

June 3, 1958

L. W. GILDART
SEMI-CONDUCTOR ALLOYS

2,837,618

Filed Aug. 6, 1954

2 Sheets-Sheet 1

Fig. 1

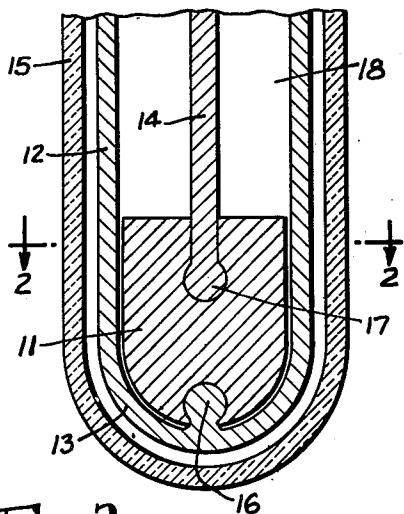


Fig. 3

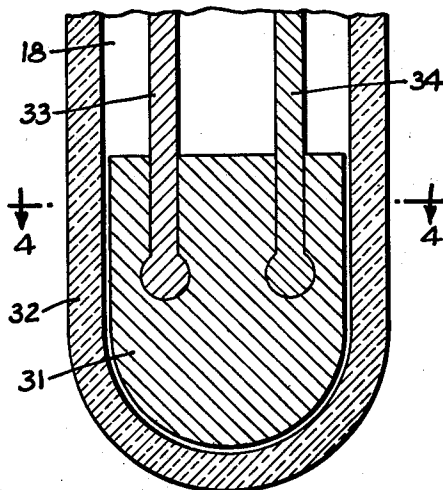


Fig. 2

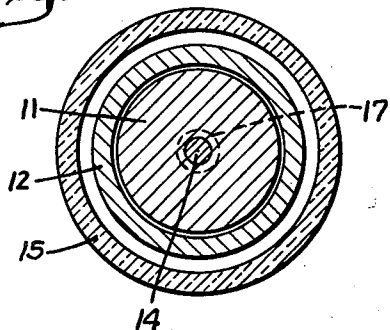


Fig. 4

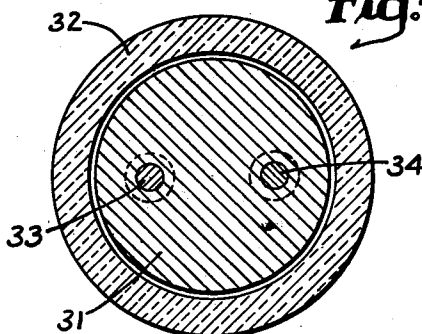


Fig. 5

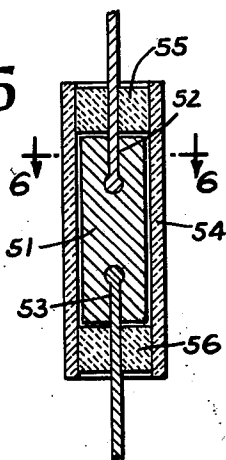
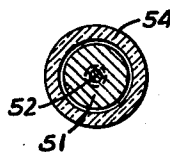


