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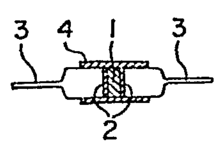
(54) **Process for the production of PTC thermistors.**

(57) A process for the production of glass sealed types PTC thermistors is disclosed wherein a positive temperature coefficient semiconductor ceramic material (1) is sealed in a glass (4) having a softening point of no higher than 560°C in the presence of air, oxygen or an air/oxygen mixture.

FIG. I



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PROCESS FOR THE PRODUCTION OF PTC THERMISTORS

The present invention relates to a process for the production of PTC thermistors.

As is well-known in the art, a thermistor aimed at sensing temperature alone includes a thermistor element sealed in glass or resin so as to keep it from being affected by other factors such as humidity or gas. Referring especially to NTC thermistors, there are available glass-sealed type thermistors which are inexpensive, easy to mass-produce and have stabilized properties, in addition to resin-sealed type disc-form thermistors.

Turning to PTC thermistors, however, glass-sealed type PTC thermistors are still not produced, and instead use is made of resin-sealed disc-form PTC thermistors or PTC thermistors in which metals are mechanically pressed onto electrodes.

This may be attributable to the properties of PTC thermistors which are significantly affected by the temperature and atmosphere at and in which the thermistor elements are sealed in glass.

Conventional NTC thermistors are prepared by glass sealing in vacuum or a reducing atmosphere such as N_2 or Ar gas so as to prevent Dumet wires or heaters from being oxidized. In consequence of the studies made by the present inventors, it has been revealed that the application of such glass sealing in a reducing atmosphere to PCT thermistors causes the properties thereof to deteriorate to a considerable extent. It has also been found that, under such conditions, the glass sealing temperature reaches as high as 650°C, at which temperature the properties of PTC thermistors deteriorate significantly.

In view of the foregoing, a main object of the present invention is to provide inexpensive glass-sealed type PTC thermistors which show a great change in resistance, especially a markedly increased change in resistance at switching temperatures, and which have stabilized properties .

According to one aspect of the present invention, there is provided a process for the production of PTC thermistors by sealing a positive temperature coefficient (PTC) semiconductor ceramic material in glass in the presence of air, oxygen or an air/oxygen mixture (wherein 0% $<$ the volume of air $>$ 100%).

According to another aspect of the present invention, there is provided a process for the production of PTC thermistors by sealing a positive temperature coefficient semiconductor ceramic material in low-melting glass having a softening point of no higher than 560^{o}C.

According to a further aspect of the present invention, there is provided a process for the production of PTC thermistors by sealing a positive temperature coefficient semiconductor ceramic material in low-melting glass having a softening point of no higher than 560^{o}C in the presence of air, oxygen or an air/oxygen mixture (wherein 0% $<$ the volume of air $>$ 100%).

The invention wil be more particularly described with reference to the accompanying drawings, in which:-

Figure 1 is a schematic view showing one embodiment of the steps of a process according to the present invention; and

Figures 2 to 4 inclusive are views showing the temperature-specific resistance characteristics of the products prepared under different conditions.

As the semiconductor ceramic material having a positive temperature coefficient used in the present invention, there are mentioned those obtained by adding to barium titanate base compositions any one of trivalent antimony, trivalent bismuth, pentavalent tantalum, pentavalent niobium or a rare earth metal. The glass used has a softening point of 450^{o}C-560^{o}C inclusive, and includes those glasses based on B_2O_3-PbO-ZnO, B_2O_3-PbO-SiO_2, B_2O_3-PbO-Ti_2O, B_2O_3-PbO-SiO_2-Al_2O_3-ZnO, B_2O_3-PbO-V_2O_5, SiO_2-PbO-K_2O, SiO_2-PbO-Na_2O and SiO_2-PbO-K_2O-Na_2O. Preference is given to a SiO_2-PbO-K_2O

base glass, since this glass shows desirous thermal expansion and wettability with respect to lead wires (Dumet wires, viz., Fe-Ni alloy wires plated with Cu).

