

[54] TEMPERATURE MEASURING RESISTANCE

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338/23, 25, 24, 28; 29/612; 106/47 R;  
252/518, 520; 317/234 V

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UNITED STATES PATENTS

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[57] ABSTRACT

A temperature measuring resistance employing a composition whose electrical resistance varies with temperature. The composition is preferably a glass containing Al<sub>2</sub>O<sub>3</sub>, LiO<sub>2</sub> and SiO<sub>2</sub>.

7 Claims, 4 Drawing Figures

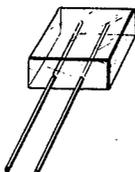


FIG. 1

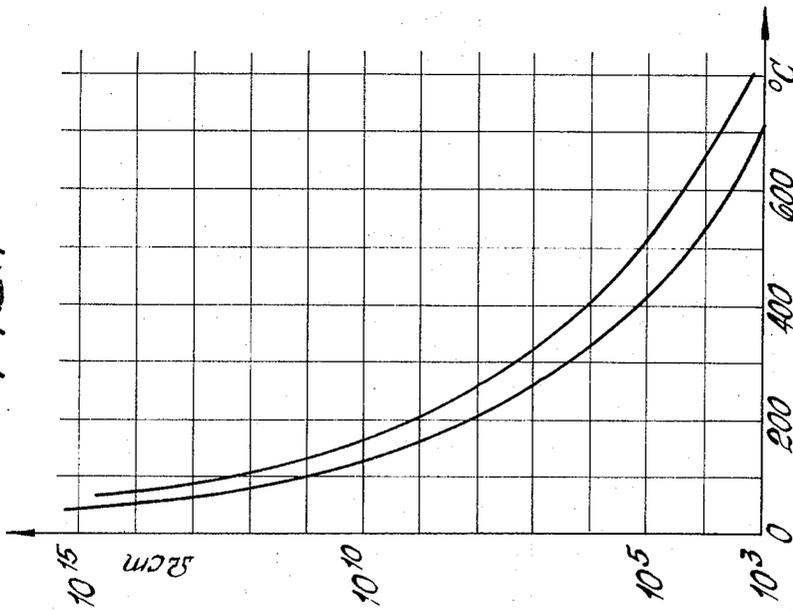


FIG. 2

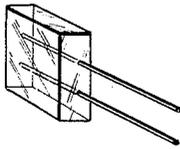


FIG. 3

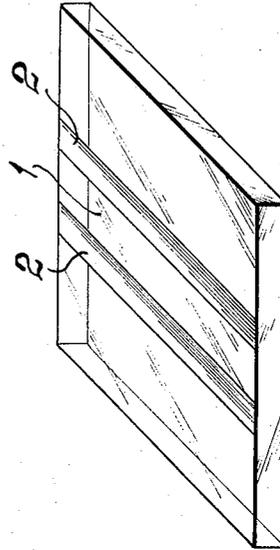
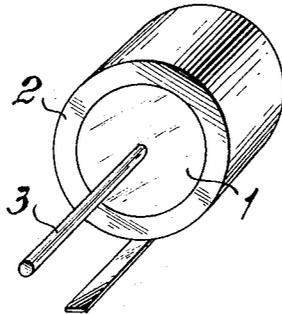


FIG. 4



## TEMPERATURE MEASURING RESISTANCE

The invention relates to a temperature-measuring resistance.

Temperature-measuring resistances having a negative temperature coefficient are already known. These are thermistors having negative temperature coefficients and consisting of n-conducting semiconductor materials. Their resistance decreases by 2.5 to 4.5 percent per degree centigrade.

The conditions which are set as regards the stability and capacity for reproduction of the resistance characteristics of the NTC resistances are only satisfied by certain metal oxides or oxidic mixed crystals with a common oxygen lattice. There are, for example:

- a. mixed crystals of  $\text{Fe}_3\text{O}_4$  (spinel) with substances which likewise present spinel lattice structures, as for example  $\text{Zn}_2\text{TiO}_4$  and  $\text{MgCr}_2\text{O}_4$
- b.  $\text{Fe}_2\text{O}_3$  with additions of  $\text{TiO}_2$ .
- c.  $\text{NiO}$  or  $\text{CoO}$  and also combinations of these oxides with small additions of  $\text{Li}_2\text{O}$ .

The dependence on temperature of the NTC resistance is represented as an approximation by the equation:

$$R_T = A \cdot e^{B/T}$$

In which

$R_T$  represents the resistance of the thermistor at the temperature  $T$ , measured in °K.

$A$  represents a constant with the dimension of ohms and dependent on the form of construction of the resistance.

$B$  represents a constant which depends on the form of construction and the material of the thermistor with the dimension °K.