Fig. 6



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2 Sheets-Sheet 2

Fig. 7

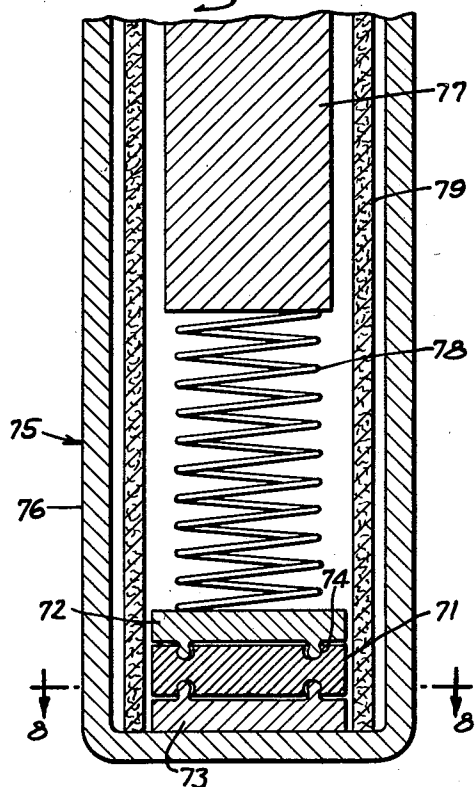


Fig. 9

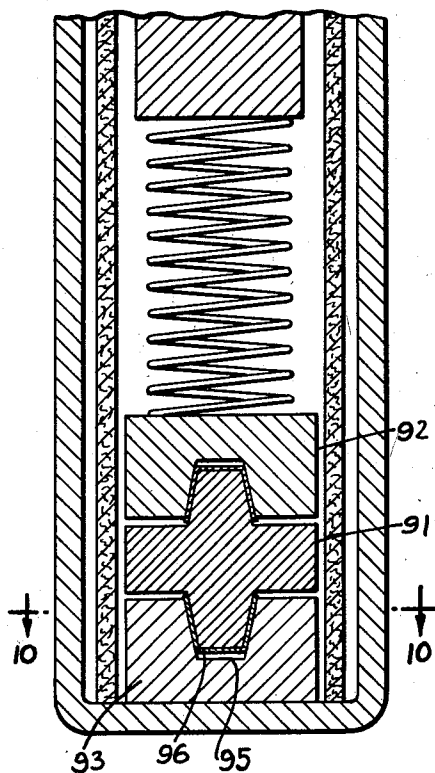


Fig. 8

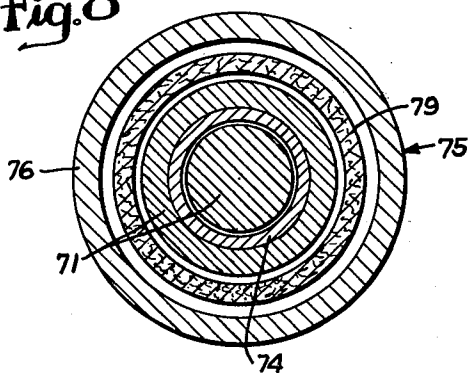
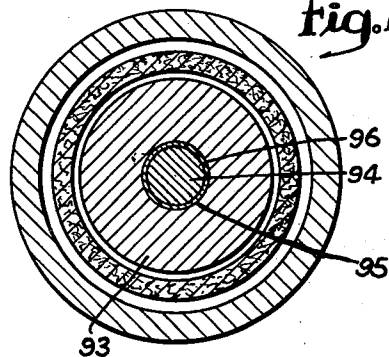


Fig. 10



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SEMI-CONDUCTOR ALLOYS

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8 Claims. (Cl. 201—63)

The instant invention relates to semi-conductor materials, suitable for use in thermistors. More particularly, the instant invention relates to thermometers of the electric resistance type in which the resistance element is of improved design and the probe of which is of novel thermistor material.

The instant application is a continuation-in-part of copending application Serial No. 348,469, filed April 13, 1953, now abandoned.

It is known that alloys of antimony and selenium, particularly an alloy having the atomic ratio of 2:3 (Sb_2Se_3), have substantial electrical resistivity and belong to the class of substances known as semi-conductors. Thermistors are thermally sensitive resistors made of semi-conductors whose resistance changes markedly with small changes in the temperature. At present thermistors have wide application as circuit elements in the radio and communications fields, and for other purposes.

Thermistors can also be used in thermometers of the electric resistance type, using a resistive element of the semi-conductor material in the form of a probe. The semi-conductor properties of pure antimony triselenide and of this compound containing 1 percent of arsenic impurity are known, but this compound has not been found of practical usefulness because its thermo-resistive behavior is erratic and unpredictable and varies widely from one batch of material to the next without definitely ascertainable reason or possibility of control.

It is an object of the instant invention to provide semi-conductor materials, the electrical properties of which are completely predictable and easily controllable.

