10 percent of polyvinyl alcohol is added and milling is continued for about an hour. The mixture is then dried at 70° C. and screened through a minus 20 mesh screen. Pellets are formed at a pressure of about 10,000–20,000 p.s.i. and fired in an electric tube furnace, preferably in air, to either 1260° C., 1315° C. at 150° C. rise per hour. The formed pellets are soaked for one to four hours and cooled to room temperature. Previous patents have suggested elabrate firing techniques using argon. This is not only costly but produces PTC thermistors of inferior quality and lower temperature coefficients of resistance than those of the claimed compositions.

The sintered bodies are then provided with electrical contacts. These contacts are applied ultrasonically using pure indium, indium-silver or lead-tin solders. Number 12 solder composed of 90% lead, 5% indium and 5% silver gives the best bond and the lowest ohmic resistance. Suitable wire leads suitably made of copper can then be soldered to the contacts.

Referring to the drawing now, FIGURE 1 shows a thermistor 2 in accordance with the invention and comprising a body prepared from the compositions herein disclosed. An upper metal contact 4 is secured in ohmic contact with the body and a suitable electric lead 6 is welded or otherwise secured thereto. A lower contact 8 and its lead 10 are similarly provided on the bottom of the thermistor member. Epoxy encapsulating material was used on thermistors designed for a maximum operating temperature of 150° C. and silicone on thermistors with a maximum operating temperature of 250° C.

In evaluating the various thermistor compositions of this invention, D.C. resistance was measured on an impedance-type bridge, with the thermistors in an oil bath which was stirred at a constant rate of speed as the bath temperature was increased by an electric hot plate.

Various sintering schedules were employed in the preparation of the thermistors of the invention. The results obtained indicate that firing in argon lowers the PTC and the initial resistance and as more air is introduced into the firing cycle, the initial resistance increases as does the PTC effect. As a general rule, optimum properties are obtained by using still air conditions. However, the PTC effect can be increased by the introduction of very

small amounts of circulating air at the expense of increasing the resistance at a given temperature.

The compositions of the invention were heated according to the following conditions.

Condition No. 1.—Room temperature to 1260° C., 150° C./hour rise, 1 hour soak, fired in still air, cooled to room temperature in 10 hours.

Condition No. 2.—Room temperature to 1315° C., 150° C./hour rise, 1 hour soak, fired in still air, cooled to room temperature in 10 hours.

Condition No. 3.—Room temperature to 1370° C., 150° C./hour rise, 1 hour soak, fired in still air, cooled to room temperature in 10 hours.

Condition No. 4.—Same as above except top temperature held two hours.

The following examples serve to illustrate but do not limit the invention:

Example 1

Following the above described method, thermistors were prepared from the following compositions:

Composition	1	2	3	4	5	6	7	8
Barium	0.998	0.997	0.995	0.998	0.997	0.995	0.999	0.997
Titanium	1.003	1.003	1.003	1.003	1.003	1.003	1.003	1.003
Praseodymium	0.002	0.003	0.005	------	------	------	------	------
Neodymium	------	------	------	0.002	0.003	0.005	------	------
Samarium	------	------	------	------	------	------	0.001	0.003

Composition	9	10	11	12
Barium	0.995	0.998	0.997	0.995
Titanium	1.003	1.003	1.003	1.003
Samarium	0.005	------	------	------
Rare earth oxide (REO)	------	0.002	0.003	0.005

Cerium, 45.6%; lanthanum, 22.8%; neodymium, 16.2%; praseodymium, 4.7%; samarium, 2.8%; gadolinium, 1.9%; yttrium, 0.2%.

These compositions have a switch point of approximately 120° C. The optimum properties are summarized in the following table:

Rare earth	Mole percent dopant	Lowest initial resistance	Maximum temp. coefficient of resistance
Praseodymium	0.005	12 ohms	+25%/° C.
Neodymium	0.005	6 ohms	+17%/° C.
Samarium	0.005	50 ohms	+25%/° C.
"REO" blend	0.003	7 ohms	+17%/° C.