$e$  represents the base of the natural logarithms (2.718)

The following applies regarding the temperature coefficient of the NTC resistances:

$$T_K = (1/R)(dR/dT) = (-B/T^2)$$

Typical  $B$ -values lie between  $2 \times 10^3$  and  $6 \times 10^3$  °K.

NTC resistances are produced by pressing the initial compositions obtained from the aforementioned materials and subsequent sintering at high temperatures.

Depending on the form of construction, the temperature range in which they can be used varies between  $-25^\circ\text{C}$  and a maximum of  $350^\circ\text{C}$ .

This relatively low maximum temperature of use is a serious disadvantage of the known NTC resistances.

The present invention has for its object a temperature-measuring resistance which does not present these disadvantages of the known NTC resistances, has the same or larger temperature coefficients, but is capable of being used in substantially higher temperature ranges, for example up to  $700^\circ\text{C}$ .

According to the present invention, there is provided a temperature-measuring resistant having two contacts and having therebetween a composition whose electrical resistances varies with temperature. The composition comprises broadly the following compounds in the following percentages by weight:

Compound	Weight Percent
$\text{Al}_2\text{O}_3$	14 to 32
$\text{Li}_2\text{O}$	1 to 6
$\text{SiO}_2$	balance

and preferably comprises:

$\text{Al}_2\text{O}_3$	14 to 32
$\text{Li}_2\text{O}$	1 to 6
$\text{TiO}_2$	0.5 to 6
$\text{ZrO}_2$	0.5 to 5
$\text{SiO}_2$	balance

In this way, there is utilized the specific resistance of glass or of glass ceramics, which is strongly variable with the temperature. What has been found to be particularly advantageous is the small linear expansion coefficient of the glass ceramics, which is in the order of magnitude of  $0$  to  $30 \times 10^{-7}/^\circ\text{C}$  and permits unrestricted use of the temperature-measuring resistances with quickly changing temperatures and large differences in temperature. The maximum temperatures of use are thus substantially higher than those of the known NTC resistance.

According to the invention, the resistance material consists of a glass ceramic with large negative temperature coefficients and has heat-expansion coefficients less than  $30 \cdot 10^{-7}/^\circ\text{C}$ .

By contrast with the NTC resistances of which the conductivity depends on the electron conduction, the conductivity of the glass ceramics is caused purely by ion conduction. The conductivity thus depends primarily on the concentration and the mobility of the alkali ions in the glass ceramic. Hence, the conduction process is very complex and if influenced by the nature and composition of the crystal phase and the glass phase, also by the absolute quantities of the glass phase and crystal phase and also by the structural formation. Consequently, suitable as thermistors are particularly alkali-containing glass ceramics, more especially glass ceramics of  $\text{SiO}_2$ — $\text{Al}_2\text{O}_3$ — $\text{Li}_2\text{O}$ , since these have, in addition to the necessary conductivity, a good resistivity to change in temperature because of their low heat-expansion coefficient of  $0$  to  $15 \times 10^{-7}/^\circ\text{C}$ . Such glass ceramics are described in the German Offenlegungsschriften 1,596,855 and 1,596,860, and also in German Patent Specification 1,596,858.

In the same way as with glasses, the curve of the specific resistance with the temperature in connection with glass ceramics for temperatures below the transformation range, is described by the law of Rasch and Minrichsen:

$$\log \rho_T = A + (B/T),$$

which, with a renomination of the constants, can also be written in the form:

$$\rho_T = ae^{b/T}$$

with which the main conformity of the resistance curve with that of the NTC resistances becomes clearly apparent.

As with glasses, the value of the constant  $B$  lies between  $3 \times 10^3$  and  $6 \times 10^3$  °K. The value  $A$  varies between  $+1.5$  and  $-4.5$ .

Using the Rasch-Hinrichsen law, and by differentiation of the temperature coefficients, there is obtained:

$$T_K = (1/\rho)(d\rho/dT) = - (B/M_{10}T^2) = -2.303 (B/T^2)$$

A glass ceramic of the aforementioned system  $\text{SiO}_2$ — $\text{Al}_2\text{O}_3$ — $\text{Li}_2\text{O}$  has for example a  $B$ -value of  $4.75 \cdot 10^3$  °K.

Thus, at  $573^\circ\text{K}$ , there is obtained a temperature coefficient of  $-3.3$  percent per degree centigrade.

Glass ceramic thermistors can only be operated with alternating current. When using direct current, the ions which participate in the conduction are depleted and in a short time the resistance is strongly increased.

Depending on the shape which is required, thermistors of glass ceramics are shaped by known glass-processing procedures such as pressing, rolling and blowing and can be transformed into a polycrystalline material in a second processing step by a controlled heat treatment.