It is a further object of the instant invention to provide processes for the production of new thermistor materials.

It is a further object of the instant invention to provide an improved thermometer probe which is reliable and durable in use and suitable for a wide range of temperatures.

It is a further object of the instant invention to provide commercially feasible processes for the production of thermometer probes containing novel semi-conductor material.

These and other objects of the instant invention will become more clearly understood from the following description.

It has been discovered that when a compound selected from the group consisting of the triselenides and the trisulfides of a metallic element of the phosphorus family is alloyed, in the manner hereinafter described, with a compound selected from the group consisting of arsenic triselenide and arsenic trisulfide, a family of improved semi-conducting materials are produced. The electrical properties of these thermistor materials are predictable and controllable, and they are suitable for use in thermometer probes as hereinafter described; and for other purposes.

In practicing the invention, the triselenide or the trisulfide salt of either antimony or bismuth is alloyed with arsenic triselenide or arsenic trisulfide. Antimony triselenide and arsenic triselenide are the preferred compounds for use in preparing the semi-conductor alloy. As previously stated, antimony triselenide is a known semi-conductor, but it has not been found satisfactory

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as a thermistor material because its thermo-resistive behavior was not easily reproducible. Arsenic triselenide at room temperature is a glass with very high resistivity and is classed as an insulator. It is surprising that in producing an alloy of these two compounds, a material which is thermo-resistively stable and predictable is obtained. Although the reason for this result is largely obscure, the fact is well established.

In order to utilize with security and continuity the semi-conducting qualities of the antimony triselenide-arsenic triselenide alloy produced in accordance with the instant invention, still further physico-chemical characteristics must be considered. Particularly, good and permanent contact must be established between the thermistor and other solids in order to insure electrical contact with the required electrodes and conductors and, in many instances, also for the purpose of insuring good thermal contact with the medium, the temperature of which is to be measured. It has been discovered that adequate contact can best be obtained in either of two ways: (1) by inserting self-heated electrodes into the body of the thermistor alloy itself, and (2) by casting and shrinking the thermistor alloy around the electrode or other solid body to be contacted. A secure electric contact seems to require additionally such performance of the casting or molding and shrinking process as to create a surface chemical reaction between the probe material and the electrode.

In practicing the instant invention, an improved probe material, an alloy of antimony triselenide and arsenic triselenide is produced, and in this embodiment it is important that the individual compounds should be uncontaminated by any other elements or traces of elements exceeding 0.1 percent by weight of the alloy. In addition, in order to insure the benefits of the stability and reproducibility of the alloy as previously mentioned, the actual weight ratios must be kept uniform between successive batches of the alloy, with at most a 0.1 percent deviation from theoretical uniformity.

For example, each of the elements, antimony and selenium, which comprise the compound, antimony triselenide, should be at least about 99.9 percent pure by weight, and each of the elements, arsenic and selenium, which comprise the compound, arsenic triselenide, should be at least about 99.9 percent pure by weight. Further, when the two compounds are weighed out for alloying one with the other, the proportions should be held within limits of better than about 0.1 percent by weight in order to produce a semi-conductor alloy of predictable and reproducible electrical properties.

The relation between the electrical resistivity and the temperature coefficient of electrical resistivity of an alloy on the one hand and the proportions in weight percentages of its components on the other are clearly established in the following table:

Sb_2Se_3 (Weight Percent)	As_2Se_3 (Weight Percent)	Electrical Resistivity (Ohm-Cm. at 25° Centi- grade)	Temperature Coefficient at 25° C. (Per- cent per Degree)
100.00	0.00	50	3.0
98.00	2.00	85	3.3
96.00	4.00	140	3.5
94.00	6.00	225	3.7
92.00	8.00	370	3.8
90.00	10.00	600	3.9
85.00	15.00	2,000	4.2
80.00	20.00	5,500	4.4
75.00	25.00	12,000	4.6
70.00	30.00	22,000	4.8
60.00	40.00	75,000	5.5
50.00	50.00	240,000	6.2
40.00	60.00	2,000,000,000	-----

