March 17, 1959 B. E. ELY, JR., ET AL 2,878,353

ELECTRICAL RESISTORS

Filed Dec. 16, 1954

FIG. 1

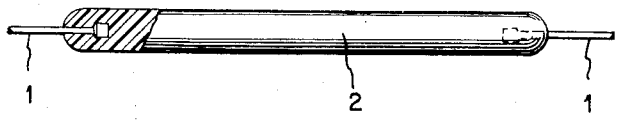


FIG. 2

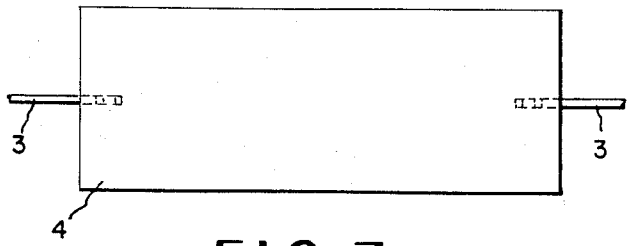
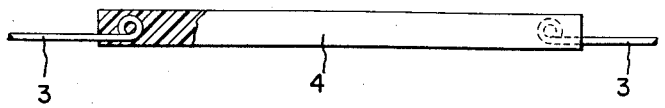


FIG. 3



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ELECTRICAL RESISTORS

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1 Claim. (Cl. 201—63)

This invention relates to improved resistors for electric circuits and more particularly to electric resistors made with tetrafluoroethylene resin and the process whereby such resistors are made.

Polytetrafluoroethylene was first obtained as a solid granular product by processes as described in U. S. Patents 2,230,654, 2,393,967 and 2,394,243. In more recent developments it was shown that concentrated aqueous dispersions of polytetrafluoroethylene could be obtained by polymerizing tetrafluoroethylene in an aqueous medium in the presence of certain surface active agents as described in U. S. Patents 2,534,058 and 2,559,752. The outstanding resistance of polytetrafluoroethylene to chemical attack and high temperatures has led to many mechanical applications of the polymer. Solid fillers such as asbestos, silica and coke flour are often added to increase rigidity and compressive strength and decrease creep of molded articles of polytetrafluoroethylene as described in U. S. Patents 2,592,147 and 2,400,099 among others. The outstanding electrical properties of the polymer have led to many applications of polytetrafluoroethylene as an insulator. The use of certain carbon filled compositions of polytetrafluoroethylene in electrical resistors, however, has not been developed heretofore.

There are numerous applications for electric resistors in electric and electronic circuits in the field of communications and other industrial fields. Resistors are, in general, resistance wires wrapped on ceramic coils and insulated with phenolic resins, phenolic resins compounded with a conductor, and the like. These resistors however have certain disadvantages. The resins in the resistors often are not useful at high temperatures in that the resin decomposes, when high electric loads giving rise to high temperatures are applied. These resins are also often subject to attack by chemicals and moisture. Resistors made by prior art processes are often too large and rigid. They will break under impact and cannot be bent.

It is therefore an object of this invention to prepare novel, high use-temperature resistors. A further object is to produce resistors from carbon filled compositions of polytetrafluoroethylene. Another object of this invention is the preparation of electric resistors by simple and inexpensive methods. Other objects will become apparent hereinafter.

The objects of this invention are accomplished by admixing from 2 to 15%, by weight of the polymer, of colloidal carbon with an aqueous dispersion of polytetrafluoroethylene until a uniform mixture is obtained, coagulating and drying the polymer, extruding the resulting curd-like compositions into the desired shape, cutting the continuous extrudate, inserting formed leads into the resistor and sintering at a temperature above 327° C. in a mold to fuse the polytetrafluoroethylene and to imbed the lead wires hermetically in the resistor. In a restricted embodiment, this invention resides in obtaining homogeneous mixtures of polytetrafluoroethylene and carbon useful in resistor applications and in a method of attaching lead wires to polytetrafluoroethylene resistors to give outstanding electric contacts.

It has now been discovered that certain compositions of polytetrafluoroethylene and carbon will give outstanding resistors. Such compositions are obtained when the carbon content is within 2 to 15% of the polytetrafluoroethylene and when the carbon is evenly dispersed throughout the polymer. Polymers having less than 2% carbon are too high in resistance to be useful and are considered insulators, polymers having more than 15% carbon are too low in resistance and could be classified as conductors. In the range of 2 to 15% of carbon the resistance of carbon polytetrafluoroethylene compositions increases almost exponentially as the carbon content is decreased; thus by varying the carbon composition any desired resistance for a standard shape can be obtained. Polytetrafluoroethylene carbon compositions, however, are useful only if the carbon is homogeneously distributed throughout the polymer. Inhomogeneities will result in the formation of hot spots causing degradation and carbonization of the polymer and thus permit the current to burn a path through the resistor, thereby lowering the resistance and making the resistor useless. By dispersing colloidal carbon in aqueous dispersions of polytetrafluoroethylene, a homogeneous mixture is obtained, and resistors made from such compositions do not vary in their resistance when used in one circuit.

