Feb. 3, 1953 C. I. HALL 2,627,570

THERMOSENSITIVE RESISTANCE ELEMENT CONTAINING EUTECTIC MIXTURES

Filed Jan. 6, 1950 4 Sheets-Sheet 1

Fig. 1.

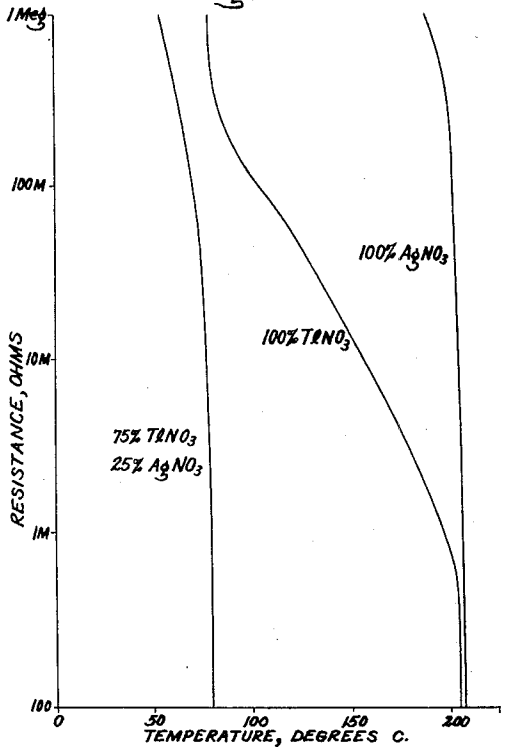


Fig. 2.

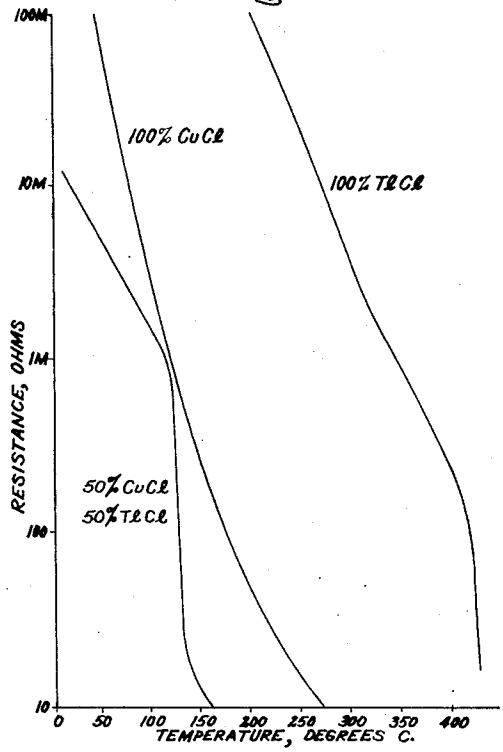
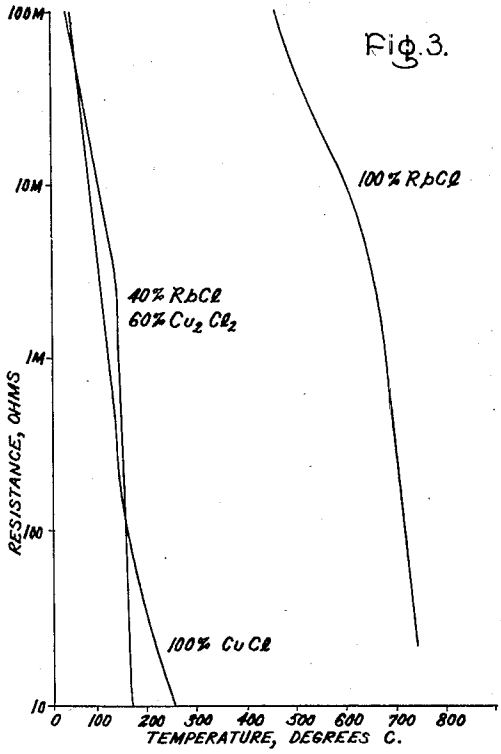


Fig. 3.