When a glass having a softening point of below 450°C is used, certain limitations are imposed upon the temperature at which the resulting glass-sealed type PTC thermistors are employed.

Referring now to Figure 1, a semiconductor barium titanate ceramic material 1 is first sliced to any suitable thickness having regard to the length of a glass tube 4 in which the finished thermistor element is to be sealed. Silver electrodes 2 and 2 are applied to both sides of the thus obtained element, and deposited thereto for 20 minutes at 600°C. Figure 1(a) shows a section of the electrode-provided element.

As shown in Figure 1(b), the element is then cut to any length corresponding to the diameter of the glass tube 4.

The element is placed in the tube 4 of a glass having a softening point of no higher than 560°C, into both ends of which Dumet wires 3 and 3 are inserted. Finally, the glass tube 4 is sealed by means of a carbon heater jig. The sealing temperature is determined depending upon the softening point of the glass used, and is generally higher than the softening point of the glass used by 50°C or more.

In the prior art NTC glass sealed thermistors, a glass having a softening point exceeding 560°C is used and sealing is carried out at a temperature exceeding 610°C. If sealing of a PTC thermistor is carried out under such conditions, there is a marked drop in the properties of the resulting PTC thermistor. According to the present invention, however, it is possible to obtain stable PTC thermistors whose properties drop only slightly by sealing the thermistor elements in a low-melting glass having a softening point of no higher than 560°C.

Figure 2 shows the results of an experiment run wherein PTC thermistor elements having a Curie point of 120°C were sealed in glasses in the art.

Although the resulting properties having slightly dropped from the initial ones (prior to sealing), yet the PTC thermistor element sealed in a glass having a softening point of 536°C or 560°C has been found to show excellent properties. It has also been found that similar results are obtained with PTC thermistor elements having different Curie points. The results of Figure 2 are also numerically given in Table 1.

Figure 3 is a characteristic diagram of a PTC thermistor sealed in glass in various atmospheres. The PTC thermistor used had a Curie point of 120°C, and sealing was carried out at 610°C.

It is clear from the diagram that sealing in air or oxygen gas yields a better PTC thermistor as compared with one treated in vacuo or in an inert or reducing gas atmosphere. The results of Figure 3 are numerically given in Table 2.

It is to be understood that similar results are obtained in an air/oxygen mixture and/or with a PTC thermistor element having a different Curie point.

Figure 4 is a graphical view showing the relation between the specific resistance and the temperature of PTC thermistors obtained by sealing a PTC thermistor element having a Curie point of 120°C in glass in air and/or oxygen gas. The results of Figure 4 are numerically given in Table 3.

From these results, it is found that by a process according to the present invention PTC thermistors are obtained which show a large change in resistance, which is comparable to the properties prior to sealing.

It is to be understood that similar results are obtained in an air/oxygen mixture and/or with PTC thermistor elements having a different Curie point.

It is to be understood that, in place of a carbon heater jig, other heater jigs, for instance, a metal heating jig, may be used for sealing the glass tube 4.

Table 1

(Ω cm)

	$R_{30°C}$	$R_{100°C}$	$R_{120°C}$	$R_{140°C}$	$R_{160°C}$	$R_{180°C}$	$R_{200°C}$	$R_{220°C}$
Before sealing	1.1×10^2	1.4×10^2	2.4×10^3	1.7×10^6	4.4×10^7	1.2×10^8	1.7×10^8	1.8×10^8
Glass: S.P. 536°C	1.1×10^2	1.4×10^2	2.4×10^3	1.7×10^6	2.5×10^7	4.8×10^7	5.9×10^7	5.7×10^7
Glass: S.P. 560°C	9.4×10	1.0×10^2	3.8×10^2	1.2×10^4	3.8×10^5	4.0×10^6	1.3×10^7	1.8×10^7
Glass: S.P. 580°C	8.7×10	9.5×10	1.6×10^2	1.1×10^3	1.1×10^4	8.0×10^4	2.1×10^5	3.0×10^5
Glass: S.P. 625°C	6.9×10	8.8×10	1.2×10^2	6.0×10^2	5.4×10^3	4.1×10^4	1.1×10^5	1.7×10^5

