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ELECTRICAL RESISTANCE ELEMENTS

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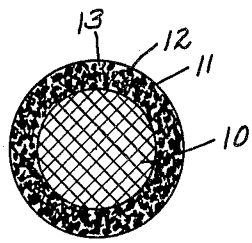

FIG. 1

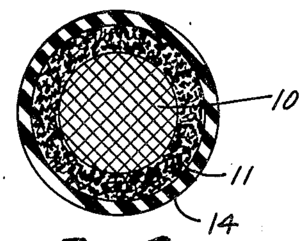

FIG. 2

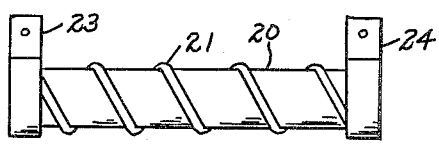

FIG. 3

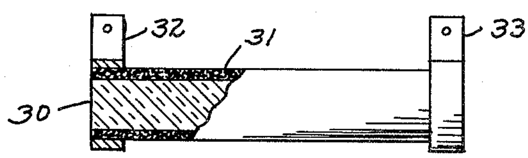

FIG. 4

LEON PODOLSKY
STANLEY O. DORST
INVENTORS

BY Arthur G. Connolly
their attorney

United States Patent Office

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ELECTRICAL RESISTANCE ELEMENTS

Leon Podolsky, Pittsfield, and Stanley O. Dorst, North Adams, Mass., assignors to Sprague Electric Company, North Adams, Mass., a corporation of Massachusetts

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8 Claims. (Cl. 201—63)

This invention relates to a new type of resistance element having unusual properties. More particularly, it concerns highly stable, elongated, flexible resistance elements of great utility, and a method of producing the same.

The present day resistance assemblies may be roughly divided into two general types, namely, the molded resistors and the wound resistors. The former consist of conducting particles, such as carbon, metal, metal oxides, or salts, dispersed in and bonded with an insulating binder, such as the phenol-formaldehyde resins. The latter consist of high resistance wires of metal or alloy, such as a nickel-chromium alloy, wound about an insulating core and coated with some insulating material to provide moisture resistance and to insulate adjacent turns of the winding.

The molded resistors are simple and inexpensive to produce with a fairly high resistance tolerance. They are particularly useful for low wattage, low temperature service which does not require great precision or heat stability. It is very difficult to obtain close tolerances in the high resistance values, and for this reason, they are unsatisfactory as meter-multipliers and for other related types of precision resistors. The wound resistors, on the other hand, can be made with fairly precise resistance values and very low temperature coefficients of resistance over a fairly wide temperature range. However, they are considerably more complicated and expensive to manufacture, and almost invariably require some external insulating material to protect them from unfavorable atmospheric conditions.

In the past, attempts to impart the more desirable properties of the wire wound resistance elements to the simpler and less expensive molded resistance elements have met with little success. For example, it has been proposed to disperse carbon particles uniformly in massive polytetrafluoroethylene. This is apparently accomplished by polymerizing the monomeric tetrafluoroethylene in the presence of the conducting particles or by incorporating the latter into the resin by milling and the like, and then heating the mixture in a mold under pressure. While polytetrafluoroethylene is indeed an unusual resin and in many respects superior to any other known at the present time, its very advantages lead to quite serious disadvantages, when one seeks to employ it in this manner. For example, the resin does not melt appreciably below its decomposition temperature, it is extremely difficult to extrude and to mill, and it is virtually insoluble in any of the ordinary solvents. Polytetrafluoroethylene with conducting particles dispersed therein has the particular disadvantage of a very high positive temperature coefficient of expansion and of resistance, irrespective of the characteristics of the particular conducting particles employed. This fact, combined with the difficulty in manufacturing resistance elements of small physical size or diameter from such material, have made this proposal of very limited practical value.

It is an object of the present invention to overcome the

foregoing and related disadvantages of the prior art resistors. A further object is to produce a new type of resistance element capable of operation over a wide range of temperatures with a low, controlled temperature coefficient of resistance. A still further object is to produce novel resistance elements that will withstand corrosive atmospheres and high humidity without appreciable change in resistance or failure. Another object is to produce new and improved resistance elements by an easily controlled, simple and inexpensive process. Additional objects will become apparent from the following description and claims.