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Fig. 4.

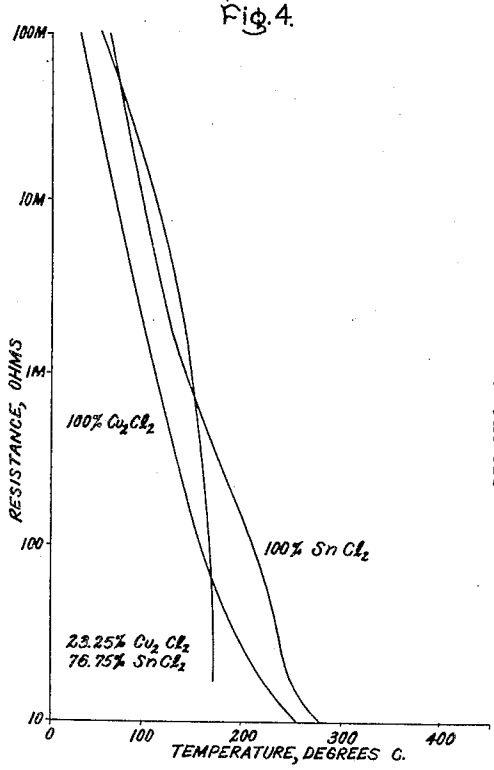
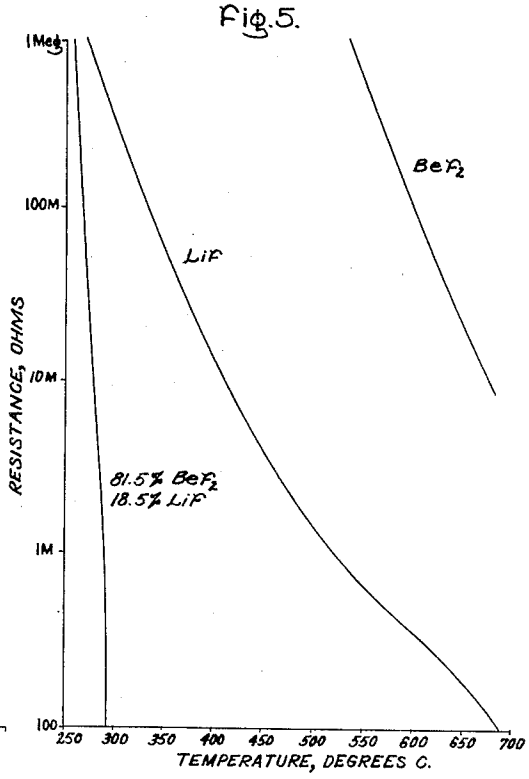


Fig. 5.



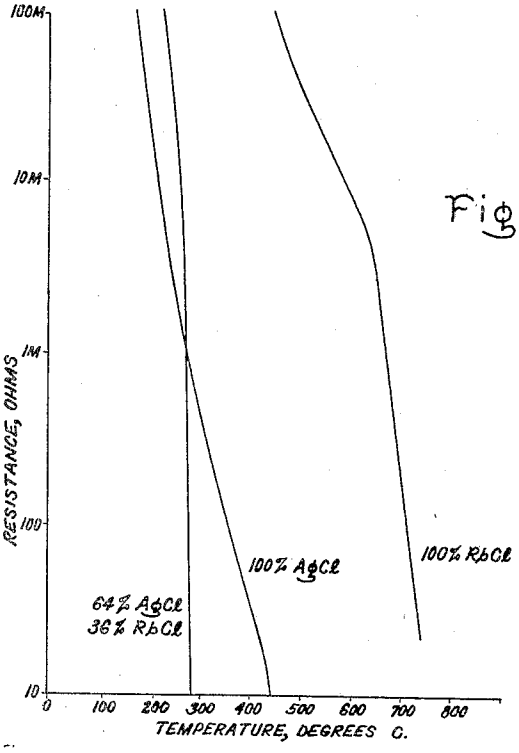


Fig. 6.

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THERMOSENSITIVE RESISTANCE ELEMENT CONTAINING EUTECTIC MIXTURES

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Fig. 7.