A factor of great importance in the manufacture of electric resistors from compounded materials is the contact between the resistor and the circuit, for which lead wires are generally used. If the contact is not steady but changes, undesirable electric disturbances, often referred to as "noises," occur in the electric circuit. It has been found that good contacts between the polytetrafluoroethylene resistor and the terminal wires can be established if the resistors are prepared by a technique which will give high shrinkage on sintering the polymer so that the electric resistor can be shrunk on to the terminal wires and thus give firmly bonded, low noise electric contacts between the polymer and the metal lead wire. This necessary shrinkage occurs when polytetrafluoroethylene admixed with a lubricant is extruded below the sintering temperature of the polymer. The extrusion of the polymer will cause an elongation as well as an interlacing of the polymer. In the subsequent sintering operation the polymer will expand slightly on heating up and then shrink up to 20% when cooled down. By using a mold and restricting the shrinkage, lead wires can thus be firmly imbedded in the resistor. The polymer is first expanded around the lead wire and then shrunk causing a hermetic seal.

The electrical resistors of this invention are prepared from aqueous dispersions of polytetrafluoroethylene containing from 10 to 60% of solid polytetrafluoroethylene having an average particle size of 0.2 micron. The aqueous dispersions are obtained by processes such as described in U. S. Patents 2,559,752 and 2,534,058. These aqueous dispersions are then stabilized against mechanical agitation by the addition of some "Triton" X–100, a non-ionic surface active agent that is chemically an alkyl aryl polyether alcohol. A further purpose for the addition of the surface active agent is to improve the dispersion of the carbon. To this stabilized dispersion, finely divided carbon, preferably calcined gas black, is added and the mixture stirred until a homogeneous distribution has been achieved. An alternate method for obtaining homogeneous distributions of the polymer and the carbon black consists of dispersing the carbon black separately in an aqueous medium with the aid of a dispersing agent and then admixing the two dispersions of

carbon black and polymer. The mixture is coagulated and the wet, curd-like composition is dried and lubricated as described in U. S. Patent 2,586,357. The resulting paste is extruded at room temperature into a beading or a ribbon or any other desirable shape. The continuous extrudate is cut into the desired length and holes are made into each end. Into the holes, formed or straight lead wires are forced. Formed lead wires used in this invention are wires having some shape at the end, such as a mushroom or a knot or loop, that will anchor the lead wire in the polymer. The lubricant is then removed by evaporation and the resistor is placed in a mold which will permit shrinkage but resist transverse expansion. The mold and the resistor are then heated at a temperature above 327° C. to cause sintering of the polymer and the hermetic sealing of the lead wires. A void-free resistor of constant resistance with good contacts to the lead wire is thus obtained. Under certain conditions, particularly where the resistor is of a massive, self-supporting structure, it is not necessary to use a mold for sintering the resistor and hermetically imbedding the lead wires, as little or no deformation with the exception of shrinkage is observed.

The attached drawings show two resistors made by the process of this invention. The first resistor illustrated was made from extruded beading of the resistor composition Figure 1, the second from extruded tape Figure 2. The terminals (1; 3) are imbedded and sealed into the body of the resistor (2; 4) by the process described hereinabove. Two types of formed lead wires are illustrated in the drawings.

The homogeneity necessary for compositions of polytetrafluoroethylene and carbon used in the process of this invention is obtained by using aqueous dispersions of polytetrafluoroethylene admixing them with colloidal carbon such as calcined gas black in the presence of a surface active agent and then coagulating the mixture. Other conductors such as metals and other forms of polytetrafluoroethylene such as granular polymer, although useful in resistors do not give the same degree of homogeneity required in electric resistors in which the resistance are to be constant. It is believed that this is due to the larger particle size of the metals and the granular polymer even when finely divided.

Polytetrafluoroethylene resistors are, however, not limited to the method of obtaining sound terminals described hereinabove. Other methods such as a graded conductor-metal terminal may be used, terminals may be clamped on to the polymer, or may be cemented to the polymer. These methods of attaching terminals to the body of the resistor however are believed to be not as convenient and efficient as the method described herein. If, however, such methods are used it is quite possible to obtain the resistors by compression molding techniques known to those skilled in the art, instead of the extrusion used in the process of this invention.