S.P. Softening Point

Table 2

(Ω cm)

	$R_{30°C}$	$R_{100°C}$	$R_{120°C}$	$R_{140°C}$	$R_{160°C}$	$R_{180°C}$	$R_{200°C}$	$R_{220°C}$
Before sealing	$1.1x10^2$	$1.4x10^2$	$2.4x10^3$	$1.7x10^6$	$4.4x10^7$	$1.2x10^8$	$1.7x10^8$	$1.8x10^8$
O_2 gas	$1.1x10^2$	$1.4x10^2$	$2.4x10^3$	$1.7x10^6$	$1.8x10^7$	$3.9x10^7$	$4.9x10^7$	$5.1x10^7$
Air	9.4x10	$1.0x10^2$	$3.8x10^2$	$1.2x10^4$	$3.8x10^5$	$4.0x10^6$	$1.3x10^7$	$1.8x10^7$
Vacuum	9.4x10	$1.0x10^2$	$3.5x10^2$	$1.8x10^3$	$1.0x10^4$	$3.4x10^4$	$7.3x10^4$	$1.2x10^5$
Ar	6.8x10	8.1x10	$1.6x10^2$	$7.5x10^2$	$2.4x10^3$	$1.2x10^4$	$2.6x10^4$	$4.1x10^4$
N_2	6.8x10	8.1x10	$1.3x10^2$	$3.5x10^2$	$9.6x10^2$	$3.0x10^3$	$7.4x10^3$	$1.4x10^4$

Table 3

(Ω cm)

	$R_{30°C}$	$R_{100°C}$	$R_{120°C}$	$R_{140°C}$	$R_{160°C}$	$R_{180°C}$	$R_{200°C}$	$R_{220°C}$
Before sealing	$1.1x10^2$	$1.4x10^2$	$2.4x10^3$	$1.7x10^6$	$4.4x10^7$	$1.2x10^8$	$1.7x10^8$	$1.8x10^8$
O_2, Glass: S.P. 536°C	$1.1x10^2$	$1.4x10^2$	$2.4x10^3$	$3.2x10^6$	$1.4x10^8$	$5.1x10^8$	$7.9x10^8$	$9.2x10^8$
Air Glass: S.P. 536°C	$1.1x10^2$	$1.4x10^2$	$2.4x10^3$	$1.7x10^6$	$2.5x10^7$	$4.8x10^7$	$5.9x10^7$	$5.7x10^7$

S.P. Softening Point

As explained above, the present invention makes it possible to inexpensively prepare PTC thermistors having excellent properties, and is therefor of industrially high value.

CLAIMS:

1. A process for the production of PTC thermistors characterised by sealing a positive temperature coefficient semiconductor ceramic material (1) in glass (4) in the presence of air, oxygen or an air/oxygen mixture (wherein 0%   the volume of air   100%).

2. A process for the production of PTC thermistors characterised by sealing a positive temperature coefficient semiconductor ceramic material (1) in a low-melting glass having a softening point of no higher than $560^{o}C$.

3. A process for the production of PTC thermistors characterised by sealing a positive temperature coefficient semiconductor ceramic material (1) in a low-melting glass (4) having a softening point of no higher than $560^{o}C$ in the presence of air, oxygen or an air/oxygen mixture (wherein 0%   the volume of air   100%).

4. A process according to claim 1, 2 or 3, characterised in that the glass (4) has a softening point of from $450^{o}C$ to $560^{o}C$ inclusive.

5. A process according to any one of the preceding claims, characterised in that the glass (4) is in the form of a tube sealed at both ends.

6. A process according to claim 5, characterised in that lead wires (3) are inserted into opposite ends of the glass tube (4) prior to the sealing thereof.

7. A process according to claim 5 or 6, characterised in that electrodes (2) are applied to opposite sides of the semiconductor material (1) prior to its insertion in the glass tube (4).