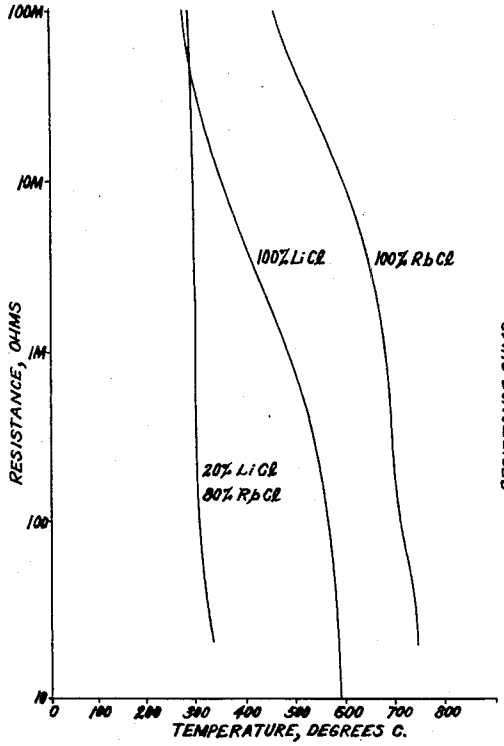


Fig. 8.

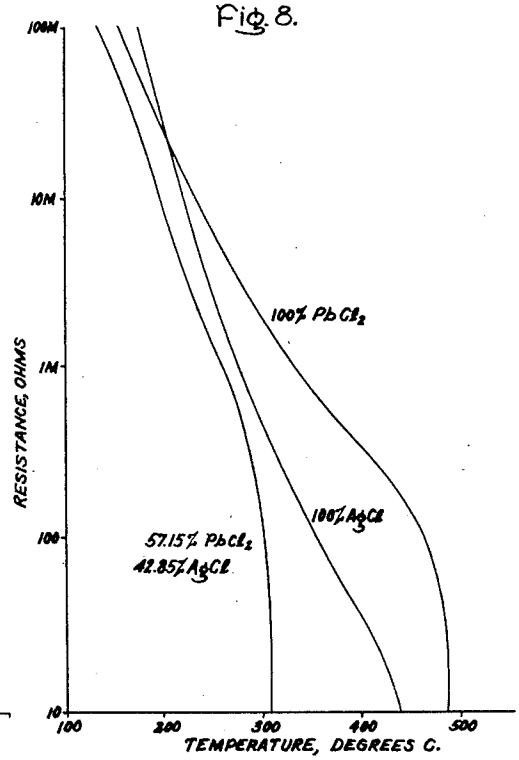
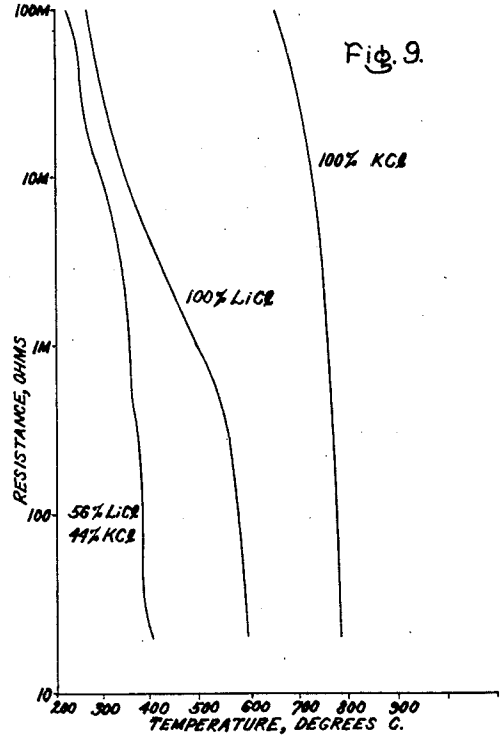


Fig. 9.



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Fig. 10.

