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(54) Title: METHOD OF MAKING A LAMINATE COMPRISING A CONDUCTIVE POLYMER COMPOSITION		
(57) Abstract		
<p>A method of making a laminate from a conductive polymer composition in which a particulate filler is dispersed in a polymeric component. The method comprises the following steps conducted sequentially in a single continuous procedure: (A) loading the polymeric component and the conductive filler into a mixing apparatus; (B) mixing the polymeric component and the conductive filler to form a molten mixture; (C) transporting the mixture from the mixing apparatus through a die; (D) forming a polymeric sheet; and (E) attaching metal foil to a least one side of the sheet to form a laminate. The laminate can be used to prepare circuit protection devices or heaters.</p>		

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## METHOD OF MAKING A LAMINATE COMPRISING A CONDUCTIVE POLYMER COMPOSITION

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### BACKGROUND OF THE INVENTION

#### Field of the Invention

10 This invention relates to a method of making a laminate comprising a conductive polymer composition and electrical devices comprising such laminate.

#### Introduction to the Invention

15 Conductive polymer compositions which exhibit PTC (positive temperature coefficient of resistance) behavior are well-known for use in electrical devices such as circuit protection devices. Such compositions comprise a polymeric component, and dispersed therein, a particulate conductive filler such as carbon black or metal. The amount and type of filler in the composition are determined by the required resistivity for each application, as well as by the nature of the polymeric component. Compositions suitable for use in circuit protection devices have low resistivities at room temperature, e.g. less than 100 ohm-cm, and generally comprise relatively high levels of conductive filler. When such highly filled compositions are prepared by conventional methods such as melt-mixing, they are subject to substantial shear. Such shear generates heat, which may degrade the polymer and result in an increased resistivity. Further shear and/or heat exposure results from the subsequent processing steps, e.g. extrusion, melt-forming, and attachment of electrodes, e.g. by lamination. Conventional processing techniques provide that some of these steps, e.g. extrusion and lamination, can be performed in a continuous process, but it is common, due to the desire to ensure adequate dispersion of the filler in the polymer, to divide the manufacturing process into several discrete, i.e. separate, steps. The more times the composition is heated, cooled, and subjected to shear, the greater the chances of degradation and resistivity change.

35 Compositions with low resistivity are desirable for use in circuit protection devices which respond to changes in ambient temperature and/or current conditions. Under normal conditions, a circuit protection device remains in a low temperature, low resistance state in series with a load in an electrical circuit. When exposed to an overcurrent or overtemperature condition, however, the device increases in resistance, effectively shutting down the current

flow to the load in the circuit. For many applications it is desirable that the device have as low a resistance as possible in order to minimize the effect on the resistance of the electrical circuit during normal operation. Although low resistance devices can be made by changing dimensions, e.g. making the distance between the electrodes very small or the device area very large, small devices are preferred because they occupy less space on a circuit board and generally have desirable thermal properties. The most common technique to achieve a small device is to use a composition that has a low resistivity. The resistivity of a conductive polymer composition can be decreased by adding more conductive filler, but this process can affect the processability of the composition, e.g. by increasing the viscosity. Furthermore, the addition of conductive filler generally reduces the size of the PTC anomaly, i.e. the size of the increase in resistivity of the composition in response to an increase in temperature, generally over a relatively small temperature range. The required PTC anomaly is determined by the applied voltage and the application. It is therefore necessary to minimize the effects of processing which result in resistivity increases, in order to achieve a composition with acceptable size and electrical properties.

#### SUMMARY OF THE INVENTION

We have now found that by using a process in which a laminate in which a conductive polymer composition is attached to a metal foil electrode (and is preferably sandwiched between two metal foil electrodes) is conducted in a single continuous procedure, devices can be prepared which have low resistivity, adequate PTC anomaly, and good electrical performance. The continuous procedure to produce the laminate allows raw, unmelted polymer and filler ingredients to be introduced into a mixing apparatus, e.g. an extruder, and to be melt-formed into a laminate, reducing the number of steps needed to produce a device. Unlike the conventional process in which the raw ingredients are melt-mixed and pelletized, then dried and extruded into a sheet to be laminated, the method of the invention allows the elimination of the pelletizing step, along with drying of the pellets before the sheet-forming step. This means that the composition is exposed to one less heating and shearing process.

In a first aspect this invention provides a method of making a laminate from a conductive polymer composition which comprises (i) a polymeric component and (ii) a particulate conductive filler dispersed in the polymeric component, said method comprising

(A) loading the polymeric component and the conductive filler into a mixing apparatus;

- (B) mixing the polymeric component and the conductive filler in the mixing apparatus to form a molten mixture;
- (C) transporting the molten mixture from the mixing apparatus through a die;
- (D) forming the molten mixture into a polymeric sheet; and
- (E) attaching metal foil to at least one side of the sheet to form a laminate,

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10 steps (A) to (E) being conducted sequentially in a single continuous procedure.