It will be noted that the electrical resistivity increases geometrically with the increasing As_2Se_3 content, and that the temperature coefficient of resistivity also increases, but much more slowly. It is impractical to set limits as to the range of percentages of Sb_2Se_3 and As_2Se_3 in the alloy which might be of the greatest use for semiconductor or thermistor materials. Whether the thermistor is to be made with low or high percentages of Sb_2Se_3 is a matter of choice, the factors of which are well known to those skilled in the art, and depends entirely on the particular application to which the material is to be put.

In other embodiments of the invention, the compounds, antimony selenide and arsenic trisulfide, antimony trisulfide and arsenic trisulfide, or antimony trisulfide and arsenic triselenide are alloyed together in the manner described herein, and the resulting alloys have electrical resistivities and thermal coefficients similar to the alloys of antimony triselenide and arsenic triselenide. However, these alloys have slightly lower mechanical strength than the antimony triselenide-arsenic triselenide alloys which are the preferred thermistor materials.

In the process of preparing the instant alloys, it is a feature of paramount importance that the constituents should be pure and their weights accurate as stated above. In practicing the invention, it is further important that in the melting and alloying step, excessively high temperatures and prolonged periods of heating be avoided in order to prevent changes in the weight proportion by evaporation or sublimation. The antimony triselenide and arsenic triselenide become fluid at temperatures slightly above about 600°C ., but inasmuch as the elements selenium and arsenic both have a tendency to sublime out of the mixture at this temperature, it is essential that the alloying and casting or molding be performed rapidly in order to avoid substantial loss of these elements. It is almost impossible to avoid loss of some of these elements, but loss is insignificant when the process is carried out at a temperature between about 630° and about 670°C ., as hereindescribed.

On the other hand, it is less important in the instant process than it was in prior attempts to prepare thermistors of antimony-selenium alloys that the exact conditions of heating and cooling be precisely duplicated between different batches for the same use. For instance, the antimony-selenium alloys exhibited major irregularity of resistivity, depending on whether the cooling down, after solidification, was rapid or slow, and on other factors. In this respect the instant alloys are considerably steadier. Of course, major divergencies should be avoided to insure the greatest possible uniformity of results; for instance, it is not advisable to cool one part of a batch abruptly and to slowly anneal another. However, the antimony triselenide-arsenic triselenide alloys as described herein are substantially free from the irregularities mentioned as long as the alloy preparation is handled in accordance with the instant process and in the manner obvious to persons skilled in the art.

It has also been found possible to formulate and prepare a probe of thermistor material so as to simplify the calibration of a thermometer containing the probe: this possibility arises from the fact that, subject to the precautions which have been stated, different mixtures or different batches of the alloys, such as the antimony triselenide-arsenic triselenide alloys, can be reheated and again mixed to produce intermediate alloys having desired electrical properties and without resulting irregularity in thermoresistive behavior. As a result, a finer adjustment of resistivity becomes possible, by remixing two or more alloys in which the proportions of antimony triselenide to arsenic triselenide are not exactly the same. No such mixing is successfully practiced with other semiconductors or thermistor materials.

It will be understood by persons skilled in the art that every batch should be calibrated, for precision work.

However such calibration is greatly facilitated by the possibility of relatively accurate pre-selection of the weight of the components in the alloying process and of mixing batches, as described. It is believed that no other material is presently known which provides such versatility together with such accuracy of pre-selection.

Actual thermometers produced in accordance with this invention can best be described in conjunction with the drawings appended hereto, wherein:

Figure 1 is an enlarged longitudinal section through a first type of thermometer probe produced in accordance herewith.

Figure 2 is a section through the probe of Figure 1, the section being taken along lines 2—2 in Figure 1.

Figure 3 is a view generally similar to Figure 1 but showing a modified probe.

Figure 4 is a view generally similar to Figure 2 and showing a section through the probe of Figure 3 along the lines 4—4 in Figure 3.