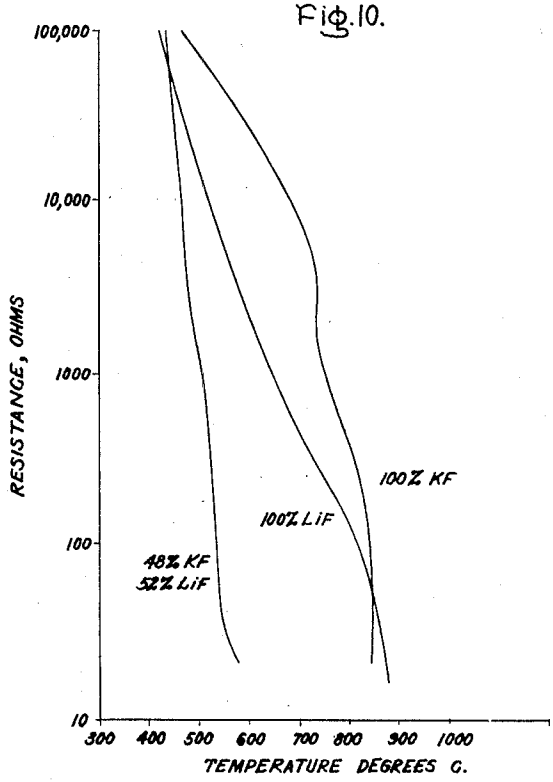


Fig. 11.

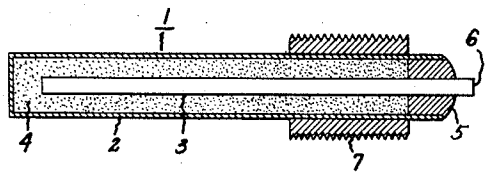
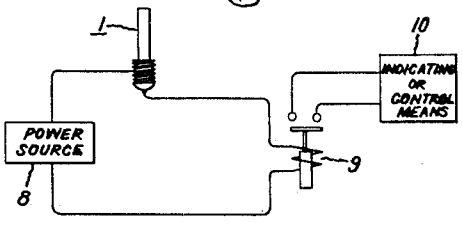


Fig. 12.



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Patented Feb. 3, 1953 2,627,570

UNITED STATES PATENT OFFICE

2,627,570

THERMOSENSITIVE RESISTANCE ELEMENT CONTAINING EUTECTIC MIXTURES

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Application January 6, 1950, Serial No. 137,233

1 Claim. (Cl. 201—63)

1

This invention relates to thermosensitive materials. More particularly, it relates to new and useful thermosensitive materials provided by eutectic mixtures of chemically stable salts having pronounced negative resistance-temperature characteristics.

It is known that many inorganic salts are thermosensitive or have negative resistance-temperature characteristics and decrease in resistance as their temperature is raised. These characteristics have been utilized to electrically indicate temperatures and control various devices and systems.

The use of simple inorganic salts or compounds as thermosensitive materials is accompanied by a number of disadvantages which detract seriously from their usefulness. One of these disadvantages is that at all temperatures except those near or at their melting point the rate of change of resistance with temperature of most simple salts is so gradual that in order to operate a relay, for example, and through it control an electrical circuit or system, the relay must be extremely sensitive and hence expensive to manufacture. With many salts or compounds, the change in resistance even at the melting point is so small as to require an extremely sensitive relay to react to the change. In addition, most salts melt at temperatures which are higher than the range of temperatures usually encountered in many devices or systems which it is desired to control or in which it is desired to give an indication of certain specific temperature conditions by electrical means.

It is an object of this invention to provide inorganic salt compositions which have a high negative rate of change of resistance at definite temperature values.

It is another object of the invention to provide thermosensitive materials as above which exhibit their pronounced resistance-temperature characteristics at temperatures which are relatively low compared to the melting points of the individual constituents thereof.

Other objects will become apparent and the invention better understood from a consideration of the following description and the drawing in which Figs. 1 through 10 show the resistance-temperature characteristics of various chemical salts and their eutectics, Fig. 11 is a cross-sectional view of a typical thermosensitive element using the present materials, and Fig. 12 shows a typical control or indicating electrical circuit utilizing the present materials in a thermosensitive element.