8. A process according to any one of the preceding claims, characterised in that the glass used is based on B_2O_3-PbO-ZnO, B_2O_3-PbO-SiO_2, B_2O_3-PbO-Ti_2O, B_2O_3-PbO-SiO_2-Al_2O_3-ZnO, B_2O_3-PbO-V_2O_5, SiO_2-PbO-K_2O, SiO_2-PbO-Na_2O or SiO_2-PbO-K_2O-Na_2O.

9. A process according to any one of the preceding claims, characterised in that the semiconductor material

(1) is a barium titanate ceramic material.

10. A process according to claim 9, <u>characterised in that</u> the barium titanate ceramic material has added thereto any one of trivalent antimony, trivalent bismuth, pentavalent tantalum, pentavalent niobium or a rare earth metal.

FIG. 1

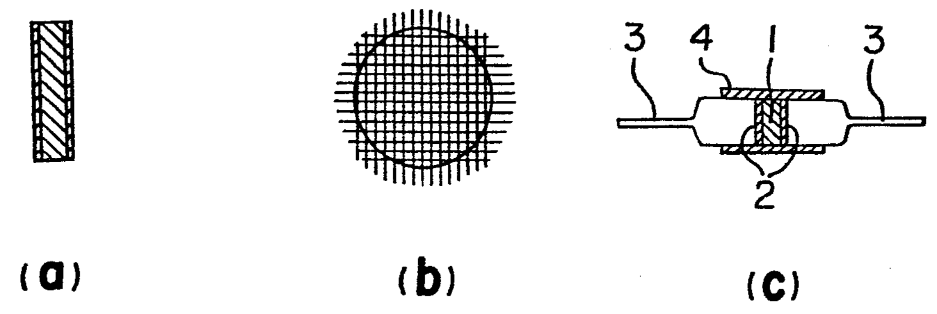

3
4
1
3
2
(a)
(b)
(c)