The resistance versus temperature curves for the above compositions are shown in FIGURE 2. Maximum temperature coefficient is achieved with praseodymium as the dopant with a value of +25%/° C. This material is ideal for static switching devices. For many commercial applications where cost is important "REO" blend as the dopant is significant. This material has a raw material cost of approximately $2 per pound as compared to $15 to $50 per pound for praseodymium, neodymium, and samarium. In certain applications requiring very low initial resistances neodymium and "REO" blend is ideal. The dopant used not only has an effect on slope of the curve but also in the initial resistance.

Example 2

Thermistors were prepared by the method of the invention using the following compositions:

Composition	13	14
Barium	0.995	0.995
Tin	0.005	0.020
Titanium	0.998	0.983
Rare earth oxide (REO)	0.005	0.005

Cerium, 45.6%; lanthanum 22.8%; neodymium, 16.2%; praseodymium 4.7%; samarium, 2.8%; gadolinium, 1.9%; yttrium. 0.2%.

The resistance versus temperature curves for the above compositions are shown in FIGURE 3. For composition No. 13 maximum temperature coefficient of resistance was +27%/° C. The addition tin improved substantially the steepness of the curve. For composition No. 14 where 0.020 mole tin were added the curve has been shifted downward somewhat and still maintained a steep curve. This type of thermistor has applications for controlling hot water.

Example 3

Thermistors were prepared by the method of the invention using the following compositions:

Composition	15	16
Barium	0.895	0.845
Lead	0.100	0.150
Titanium	1.003	1.003
Rare earth oxide (REO)	0.005	0.005

Cerium, 45.6%; lanthanum 22.8%; neodymium, 16.2%; praseodymium, 4.7%; samarium, 2.8%; gadolinium, 1.9%; yttrium, 0.2%.

The resistance versus temperature curves for the above compositions are shown in FIGURE 4. The use of lead has increased the switch points from 120° C. for compositions 1–12 (Example 1) to 160° C. for composition 15 and to 180° C. for composition 16. These types of thermistors have high temperature applications up to 250° C.

Example 4

Thermistors were prepared by the method of the invention using the following compositions:

Composition	17	18	19	20	21	22
Barium	0.898	0.897	0.895	0.798	0.797	0.795
Strontium	0.100	0.100	0.100	0.200	0.200	0.200
Titanium	1.003	1.003	1.003	1.003	1.003	1.000
Samarium	0.002	0.003	0.005	0.002	0.003	0.005

Composition	23	24	25
Barium	0.698	0.695	0.690
Strontium	0.300	0.300	0.300
Titanium	1.003	1.003	1.003
Rare earth oxide (REO)	0.002	0.005	0.010

Cerium, 45.6%; lanthanum, 22.8%; neodymium, 16.2%; praseodymium, 4.7%; samarium, 2.8%; gadolinium, 1.9%; yttrium, 0.2%.

The resistance versus temperature curves for the above compositions are shown in FIGURE 5. The effect of strontium additions is to shift the switch point from 120° C. to 80° C. for composition 19 (.100 Sr) to 60° C. for composition 22 (.200 Sr) to 30° C. for composition 24 (.300 Sr).

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is, therefore, to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A thermistor composition consisting essentially of a fired body formed from a mixture of 0.998 mole percent of barium oxide, 1.003 mole percent of titanium dioxide and 0.002 mole percent of praseodymium oxide.

2. A thermistor composition consisting essentially of a fired body formed from a mixture of 0.998 mole percent of barium oxide, 1.003 mole percent of titanium dioxide and 0.002 mole percent of neodymium oxide.

3. A thermistor composition consisting essentially of a fired body formed from a mixture of 0.997 mole percent of barium oxide, 1.003 mole percent of titanium dioxide and 0.003 mole percent of samarium oxide.

4. A thermistor composition consisting essentially of a fired body formed from a mixture of 0.898 mole per-

cent of barium oxide, 0.100 mole percent of strontium oxide, 1.003 mole percent of titanium dioxide and 0.002 mole percent of samarium oxide.

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