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It has been found that thermosensitive materials having a high negative rate of change of resistance with a slight change in temperature may be provided by a eutectic mixture of chemically stable salts.

More particularly, it has been found that such thermosensitive materials may be provided by a eutectic mixture of chemically stable salts having boiling points which are relatively high compared to their melting points and which are nonreactive with electrode and sheathing materials used.

By a suitable choice of salts, a series of eutectic mixtures whose resistance will decrease precipitately at different temperatures may be prepared and used in thermosensitive elements which are extremely sensitive to a very slight change in temperature.

The following are given as typical examples of the pronounced behavior of eutectic mixtures of chemically stable salts as compared with the behavior of their individual constituents. These combinations are presented as indicative of the behavior of eutectic mixtures of chemically stable salts in general and are not to be considered as limiting the scope of the present invention.

Example 1

A eutectic mixture of 75%, by weight, thallous nitrate and 25%, by weight, silver nitrate was prepared which melted at 83° C. This low melting point compares with a melting point of 206° C. for thallous nitrate and 212° C. for silver nitrate. As shown in Fig. 1, the thallous nitrate-silver nitrate eutectic has a very steep negative resistance-temperature curve in the vicinity of 80° C., whereas such a characteristic is available in the individual constituents only at a much higher temperature. The extreme steepness of the eutectic resistance curve at about 80° C. representing a change of over two decades (from 25,000 ohms to 100 ohms) from about 75° to 85° C. makes possible the use of a relatively insensitive and inexpensive relay device to signal approximately an 80° C. temperature condition in any desired installation or to actuate controls at that temperature. On the other hand, the resistance of silver nitrate alone drops sharply only at over 200° C. as does that of thallous nitrate. There is thus provided a eutectic mixture of these salts which is very thermosensitive at a much lower temperature than either of its constituents.

Example 2

A eutectic mixture of 50%, by weight, cuprous chloride and 50%, by weight, thallium mono-

chloride melting at 132° C. was prepared. The melting point of cuprous chloride alone is 422° C., and the melting point of thallium mono-chloride is 430° C. This eutectic as shown in Fig. 2 exhibits a very sharp drop in resistance at about 130° C., decreasing about one and one-half decades within five degrees from 130° C. to 135° C. Cuprous chloride alone exhibits a very gradual decrease in resistance while thallium mono-chloride decreases gradually and then more sharply but at a much higher temperature and in a much lower resistance range.

Example 3

Reference to Fig. 3 shows that while rubidium chloride, melting at 715° C., and cuprous chloride, melting at 422° C., have a gradual decrease of resistance with temperature in the usable resistance range, the eutectic mixture of these two salts exhibits a very sharp drop in resistance in the vicinity of 150° C. of over two decades in about twelve degrees from 150° C. to 162° C. This eutectic consists of 40%, by weight, rubidium chloride and 60%, by weight, cuprous chloride and melts at 150° C.

Example 4

A eutectic mixture of 23.25%, by weight, cuprous chloride and 76.75%, by weight, stannous chloride melting at 172° C. exhibits a relatively sharp drop in resistance at about 170° C., as shown in Fig. 4, of approximately one decade in ten degrees from 165° C. to 175° C. which makes it useful for causing a change in an electrical circuit at this temperature. This compares with a very gradual drop in resistance for either of the constituents alone in this as well as higher temperature ranges.

Example 5

A eutectic mixture of 81.5%, by weight, beryllium fluoride and 18.5%, by weight, lithium fluoride with a melting point of 420° C. was prepared. This mixture exhibited a pronounced drop in resistance at between 260° C. and 300° C. with the sharpest decrease at about 295° C. for a drop of four decades in forty degrees. On the other hand, the lithium fluoride constituent had a very gradual decrease in resistance with temperature as shown in Fig. 5 as does beryllium fluoride.