In a second aspect, this invention provides an electrical device which

- (1) comprises (a) a resistive element which is composed of a conductive polymer composition which exhibits PTC behavior and which comprises (i) a polymeric component which has a melting temperature  $T_m$ , and (ii) dispersed in the polymeric component a particulate conductive filler; and (b) two electrodes which (i) are attached to the resistive element, (ii) comprise metal foil, and (iii) can be connected to a source of electrical power;

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- (2) has a resistance at 20°C,  $R_{20}$ , of at most 50.0 ohm;
- (3) has a resistivity at 20°C,  $\rho_{20}$ , of at most 50.0 ohm-cm; and

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- (4) has been made by a method which comprises

(A) loading the polymeric component and the conductive filler into a mixing apparatus;

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(B) mixing the polymeric component and the conductive filler in the mixing apparatus to form a molten mixture;

(C) transporting the molten mixture from the mixing apparatus through a die;

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(D) forming the molten mixture into a polymeric sheet;

(E) attaching metal foil to two sides of the sheet to form a laminate; and

(F) cutting the laminate to form the device,

5 steps (A) to (E) being conducted sequentially in a single continuous procedure.

#### DETAILED DESCRIPTION OF THE INVENTION

10 The method of the invention is used to make a laminate of a conductive polymer composition. The conductive polymer composition comprises a polymeric component, and, dispersed in the polymeric component, a particulate conductive filler.

15 The polymeric component of the composition comprises one or more polymers, one of which is preferably a crystalline polymer having a crystallinity of at least 20% in its unfilled state as measured by a differential scanning calorimeter. Suitable crystalline polymers include polymers of one or more olefins, particularly polyethylene such as high density polyethylene; copolymers of at least one olefin and at least one monomer copolymerisable therewith such as ethylene/acrylic acid, ethylene/ethyl acrylate, ethylene/vinyl acetate, and ethylene/butyl acrylate copolymers; melt-shapeable  
20 fluoropolymers such as polyvinylidene fluoride and ethylene/tetrafluoroethylene copolymers (including terpolymers); and blends of two or more such polymers. For some applications it may be desirable to blend one crystalline polymer with another polymer, e.g. an elastomer or an amorphous thermoplastic polymer, in order to achieve specific physical or thermal properties, e.g. flexibility or maximum exposure temperature. The polymeric component has  
25 a melting temperature, as measured by the peak of the endotherm of a differential scanning calorimeter, of  $T_m$ . When there is more than one peak, as for example in a mixture of polymers,  $T_m$  is defined as the temperature of the highest temperature peak. The polymeric component generally comprises 40 to 90% by volume, preferably 45 to 80% by volume, especially 50 to 75% by volume of the total volume of the composition.

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The particulate conductive filler which is dispersed in the polymeric component may be any suitable material, including carbon black, graphite, metal, metal oxide, conductive coated glass or ceramic beads, particulate conductive polymer, or a combination of these. The filler may be in the form of powder, beads, flakes, fibers, or any other suitable shape.  
35 The quantity of conductive filler needed is based on the required resistivity of the composition and the resistivity of the conductive filler itself. For many compositions the

conductive filler comprises 10 to 60% by volume, preferably 20 to 55% by volume, especially 25 to 50% by volume of the total volume of the composition.

The conductive polymer composition may comprise additional components, such as antioxidants, inert fillers, nonconductive fillers, radiation crosslinking agents (often referred to as prorads or crosslinking enhancers, e.g. triallyl isocyanurate), stabilizers, dispersing agents, coupling agents, acid scavengers (e.g.  $\text{CaCO}_3$ ), or other components. These components generally comprise at most 20% by volume of the total composition.

The composition generally exhibits positive temperature coefficient (PTC) behavior, i.e. it shows a sharp increase in resistivity with temperature over a relatively small temperature range, although the method of the invention may be used to prepare compositions which exhibit zero temperature coefficient (ZTC) behavior. In this application, the term "PTC" is used to mean a composition or device which has an  $R_{14}$  value of at least 2.5 and/or an  $R_{100}$  value of at least 10, and it is preferred that the composition or device should have an  $R_{30}$  value of at least 6, where  $R_{14}$  is the ratio of the resistivities at the end and the beginning of a  $14^\circ\text{C}$  range,  $R_{100}$  is the ratio of the resistivities at the end and the beginning of a  $100^\circ\text{C}$  range, and  $R_{30}$  is the ratio of the resistivities at the end and the beginning of a  $30^\circ\text{C}$  range. Generally the compositions used in devices of the invention which exhibit PTC behavior show increases in resistivity which are much greater than those minimum values. It is preferred that compositions used to form devices of the invention have a PTC anomaly at at least one temperature over the range from  $20^\circ\text{C}$  to  $(T_m + 5^\circ\text{C})$  of at least  $10^4$ , preferably at least  $10^{4.5}$ , particularly at least  $10^5$ , especially at least  $10^{5.5}$ , i.e. the  $\log[\text{resistance at } (T_m + 5^\circ\text{C})/\text{resistance at } 20^\circ\text{C}]$  is at least 4.0, preferably at least 4.5, particularly at least 5.0, especially at least 5.5. If the maximum resistance is achieved at a temperature  $T_x$  that is below  $(T_m + 5^\circ\text{C})$ , the PTC anomaly is determined by the  $\log(\text{resistance at } T_x/\text{resistance at } 20^\circ\text{C})$ .