These objects are attained in accordance with the present invention by producing an electrical resistance element comprising a non-conducting base material provided with a coating consisting of a mixture of conducting particles and a polytetrahaloethylene resin. In a more restricted sense this invention concerns an electrical resistance element comprising an inorganic base material bonded to and coated with a uniform dispersion of conducting particles in a polytetrahaloethylene resin, said dispersion being sufficiently thin to cause its expansion characteristics to be determined by those of the base material. In a still more restricted sense, this invention provides an electrical resistance element comprising a flexible glass string bonded to and coated with a layer of carbon particles uniformly dispersed in polytetrafluoroethylene not greater than .0025" in thickness. In one of its preferred embodiments, the invention concerns an electrical resistance element comprising a flexible woven glass string bonded to and coated with a layer consisting from about 5% to about 90% by weight of conducting particles predominating in carbon uniformly dispersed in from about 10% to about 95% of polytetrafluoroethylene, said layer of conducting particles in polytetrafluoroethylene being less than .0025" thick and being coated in turn with a top layer of polytetrafluoroethylene.

In accordance with the present invention, a novel resistance element is produced by forming a uniform suspension of the resin particles and conducting particles in a suitable liquid suspending medium, applying a coating of this suspension to the surface of a suitably shaped non-conducting base, generally inorganic, and thereafter heating the coated base to drive off the suspending medium, and sinter and bond the resin and conducting particles together and to the base. The high temperature coefficient of resistance and the processing difficulties inherent in the molded resistors employing polytetrafluoroethylene, are eliminated in accordance with this invention by depositing and bonding a layer of a uniform mixture of the resin and the conducting particles from a suspension thereof upon an inorganic base material, the layer being of a thickness such that the expansion characteristics thereof are determined by the expansion characteristics of the base. In accordance with one of the preferred embodiments of the invention, this base material is a flexible glass string woven from glass fibers. It is important that the coating should wet and bond to the base. As a general rule, the thickness of the layer should be less than about .050" and for optimum results, less than about .0025".

The resin particle binder of the invention may be prepared in various ways, so long as a uniform dispersion thereof in a liquid medium may be obtained. Water is the most common suspending medium and is preferably used as later described. The resin particle suspension may be obtained by polymerizing the monomeric material in the presence of water, or by dispersing the polymer with suitable milling in water, preferably with the aid of a dispersing agent. The resin particles are composed of single polymers, mixed polymers or copolymers predominating in tetrahaloethylene. Very desirable results are obtained by using particles composed of polytetrafluoroethylene. Polymers of tri-fluoro-mono-chloro-ethylenes and polytetrochloroethylene are also desirable as binder resins possessing properties similar to polytetrafluoroethylene. It is contemplated that other high temperature elastomers may be employed in lieu of polytetrahaloethylenes.

The conducting particles may be of any type that can be dispersed in the same suspending medium as are the resin particles or in one compatible therewith. There are many types of conducting particles which may be utilized, such as metals, alloys, metal oxides, metal salts, spinels, carbon in the form of carbon black and graphite. Carbon and graphite are particularly desirable, since they may be dispersed in water or other hydrophilic liquids with a minimum of effort. Carbon black, acetylene black, vitreous carbon and natural and synthetic graphites may be used. Ammonia and tannic acid in combination are excellent dispersing agents for carbon and graphite, and may be readily removed from the resistance layer during subsequent processing steps.

A number of metals and alloys are useful in producing semi-conducting coatings. Among these are nickel-chrome alloys, bismuth, constantan, tungsten, chromel, alumel, etc. Useful metal derivatives include iron oxide, chromium titanate, copper oxide, lower oxides of titanium and zirconium, molybdenum sulfide, copper sulfide, etc.

Mixtures of the conducting particles may be employed where special resistance characteristics are required.

The invention will be further described with reference to the appended drawings in which

Fig. 1 represents a cross section of a resistance element of the invention;

Fig. 2 represents a cross section of resistance element of the invention;

Fig. 3 represents a side view of a resistor embodying a resistance element of the invention; and

Fig. 4 represents a partial cross section of another resistor of the invention.