FIG. 2

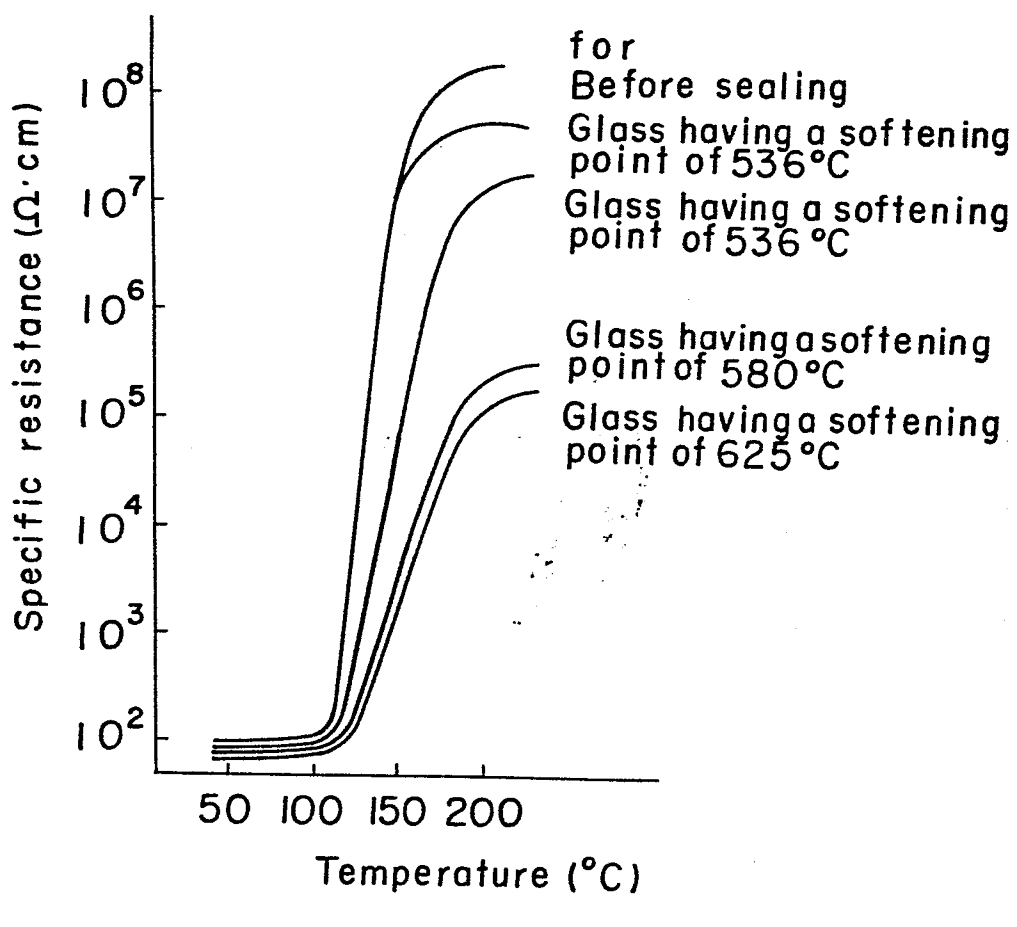

Specific resistance (Ω·cm)
10^8
10^7
10^6
10^5
10^4
10^3
10^2
50 100 150 200
Temperature (°C)
for
Before sealing
Glass having a softening point of 536°C
Glass having a softening point of 536 °C
Glass having a softening point of 580 °C
Glass having a softening point of 625 °C