Example 6

As pointed out heretofore, rubidium chloride, melting point 715° C., has a rather gradual drop of resistance with temperature. Silver chloride, melting point 455° C., also exhibits a slow change of resistance with rising temperature. However, when the eutectic mixture of these two chemically stable salts is made consisting of 64%, by weight, silver chloride and 36%, by weight, rubidium chloride and having a 270° C. melting point, a very sharp drop in resistance is obtained at about 270° C. which can be utilized to readily indicate this temperature. This drop is about three decades in approximately ten degrees from about 270° C. to 280° C. This pronounced negative resistance-temperature characteristic is shown in Fig. 6.

Example 7

A eutectic mixture of 80%, by weight, rubidium chloride and 20%, by weight, lithium chloride melting at 318° C. exhibits a very sharp drop in resistance at about 290° C. of over one decade within ten degrees from 280° C. to 290° C. This is in contrast to the decrease of resistance with temperature exhibited by lithium chloride alone

which melts at 613° C. and rubidium chloride which melts at 715° C. The contrast between the eutectic mixture and the individual constituents is best shown in Fig. 7 which shows a gradual drop in resistance with increase in temperature as compared to the eutectic.

Example 8

As shown in Fig. 8, lead chloride ($PbCl_2$), melting at 501° C., and silver chloride, melting at 455° C., show a gradual drop in resistance with increase of temperature at around 300° C. However, the eutectic of 57.15%, by weight, lead chloride ($PbCl_2$) and 42.85%, by weight, silver chloride, melting at 310° C., exhibits a sharp decrease of about over one decade in resistance in about ten degrees at about 310° C. or from 300° C. to 310° C. which makes it useful for indicating a temperature of this magnitude.

Example 9

Whereas, as shown in Fig. 9, potassium chloride, melting at 776° C., and lithium chloride, melting at 613° C., show a rather sharp decline in resistance near their melting point, their eutectic mixture, 44% by weight potassium chloride and 56% by weight lithium chloride, melting at 355° C., exhibits an even sharper decrease at the much lower temperature of about 370° C. The resistance drop is about over one decade in approximately twenty degrees from about 360° C. to 380° C. This characteristic makes this eutectic useful for indicating temperatures in this latter range.

Example 10

The eutectic consisting of 48%, by weight, potassium fluoride and 52%, by weight, lithium fluoride melting at 530° C. is useful for indicating temperatures of about 520° C. by reason of its sharp decrease in resistance at around this temperature as shown in Fig. 10. This decrease is approximately one decade in twenty degrees from about 500° C. to 520° C. In contrast to this phenomenon, lithium fluoride, melting at 870° C., has a gradual decrease in resistance with temperature even around its melting point, whereas potassium fluoride, melting at 880° C., has a sharp decrease in resistance only at the much higher temperature of about 850° C. as compared to 520° C. for the eutectic.

From the above examples it will be seen that the eutectics of chemically stable salts offer definite advantages over the individual salts as temperature indicators. In general, the eutectic mixtures exhibit a much sharper decrease in resistance at temperatures at or near their melting points than do the single salts. This makes possible the use of relatively insensitive relay or other resistance reactant instruments or controls which it is desired to operate at the particular temperature. On the other hand, very sensitive and much more expensive relays are required to react at a certain specific temperature when the resistance is decreasing only gradually at that point. This is true of the simple salts except in certain cases where the resistance drop is great around their melting points. However, in general, the melting points of chemically stable salts are relatively high so that at lower temperatures the large drop in resistance with temperature cannot be utilized. However, as shown above, in the case of eutectic mixtures the sharp decrease in resistance occurs at lower temperatures. By a proper selection of eutectic mixtures of chemically stable, non-corrosive salts, thermosensitive

materials each reacting at a specific temperature in a wide range may be made available. Thus, eutectic mixtures as herein described may be used as the thermosensitive element in heating system thermostats, bearing heat detectors, fire detectors and the like.

In order that best results may be attained, the resistance of the present eutectic mixtures should exhibit a resistance drop of at least one decade in five degrees at temperatures up to 150° C. For those whose sharp resistance drop occurs between 150° C. and 300° C., the drop should be at least about one decade in ten degrees, and for those exhibiting the rapid decrease above 300° C., the drop should be at least about one decade in twenty degrees. This insures the rapid and certain actuation of relatively insensitive and inexpensive electrical circuits.