Referring more specifically to Fig. 1, **10** represents a cross section of an elongated, inorganic base material, preferably consisting of a flexible, glass fiber string. The type of glass employed is determined by the temperature of processing to be encountered, the flexibility required and other characteristics relating to the utility of the resistance element. Fibers of glass may be woven into flexible strings varying in diameter from a minimum of about 1 mil (.001") to much larger diameters. Strings of diameters between about 5 and 200 mils are particularly useful in accordance with the present invention.

The resistance layer **11** consists of conducting particles **12** and a resin binder **13**. The conducting particles are generally composed of a low resistance material and are of a size and configuration adapted for the purpose. The resin binder **13** consists of sintered particles of a polytetrahaloethylene resin, for example, unadulterated polytetrafluoroethylene, which bind the conducting particles **12** to each other, giving continuity, and to the base **10**.

The resistance element illustrated in Fig. 1 possesses excellent physical and chemical properties, particularly a remarkable resistance to humidity and corrosive atmospheres and a pronounced flexibility and resistance to damage through handling. From an electrical standpoint, it is of special value in that the temperature coefficient of resistance may be zero or positive or negative, as desired, depending upon the nature of the inorganic base material employed and the nature and concentration of the conductor. At the same time, the element may be operated over an extreme temperature range, e. g. from minus 50° C. or less to about 300° C.

Fig. 2 represents a modified resistance element in which core material **10** with its resistance layer **11** is provided with an insulating top coating **14** of sintered particles of a polytetrahaloethylene resin. This insulating layer adds, of course, somewhat to the resistance to abrasion and the like, but is generally employed only to permit the fabrication of multi-layer resistance windings, to prevent short circuiting between turns, at high voltage levels.

Fig. 3 illustrates a simple wound resistor embodying the novel resistance element of the invention. **20** represents an insulating core of steatite or other refractory material. It is generally advisable to employ a shock resistant ceramic material, since the latter may be employed over the very wide temperature range within which the resistance elements of the invention are applicable, while at the same time it can withstand thermal shocks. Resistance element **21** is wound about core **20** and attached to terminal straps **23** and **24** at the extremities of core **20**. If so desired, the wound resistor assembly shown in Fig. 3 may be provided with a top coating of sintered particles of a polytetrahaloethylene resin, or it may be inserted in a hermetically sealed glass tube with metal end ferrules. However, such exterior protection is generally not required, since the resistance element is relatively insensitive to conditions that would be fatal to the conventional resistor.

Fig. 4 shows a partial cross-section of a resistor produced by depositing the resistance coating of the invention upon an inflexible, inorganic base material. The inorganic base material may be of any shape such as rectangular or sheet-like shape. **30** represents the insulating base, preferably of steatite, with resistance coating **31** bonded to the surface thereof. Terminal elements **32** and **33** are affixed to the ends of the base **30** for electrical connection into circuits. The base is generally cylindrical in shape, but may be of square, flat, oval or other configuration. If so desired, the base may be a tubular insulator coated on the inside, on the outside or even on both sides of the tube. The inside coated resistor is useful when the resistance element must be shielded from other devices and components.

The following examples will serve to illustrate how the novel resistance elements described herein may be prepared and embodied in a resistor. The invention is obviously not limited to the specific materials, proportions and conditions set forth therein, as these may be varied widely within the scope of the general disclosures contained herein.

Example 1

An aqueous suspension containing 30% by weight of graphite particles, was mixed in equal proportion with an aqueous suspension containing 55% of polytetrafluoroethylene particles. The resultant mixture was a uniform dispersion of graphite and polytetrafluoroethylene particles in water. A glass fiber string possessing a diameter of 0.018" was passed through the mixed suspension and thence through an oven which was held at 500° C. The oven was 3 feet long and 1 inch in diameter and the rate of travel of the string was about 10 feet per minute. The coated glass string reached a temperature in the neighborhood of 350–400° C. in the oven. By such heating the residual water was removed from the coating and the particles of polytetrafluoroethylene were sintered together and to the glass base. The resultant resistance element, possessing a diameter of about 23 mils, was wound upon a steatite core, 4" long by ½" in diameter with a total length of the resistance element of 40".

Example 2

The suspension of resin and graphite particles referred to in Example 1 was used as a coating suspension for steatite rods, .250" in diameter and 1⁹⁄₁₆" long. The resistor was produced by dipping the steatite rod in the suspension, air drying the coated rod for 10 minutes and sintering the resin particles to each other and to the rod by placing the latter in an oven held at 400° C. for about 5 minutes. This process was repeated three times, to give a total coating thickness of about .0025". The resistor was provided with terminals at the ends of the rod, as shown in Fig. 4.