Figure 5 is a view generally similar to Figure 1 but showing a second modification.

Figure 6 is a view generally similar to Figure 2, taken along the lines 6—6 in Figure 5.

Figure 7 is a view generally similar to Figure 1 but showing a third modification.

Figure 8 is a view generally similar to Figure 2, taken along lines 8—8 in Figure 7.

Figure 9 is still another view generally similar to Figure 1 and showing a fourth modification.

Figure 10 is a view generally similar to Figure 2 taken along lines 10—10 in Figure 9.

In all views the numeral 11 indicates the temperature sensitive probe, slug or cartridge. Preferably this element is made from the antimony triselenide-arsenic triselenide $\text{Sb}_2\text{Se}_3\text{-As}_2\text{Se}_3$ alloy described above, and particularly from a suitably predetermined batch, for such resistivity as may be suitable for the electric system to be used, wherein the thermometer forms a variable resistance element. However, certain aspects of the thermometer probe design to be described presently are applicable also to other thermistor materials.

Referring first to Figures 1 and 2: the $\text{Sb}_2\text{Se}_3\text{-As}_2\text{Se}_3$ probe 11, preferably containing less than 30.00 percent by weight of As_2Se_3 , is disposed within a nickel-silver shell 12 at the closed tip thereof. This shell serves as one of the electrodes in the circuit containing the probe as a variable resistor; the other electrode 14 being a nickel-silver, Kovar, rodar or Nichrome wire inserted in the central upper part of the probe 11. Kovar and rodar are alloys containing nickel, cobalt, manganese and iron. In order to avoid inadvertent grounding of the outer electrode 12, this electrode may be provided with an insulating envelope or shield 15 which may consist in a plastic coating, a removable glass envelope or the like, depending upon the service to which the outer thermometer surface is subjected.

Attention is drawn to the fact that, while the nickel-silver electrode 12 surrounds and mechanically protects the bulk of the probe 11, a central projection or finger 16, formed integrally or otherwise in or on the inside of the tip 13, is surrounded by the probe material, as is the end or tip 17 of the electrode wire 14. This arrangement is important for the production and maintenance of contact.

In the process of producing the thermometer probe, the suitably selected material for the probe, for example, an antimony triselenide-arsenic triselenide alloy, is filled into the tip 13, in powdered or granulated condition, the wire 14 being held in position in well known manner. The tip is then heated in order to remelt and re-fuse the probe material, subject to substantially the same precautions as have been mentioned above in connection with the original fusion process. Thereupon the casting or molding of the probe is completed by cooling it down to normal temperatures, incident to which the differential

shrinkage of the probe material compared with the metal of the electrodes causes tight engagement and squeezing of the tips 16 and 17.

More particularly, it has been found preferable to provide some little time delay in one of the later stages of this cooling process, although the melting temperature, for reasons stated above, should be maintained only for the shortest possible time, required for complete melting. At some suitable temperatures below 600° C., for instance at approximately 550° C., it is desirable to provide a stabilization period, for example between about 5 and about 60 minutes, preferably of about 5 minutes. A more durable contact is thus provided, probably due to the formation of metal selenides on the electrode surfaces.

It is unnecessary at this point to describe the use of the thermometer, or the remaining structures involved in such use, such as the source of current, the measuring or indicating device and the like, which can be formed and used in manners well known to persons skilled in the art.

The field of application for thermometers according to Figures 1 and 2 is very wide. It can be used to measure temperatures from about minus 100° C. to about plus 200° C. The thermometer may be used for instance for clinical purposes, in which event the probe material, desirably, is prepared for high sensitivity in the usual clinical temperature range, that is, in the vicinity of about 100° F. In this connection it will be understood by persons skilled in the art that semi-conductors of different formulations have maximum temperature coefficient and sensitivity in one particular part of their basic temperature range. Furthermore, this thermometer probe will best be formulated for such resistance as allows the use of weak, clinically inoffensive electric currents, so that in suitable cases the metal shell 12, 13 can be contacted with the body of the patient direct, without any electric insulation and therefore without heat insulation. The use of a stainless steel shell 15 is also desirable, from the clinical viewpoint, because the outside of such a shell can be sterilized in an autoclave. This cannot be done with an ordinary fever thermometer. The new probe material is not injured and not over expanded by autoclave steam temperatures ranging suitably upwards of 220° F.