The process of this invention is further illustrated by the following example in which all parts are by weight.

Example.—To an aqueous dispersion containing 60% by weight of colloidal polytetrafluoroethylene and 6% by weight of "Triton" X–100 was added under agitation, 3%, by weight of the polytetrafluoroethylene, of calcined gas black. The resulting mixture was agitated by a paddle stirrer at 150 R. P. M. until all the carbon had been dispersed. To this mixture was added under agitation sufficient acetone to cause coagulation of the dispersion. The resulting curd-like coagulated composition was dried at 150° C. to remove the water remaining in the coagulated material. To this dried mixture was added 20% by weight of polymer of n-decane as a lubricant and the resulting mixture was rolled in a container for a period of 20 minutes, which caused the lubricant to be uniformly distributed. This lubricated paste was then extruded through a tapered die having a ⅛" diameter orifice at room temperature using a ram pressure of 2000 p. s. i. The extruded beading was cut into ¾ inch lengths. The thus formed unsintered resistor was inserted into a 1 inch long glass tube. Small holes were drilled into the ends of the resistor and upturned lead wires were forced into the holes. The assembly was then placed into an oven at a temperature of 150° C. to remove the lubricant and then in an oven at 360° C. for a period of 30 minutes, to fuse the resistor. Upon removing the sintered polymer, the lead wires were firmly imbedded in the resistor. This operation was repeated for a series of compositions varying only in carbon content. The following results were obtained:

Table I

Weight of calcined channel black:	Resistance in ohms
2.0	3.9×10^{9}
3.0	3.1×10^{9}
3.5	1.9×10^{9}
4.0	4.3×10^{7}
4.1	4.1×10^{6}
4.4	9.6×10^{5}
4.5	9.3×10^{5}
5.0	6.4×10^{4}
6.0	1.9×10^{4}
7.0	1.3×10^{3}
8.0	1.1×10^{3}
9.0	2.5×10^{2}
10.0	1.2×10^{2}
12.0	0.7×10^{2}

The invention has been described in the example as applied to ⅛" diameter beading. The invention, however, is not limited to this size or shape. Depending on the nature of the electric current and the nature of the circuit the size and shape of the resistor may be varied. Thus thicker beading may be extruded. The cross-section of the resistor may assume that of a circle, a square, an oval, a flat ribbon or any desired shape that is extrudable. The length of the resistor may also be varied for specific purposes. The resistances obtained from such variations are of course subject to the laws of electricity. The resistors may further be enclosed in insulators such as unfilled polytetrafluoroethylene tubing or film.

From the experimental data presented hereinabove a rapid change of resistance with increase in carbon content is observed in the resistor compositions of this invention. This steep change of resistance may be levelled out by the addition of a semiconductor to the filled composition in the same manner that the carbon was added. Semiconductors useful for such purposes are ferrites, barium titanates, and the like. Large quantities of such semiconductors should be avoided as they may affect the fabrication of the filled composition, give rise to weak and brittle compositions and may lead to gross inhomogeneities in the composition.

The advantages gained by using polytetrafluoroethylene resistors are due to the nature of the polymer. Polytetrafluoroethylene resistors are insensitive to all common chemicals. The resistors are flameproof and can be used at temperatures up to 250° C. for continuous operation and higher for short periods. Since the nature of resistors is such that electrical energy is dissipated as heat energy, polytetrafluoroethylene is well suited for resistors as the polymer is not changed by prolonged heating. Furthermore the resistors of this invention are tough and resilient, they can therefore be flexed, bent, and can sustain high impacts without breaking. In addition they can be made in very small sizes for all ranges of resistance and are therefore extremely useful in miniature electric and electronic circuits. Simple and economic methods can be used for the fabrication of polytetrafluoroethylene resistors. The resistors of this invention are especially useful in electric and electronic circuits.

We claim:

The method of producing a polytetrafluoroethylene

resistor, which comprises admixing an aqueous colloidal dispersion of polytetrafluoroethylene with 2 to 15% by weight of the polymer of finely divided carbon, coagulating and drying said composition, extruding said composition in the presence of 5 to 50% by weight of the polymer of a liquid hydrocarbon lubricant introducing metal terminals into said extrudate and thereafter heating said extrudate to a temperature above 327° C. to remove the lubricant and sinter the extrudate.

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