Example 3

A coating dispersion of about 30% polytrifluorochloroethylene and about 70% iron oxide particles in water was prepared. This dispersion was applied to a woven glass string as described in Example 1, with a sintering temperature of about 300° C. After aging at 250° C., the resistance string was measured and found to possess a negative temperature coefficient of resistance over a temperature range of 25° C. to 150° C.

A resistor produced in the usual manner by combining graphite and massive polytetrafluoroethylene possesses a large positive temperature coefficient of resistance and is particularly unsatisfactory between about 150° C. and 200° C., over which range the resistance value is almost doubled. Therefore, to operate a resistor at high efficiency per unit volume—thus at a higher hot spot temperature—the massive polytetrafluoroethylene resistor is unsatisfactory, particularly for precision applications. In comparison, the resistors of the present invention are very adaptable to precision applications, even at the higher temperatures.

The resistor of Example 1 possessed a resistance value of 1.09 megohms at 30° C., while the resistor produced in Example 2 had a resistance value of 936 ohms at 30° C. The average temperature coefficient of resistance of the resistor of Example 1 is about −0.1% per degree centigrade from 30° C. to 190° C. The average temperature coefficient of resistance of the resistor of Example 2 is about −0.054% per degree centigrade. The flexibility, resistance to humidity, stability and inertness of both of these resistors were outstanding. Further, they do not sustain flame.

It is apparent that there are a number of variables which may be employed and controlled in accordance with the invention to produce resistance elements of almost any desired characteristics, and particularly such having negative, zero, or positive temperature coefficients of resistance. These are discussed in the following paragraphs.

The base material, as heretofore mentioned, should preferably have a thickness greater than the thickness of the layer of resistance material bonded thereto. It is preferable that the temperature coefficient of volume expansion of the base material be less than about 2.0×10^{-5}/° C. over the temperature range within which the resistor is to be operated. Base materials with volume coefficients beyond this value are not contemplated in the present invention.

The concentration of conducting particles in the polytetrahaloethylene resin binder is preferably between about 5% and about 90% although for special applications, higher and lower concentrations are possible. It is necessary that contact between adjacent conducting particles be maintained, and for this reason the particular concentration selected depends upon the size and nature of the conducting particles. With smaller particle sizes, a higher concentration thereof is desirable.

The conducting particles may be of metal, metal oxides, metal salts, carbon, etc. The conductivity of the particles per se may be very high, e. g. silver, copper, etc., or relatively low, e. g. chromium titanate, iron oxide, etc. Carbon and graphite particles are particularly useful and are stable up to the temperature limit imposed by the binder. Spinels, especially iron, manganese and nickel spinels, and solid solutions of spinels may be incorporated into the flexible coatings. The size of such conducting particles should lie between about 0.3 and about 100 microns for optimum results. Mixtures of different kinds of particles are sometimes of value.

Special resistance characteristics may be achieved with particles of chromium titanates, metal spinels, as mentioned above, and various voltage sensitive resistance materials that are employed in the manufacture of thermistors and other special devices. Further, in accordance with the invention, particles of high permeability iron, iron derived from iron-carbonyl, metal alloys, etc., may be incorporated in the coating and the resultant element used in the preparation of inductive assemblies.

The thickness of the resistance layer, as discussed heretofore, is likewise of importance. It should be preferably between about 0.0001" and about 0.050" for best results. For high power (wattage) purposes, heavier coatings have utility.

Inorganic base materials which may be employed in accordance with the invention are borosilicate glass rods, tubes, plates and strings; porcelain and steatite; quartz, etc. It is contemplated that insulating or poorly conducting organic bases may be employed. For example, a sheet or rod of a polytetrahaloethylene resin might be useful as a base material, although the temperature coefficient of volume expansion is quite high.

The tension of the elongated inorganic base material during processing and during assembly of the resistance element into a resistor is an important factor. The base material, if a glass string, is capable of being stretched, causing an increase in resistance value, if the resistance layer is present.