Fig. 11 shows a simplified thermosensitive element of the type which may be used in conjunction with the thermosensitive materials disclosed herein. The element 1 comprises a tube 2 closed at one end which may serve as one electrode. The second electrode 3 may be in the form of a rod or strip of metal or other suitable electrically conducting material which extends into and is spaced from the other electrode 2. The intervening space between the electrodes may be filled with any of the thermosensitive materials 4 of this invention and a leak-proof plug 5 of suitable insulating material placed at the open end of the tube electrode 2 and around electrode 3 to insulate the electrodes from one another and hold them in fixed relative positions as shown. Lead wire 6 may be used to connect electrode 3 in circuit, and electrode 2 may conveniently be so connected by means of a threaded collar 7 fixed to it. It will be understood, of course, that other means of connecting the electrodes in an electrical circuit may be resorted to without departing from the scope and spirit of this invention. For example, lead wires may be led from both electrodes or the necessary contact may be made by employing a socket-fitting arrangement such as is used on the conventional electric light bulb.

A thermosensitive element such as described may be used for a number of purposes. It may be used as a fuel control, for example, in an oil or gas-fired furnace. An element containing a thermosensitive material having a low resistance at flame temperature might be placed in contact with the pilot flame of such a furnace. As long as the fuel supply is on and the pilot flame lit, the material would have certain resistance which would act through an electric relay system to regulate the main fuel feed. If the pilot flame fails, the material in the element would assume a sharply different resistance which could be utilized to so affect the current in the electrical system as to shut off the fuel supply. The thermosensitive element could also be used to detect fires, detect hot boxes in railroad car trucks, give an indication of hot motor bearings and in general actuate a visual or audible signal whenever such is desired to indicate a change in temperature in a particular range or to control the system at a particular temperature.

A typical electrical circuit in which the thermosensitive materials of the present invention may be used is shown in Fig. 12. Thermosensitive element 1 may be connected in series with a power source and relay 9, the latter being connected to the indicating or control means 10. Thermosensitive element 1 may be placed at any point in a device or apparatus where the temperature condition which it is desired to indicate or control exists. Thus, the element may be placed in a railway or motor bearing in a heating thermostat system, a fire detection system or the like, the thermosensitive material in the element being selected to give a sharp decrease in resistance at the temperature at which the circuit is to be actuated. When the thermosensitive material in the element reacts, relay 9 is actuated and the indicating or control means 10 actuated. The indicating means may be an electric light or a loudspeaker or other audible means which signals the temperature condition to which the element 1 is sensitive. Alternatively, 10 may be a controlling means which, upon the critical temperature being reached, will cut off the power to the apparatus or device. The controls may also be arranged to turn on a power supply at a particular temperature. Thus, in the case of heating thermostats, when the critical temperature is reached, the heating means might be shut off. In a railway bearing application, usually a visual or audible signal would be used to warn the trainmen of the condition to be corrected. In a motor bearing, both a visual and audible signal to warn of the condition and controlling means to shut off the motor might be used. In a fire detection system, a visual and audible signal might be used and, additionally, means to turn on a fire extinguishing system.

What I claim as new and desire to secure by Letters Patent of the United States is:

A thermosensitive electrical resistance element composed of a tubular electrode closed at one end, a second electrode extending into the other end of said tubular electrode and spaced therefrom by a plug of insulating material sealing said other end of the tubular electrode, and a body of resistance material within said tubular electrode in electrical contact with both of said electrodes, said body of resistance material consisting of a eutectic mixture of chemically stable salts having a rate of change of resistance in the unfused state in excess of that of the single constituent salts, said eutectic mixture consisting of one of the combinations of salts, thallous nitrate-silver nitrate, cuprous chloride-thallium monochloride, rubidium chloride-cuprous chloride, cuprous chloride-stannous chloride, beryllium fluoride-lithium fluoride, rubidium chloride-silver chloride, rubidium chloride-lithium chloride, lead chloride-silver chloride, potassium chloride-lithium chloride, and potassium fluoride-lithium fluoride.

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