For other applications, it may be preferable to use higher voltages and to formulate the probe 11 accordingly, in order to simplify the circuit system or for other reasons. In such cases it is usually desirable to utilize an insulating sheath of glass or the like, in place of the stainless steel shell 15, in the actual use of the thermometer.

In the modified form of Figures 3 and 4, the probe 31 is directly enclosed in a shell 32 which has electric insulating properties and which may, for instance, consist of Pyrex glass; the thickness of the shell being suitably selected for the desired sensitivity of the thermometer. In this event an outer shell, stainless steel or the like, not shown, may be used in order to protect the thermometer from breakage when it is not in actual use. Two parallel and similar electrodes 33 and 34 are used in this case, both being inserted in and clamped by the upper part of the probe material.

In both forms, Figures 1 and 2 as well as 3 and 4, the interior space 18 of the thermometer shell 12 or 32, above the probe (and also around the same, in view of the shrinkage of the probe material, incident to the manufacture of the thermometer) is desirably filled with an inert gas such as nitrogen or argon or the like, at such pressure or rarefaction as may be suitable for the temperature range contemplated. The life expectancy of the probe and particularly of its contact surfaces engaging the electrodes is improved by such use of neutral gases; the presence of oxygen in this space may tend to produce chemical changes in the probe material. The

details of the thermometer seal and electrode construction, in the upper part remote from the probe, are not shown herein, being well known to persons skilled in the art.

Figures 5 and 6 show a particularly simple or cartridge type of application, suitable mainly for the application of relatively small thermometer elements forming permanent parts of flow systems or the like. Here the probe 51, preferably made of the above described alloy and also preferably cast around the electrode ends or tips 52, 53, or opposite one another, has a generally cylindrical form and is suitably inserted in a protective sleeve 54 of Pyrex, ceramic material, stainless steel, or the like. In the event that a conductor such as stainless steel is used, of course it is necessary either to insulate the inside thereof or to make the radial distance from the tips 52, 53 to the shell much greater than the longitudinal distance between said tips. Even then a certain shunting effect of the shell will exist, which however need not interfere with proper thermometric measurement if the circuit system is properly designed in manners known to the art. The ends of the cartridge may be closed by plugs 55, 56 of wax or cement or other suitable sealing material, insulating the electrode wires from the outside and preventing the access of corrosive fluids and the like.

In Figures 7 and 8 the probe 71 forms a flat cylinder or slug rather than a long cylinder or cartridge, and is engaged by similar slug-shaped electrodes 72, 73, at the two flat sides of the probe, for the passage of a relatively dense current as may be required in industrial applications where the probe material has appropriate resistivity for such current. Again the probe is adapted to engage the electrode firmly, in the casting and cooling process. For this purpose each electrode slug in this case has, on its probe-engaging surface, a preferably annular ridge or bead 74, the outside of which is firmly compressed as the probe material shrinks around the same. A wafer or button 71, 72, 73 is formed of the probe and the two electrodes, which can be inserted in the working end of a thermometer 75 in a manner basically known to the art, providing excellent electrical as well as thermal contact. The thermometer may have, for instance, an outer shell 76 of stainless steel, brass or the like, acting as conductor in contact with the lower electrode 73; an inner conductor 77 connected with the upper electrode 72 by a spring 78, and an insulating shield of fiber, plastic or the like, 79, to separate the inner conductor 77, 78 and wafer 71, 72, 73 from the outer side wall 76.