Processing at elevated temperatures should be carried out under conditions such that the suspending medium, such as water, will be removed and the particles of the resin sintered together without decomposition thereof. The temperature range should be from about 300° C. to about 425° C. and preferably about 350° C., in the case of polytetrafluoroethylene. The temperature range for the polytrifluorochloroethylene depends upon the molecular weight thereof.

It is readily seen that the invention can be applied to the preparation of elements which are not simple resistors. This invention can be applied to the manufacture of thermistors, inductors and the like. The broad operational temperature range of the novel resistance elements makes possible new applications for which conventional resistance elements are not satisfactory. Non-inflammable radiant heating panels may be produced. The qualities of the elongated flexible elements manufactured according to this invention are such that these elements may be used in washable heating blankets.

Further, the resistance material may be utilized to compensate the slight positive temperature coefficient of resistance of other materials, such as nickel-chrome alloys, which are widely used in the manufacture of wire-wound resistors. In such an application, a negative resistivity coefficient resistance material of the invention may be deposited upon the wire in much the same manner as it is applied to the flexible conductor in Example 1. The thickness and constitution of the deposited layer will be selected upon consideration of the characteristics of the base resistance material. Extremely thin coatings are useful in this application.

While we do not fully understand the reasons for the remarkable behavior of the composite materials of the invention, which are not predicted from the bulk or massive properties of the substances employed, we believe we have produced an oriented overgrowth, e. g., so that the resistance film acts as if it were glass, at least in its mechanical properties.

This application is a continuation in part of our copending application, Serial No. 29,318 filed May 26, 1948, now abandoned.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope hereof, it is to be understood that the invention is not limited to the specific embodiments hereof except as defined in the appended claims.

What is claimed is:

1. An electrical resistor comprising a non-conductive elongated inorganic base material having a temperature coefficient of volume expansion of less than about $2.0\times10^{-5}/°$ C., coated with a uniform dispersion of conducting particles in a polytetrahaloethylene resin said dispersion containing from about 5 to about 90% by weight of conducting particles, the thickness of the coating being appreciably less than that of the base material, whereby the expansion characteristics of the base determine the expansion characteristics of the coating, and terminal connections adapted to be inserted in an electric circuit, secured to said coating.

2. An electrical resistor comprising a non-conductive, elongated, inflexible, inorganic base material having a temperature coefficient of volume expansion of less than about $2.0\times10^{-5}/°$ C. provided with a coating consisting of a layer of conducting particles uniformly dispersed in polytetrafluoroethylene, said dispersion containing from about 5 to about 90% by weight of conducting particles, the thickness of the coating being such that expansion characteristics are determined by the expansion characteristics of the base material, and end terminal straps suitable for connection into an electrical circuit fastened to said coating and said base material at opposite ends of said base material.

3. An electrical resistance element comprising a flexible glass string coated with a layer consisting of from about 5% to about 50% by weight of conducting particles uniformly dispersed in from about 50% to about 95% of fused particles of polytetrafluoroethylene, the thickness of the coating being less than about .050" whereby the expansion characteristics are determined by the expansion characteristics of the string, and terminals suitable for connection into an electrical circuit attached to the ends of said string.

4. An electrical resistor comprising a flexible glass string having a diameter between about 0.005" and 0.200", a flexible conductive coating consisting of a mixture of conducting particles and polytetrafluoroethylene resin of a thickness between about 0.0001" and 0.050" on said string, whereby the expansion characteristics of said coating are determined by the expansion characteristics of said string, and terminal connections adapted to be inserted in an electric circuit, secured to the ends of said string.

5. A resistor as defined in claim 4 in which the conducting particles are predominantly carbon.

6. A process of producing an electrical resistance element, which comprises coating a flexible, elongated, inorganic base material with an aqueous suspension of conducting particles and polytetrafluoroethylene particles, heating said base material to remove water and to sinter the polytetrafluoroethylene particles together and to said base, and then fastening end terminals to the ends of said base.

7. A process of producing an electrical resistance element, which comprises coating an inorganic base material with a suspension of conducting particles and particles of a polytetrahaloethylene resin, removing the suspension medium, and sintering the resin particles together and to the base.

8. A process of producing an electrical resistance element, which comprises coating a flexible, elongated, inorganic base material with an aqueous suspension of conducting particles and polytetrafluoroethylene particles, and then heating to remove water and to sinter the polytetrafluoroethylene particles together and to the base.

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