FIG. 4

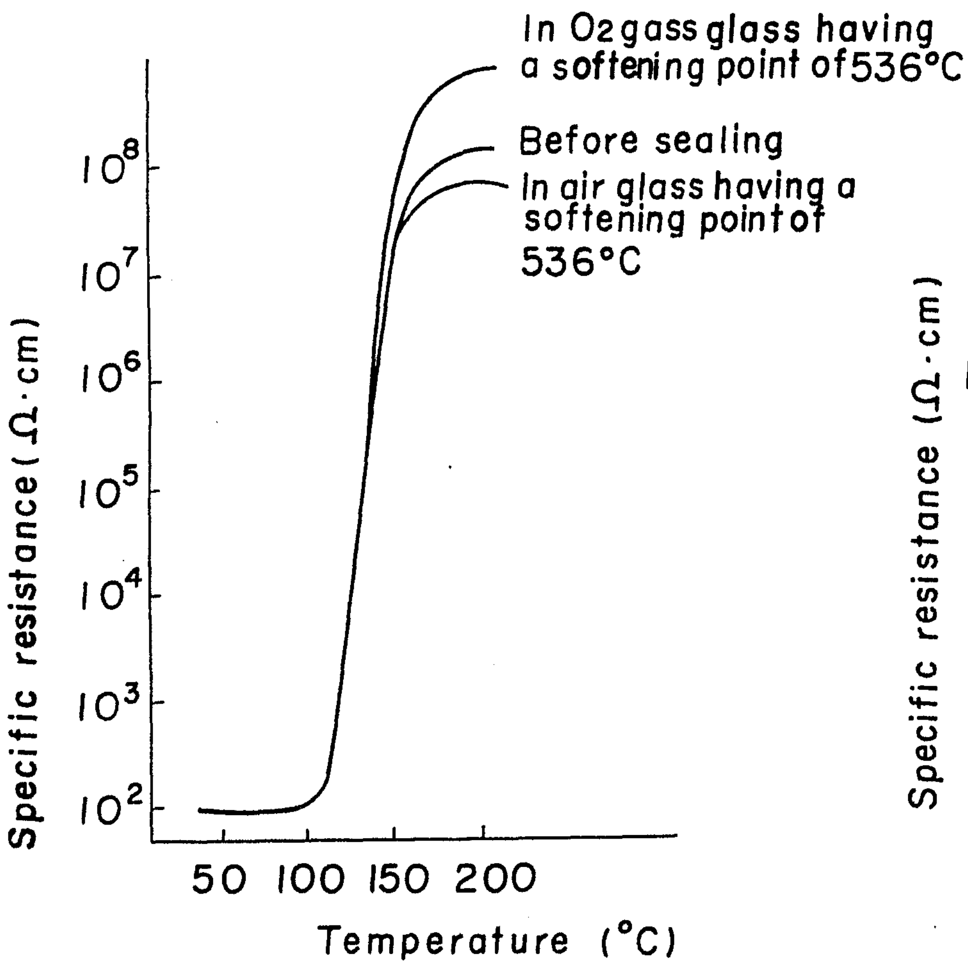
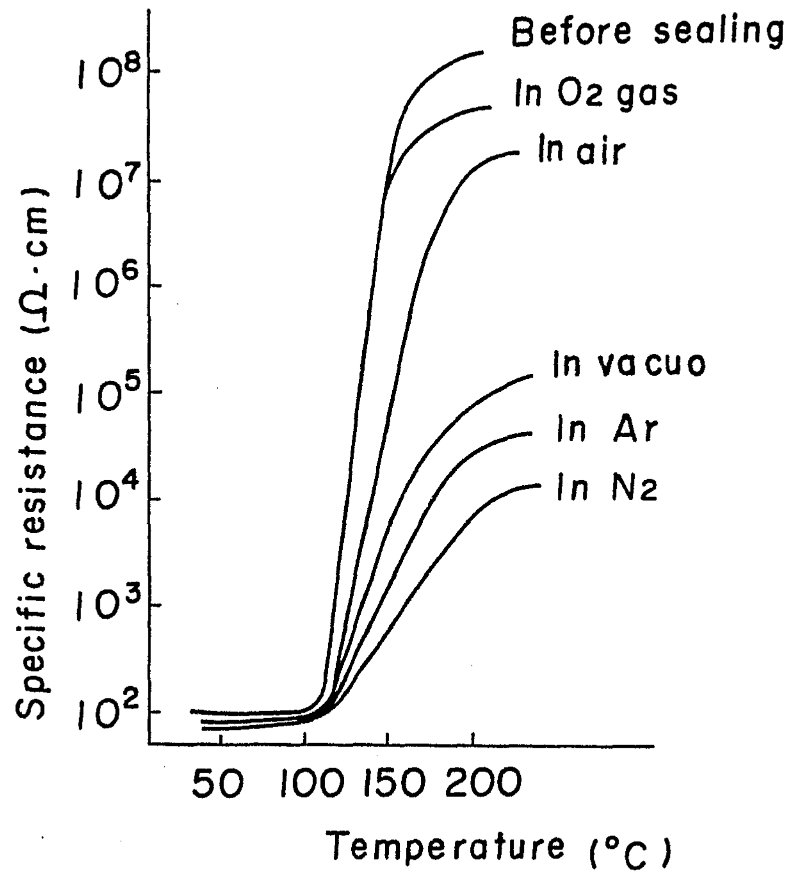

In O2 gass glass having a softening point of 536°C
Before sealing
In air glass having a softening point of 536°C
Specific resistance (Ω·cm)
10^8
10^7
10^6
10^5
10^4
10^3
10^2
50 100 150 200
Temperature (°C)

FIG. 3


Before sealing
In O2 gas
In air
In vacuo
In Ar
In N2
Specific resistance (Ω·cm)
10^8
10^7
10^6
10^5
10^4
10^3
10^2
50 100 150 200
Temperature (°C)

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EUROPEAN SEARCH REPORT

Application number

EP 84 30 3796

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X	US-A-3 377 561 (H.A. SAUER) * Claims 1,3; column 4, lines 20-31; column 5, lines 19-59; figure 3 * ---	1,5,7, 9,10	H 01 C 17/02 H 01 C 7/02 H 01 C 1/024
A	GB-A- 992 926 (CONSTRUCTA-WERKE GmbH) * Claims 1,2 * ---	1	
A	US-A-4 276 536 (J.A. WISNIA) * Claims 1,7 * ---	1	
A	LU-A- 69 220 (SIEMENS A.G.) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			H 01 C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	12-09-1984	DECANNIERE L.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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