Figures 9 and 10 show still another modification, utilizing a thermometer structure similar to that shown at 75. Here however the probe slug 91 is connected with the electrode slugs 92, 93 by means of a projection 94 on each side of the probe slug, which is pressed into a recess 95 in the electrode slug. Plastic conducting material 96, such as lead foil, may be interposed between the elements 94, 95. In this manner electric contact may be provided by a press fit rather than the casting shrinkage and selenide formation used in the other examples. Furthermore the slug and electrode can thus be made separable and replaceable, for instance for laboratory use and the like, wherein differently formulated alloy probes may be successively clamped between the same set of electrodes.

In order to give additional understanding of the instant invention, the following examples are included; however it is to be understood that they are illustrative only and the invention is not to be understood as limited thereto.

Example I

A thermistor material was produced by alloying antimony triselenide of at least 99.9% purity with arsenic triselenide of 99.9% purity by heating at a temperature

of about 650° C. The weight ratio was about 96.00% of the antimony triselenide to about 4.00% of the arsenic triselenide. The resulting alloy was cooled. The resulting material had a resistivity of about 140 ohm-centimeters at 25° C. and a temperature coefficient of approximately 3.5% per degree centigrade.

Example II

A thermistor material was prepared in the manner described in Example I, except that the weight ratio was about 92.00% antimony triselenide to about 8.00% of arsenic triselenide. At 25° C. the resistivity of this thermistor was about 370 ohm-centimeters, and the temperature coefficient was approximately 3.8% per degree centigrade.

Example III

A thermistor alloy was produced by remelting a portion of the alloys obtained in Example I and in Example II and mixing them in a ratio by weight of 1:1. The resulting semi-conductor had a resistivity of about 225 ohm-centimeters at 25° C., and the temperature coefficient was approximately 3.65% per degree centigrade.

Example IV

A thermistor alloy was prepared in the manner described in Example I in which about 75.00% by weight of antimony and about 25.00% by weight of arsenic triselenide were alloyed and cooled. The resulting material had an electrical resistivity of about 12,000 ohm-centimeters at 25° C., and had a temperature coefficient of approximately 4.6% per degree centigrade.

Having thus fully described and illustrated the character of the instant invention, what is desired to be protected and secured by Letters Patent is:

1. A semi-conductor alloy suitable for use in thermistors consisting of a compound selected from the group consisting of the triselenides and the trisulfides of the group consisting of antimony and bismuth, alloyed with at least about 2% by weight of a compound selected from the group consisting of arsenic triselenide and arsenic trisulfide.

2. A semi-conductor alloy suitable for use in thermometer probes consisting of a major amount of a compound selected from the group consisting of the triselenides and the trisulfides of the group consisting of antimony

and bismuth, and at least 2% by weight of a compound selected from the group consisting of arsenic triselenide and arsenic trisulfide.

3. A semi-conductor alloy suitable for use in thermistors consisting of an alloy of antimony triselenide and at least about 2% by weight of arsenic triselenide.

4. A thermometer probe material comprising an alloy containing between about 70% and about 95% by weight of antimony triselenide and between about 30% and about 5% by weight of arsenic triselenide.

5. In a process for the production of thermistors including production of semi-conductor material and forming a resistance element therefrom, the improvement comprising alloying substantially pure arsenic triselenide and substantially pure antimony triselenide at a temperature between 630° and about 670° C., and cooling the resulting thermistor material.

6. A method of producing a thermometer probe comprising melting a body of an alloy containing between about 70% and about 95% by weight of antimony triselenide and between about 30% and about 5% by weight of arsenic triselenide around a pair of electrode tips at a temperature between about 630° and about 670° C., cooling the body to a temperature between about 550° and about 600° C., allowing the partially cooled material to stand at such temperature for between about 5 and about 60 minutes, and then cooling the resulting material to about atmospheric temperature.

7. A thermometer probe comprising a solid body of an antimony selenium arsenic alloy cast around and thereby shrunk upon a pair of electrodes, wherein one of the electrodes cast into the probe body substantially consists in an inward projection of a metallic body also forming an outer shell for the probe.

8. A thermometer probe as described in claim 7, wherein the outer shell and inward projection thereof substantially consists of stainless steel.

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