The temperature range in which the glass ceramic thermistors can be used has an upper limit, which is the temperature at which the permanent deformations, for example, due to a continuation of the crystallization, are produced. The lower limit as regards the range of use is only given by the maximum resistance which can still be accepted for the respective purpose of use.

In the Drawings

FIG. 1 shows in the form of a graph the typical curve of the resistance, depending on the temperature for the temperature-measuring resistance according to the invention.

FIGS. 2 and 3 show two constructional examples of temperature-measuring resistances according to the invention.

FIG. 4 shows an embodiment of the temperature measuring resistances in the form of a pressed glass melt.

The temperature-measuring resistance shown in FIG. 2 can for example be produced by a platinum wire loop being placed between two glass ceramic wafers which have still not assumed ceramic form and this sandwich is then melted under pressure at high temperature and simultaneously converted into the polycrystalline state. After terminating the temperature treatment, the platinum wire loop is severed and the temperature-measuring element is brought to its final shape by grinding and polishing.

FIG. 3 shows a glass ceramic article, namely, a glass ceramic plate, which has a zone 1 formed as a temperature-measuring resistance. This zone 1 is produced by two conductive silver strips 2 being fired on the said plate. When the plate is heated, the zone as thus defined can serve as temperature detector for controlling the plate temperature. As compared with the use of a thermoelement, it has proved to be advantageous that the mean temperature of a surface and not just the temperature of a point is determined.

FIG. 4 shows an embodiment of the temperature-measuring resistances in the form of a pressed glass melt. The glass 1 is located between an outer electrode 2 in the form of a ring and an inner electrode 3 of a suitable metal.

In order to minimize the adverse effects of rapid temperature changes, the use of glass as a resistance material is possible. The relation of specific electrical resistance to temperature is quantitative in the case of glasses as in the case of glass ceramics. Among the advantages of the use of glass as a resistance material is the ability to use mixtures of glasses whose resistance gradient can be made to vary over wide ranges. Above all, it is possible to provide given resistance values for given temperatures.

Temperature-measuring resistances having an outstanding temperature expansion coefficient can be provided in different physical forms. For example, the

temperature-measuring element can be provided in the form of a pressure glass melt or as an element having a very small mass.

The invention may be better understood by reference to the following specific example employing a specific glass composition.

Example

A temperature-measuring resistance is fashioned as shown in FIG. 2 employing as the wafers the glass ceramic shown in Column 1 of Table I beginning at Line 27, Column 5 of Auslegeschrift 1,596,858. The resultant temperature-measuring resistance functions satisfactorily.

Although the invention has been described in considerable detail with reference to certain preferred embodiments thereof, it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described above and as defined in the appended claims.

What is claimed is:

1. A temperature-measuring resistance having two contacts and having therebetween a composition whose electrical resistance varies with temperature, said composition comprising the following compounds in the following percentages by weight:

Compound	Weight Percent
Al <sub>2</sub> O <sub>3</sub>	14 to 32
Li <sub>2</sub> O	1 to 6
SiO <sub>2</sub>	balance

2. The resistance of claim 1 wherein the composition comprises the following compounds in the following percentages by weight:

Compound	Weight Percent
Al <sub>2</sub> O <sub>3</sub>	14 to 32
Li <sub>2</sub> O	1 to 6
TiO <sub>2</sub>	0.5 to 6
ZrO <sub>2</sub>	0.5 to 5
SiO <sub>2</sub>	balance

3. A temperature-measuring resistance according to claim 1, characterized in that the composition consists of a glass ceramic with a high negative temperature coefficient.

4. A temperature-measuring resistance according to claim 1 characterized in that the glass ceramic of the resistance material has a thermal expansion coefficient smaller than  $30 \times 10^{-7}/^{\circ}\text{C}$ .

5. A temperature-measuring resistance according to claim 1 characterized in that a glass ceramic article shows certain measuring ranges due to defining contacts.

6. A method of measuring temperature by passing a current through a composition whose electrical resistance varies with temperature, said composition comprising the following compounds in the following percentages by weight:

Compound	Weight Percent
Al <sub>2</sub> O <sub>3</sub>	14 to 32
Li <sub>2</sub> O	1 to 6
SiO <sub>2</sub>	balance

7. The method of claim 6 wherein the composition comprises the following compounds in the following percentages by weight:

Compound	Weight Percent
Al <sub>2</sub> O <sub>3</sub>	14 to 32
Li <sub>2</sub> O	1 to 6
TiO <sub>2</sub>	0.5 to 6
ZrO <sub>2</sub>	0.5 to 5
SiO <sub>2</sub>	balance.

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