The resistivity of the composition depends on the application and what type of electrical device is required. When, as is preferred, the composition is used to make laminate for circuit protection devices, the composition has a resistivity at  $20^\circ\text{C}$ ,  $\rho_{20}$ , of at most 100 ohm-cm, preferably at most 50 ohm-cm, more preferably at most 20 ohm-cm, particularly at most 10 ohm-cm, more particularly at most 5 ohm-cm, especially at most 2.0 ohm-cm, most especially at most 1.0 ohm-cm. When the composition is used in a heater, the resistivity of the conductive polymer composition is preferably higher, e.g. at least  $10^2$  ohm-cm, preferably at least  $10^3$  ohm-cm.

Suitable conductive polymer compositions are disclosed in U.S. Patent Nos. 4,237,441 (van Konynenburg et al), 4,388,607 (Toy et al), 4,534,889 (van Konynenburg et al), 4,545,926 (Fouts et al), 4,560,498 (Horsma et al), 4,591,700 (Sopory), 4,724,417 (Au et al), 4,774,024 (Deep et al), 4,935,156 (van Konynenburg et al), 5,049,850 (Evans et al), and 5,250,228 (Baigrie et al), 5,378,407 (Chandler et al), 5,451,919 (Chu et al), and 5,582,770 (Chu et al), and in International Publications Nos. WO96/29711 (Raychem Corporation, published September 26, 1996) and WO96/30443 (Raychem Corporation, published October 3, 1996).

The method of the invention comprises five steps, steps (A) to (E), which are conducted sequentially in a single continuous procedure. Additional process steps, e.g. heat-treatment or irradiation, may be conducted between two steps of the invention so long as the process remains continuous. At least parts of two steps may be conducted simultaneously, e.g. transporting the molten mixture through a die (step (C)) which has a shape which forms the molten mixture into a polymeric sheet (step (D)).

In step (A), the polymeric component and the particulate conductive filler are loaded into a mixing apparatus. In a preferred embodiment, both the polymeric component and the conductive filler are in the form of dry powders, flakes, fibers, or pellets which can be readily fed into the mixing apparatus. Although these two components can be fed separately into the mixing apparatus, preferably the polymeric component and the conductive filler are "premixed" in the dry state, e.g. by means of a blender or mixer such as a Henschel™ mixer, to improve the uniformity and flow of the components during the loading step. Additional components, in the form of powder, pellets, or liquid, may be premixed with the polymer component and the particulate component, or may be added at different points in the process. Loading may be achieved by any means, although loss-in-weight feeders such as those sold by K-Tron America under the tradename "K-Tron", are preferred to ensure consistent feeding into the apparatus. The mixing apparatus is preferably an extruder, although other types of mixing equipment, including internal mixers such as Banbury™ mixers, Brabender™ mixers, and Moriyama™ mixers, may be used with suitable attachments for conveying material to complete the required steps of the invention. Suitable extruders include single screw extruders, co-rotating twin screw extruders, counter-rotating twin screw extruders, or reciprocating single screw extruders, e.g. a Buss™ kneader. When an extruder is used, various additives, e.g. crosslinking agents such as peroxide, can be added continually at a feed port downstream from the port in which the polymeric component and conductive filler are introduced. Unlike conventional methods in which adding a crosslinking agent to a



composition would result in a crosslinked mass which could not easily be subsequently formed into a uniform sheet or other shape, the method of the invention is particularly suited for in-line chemical crosslinking. The continuous procedure allows the crosslinking agent to be added just before the material is transported through a die.

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In step (B), the polymeric component and the conductive filler are mixed in the mixing apparatus to form a molten mixture, i.e. one which has a temperature above the melting temperature  $T_m$  of the polymeric component. During step (B), the conductive filler, as well as other components such as inorganic fillers or pigments, is dispersed in the polymeric component. To ensure that adequate mixing and dispersion is achieved, the screw of an extruder may be designed to have mixing or kneading sections, as well as conveying sections. For example, we have found that incorporating kneading sections in at least 10% of the total screw length for a corotating twin screw extruder has produced acceptable dispersion. When an extruder is used, it is preferred that the ratio of the screw length to its diameter, i.e. the L/D ratio, is at least 10:1, preferably at least 15:1, particularly at least 20:1, especially at least 30:1, e.g. 40:1, in order to achieve adequate dispersion of the conductive filler. The mixing apparatus may be heated, e.g. electrically or by oil, in one or more sections (zones). A vacuum apparatus, to remove volatiles generated during mixing, can be positioned appropriately in combination with the mixing apparatus.

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In step (C), the molten mixture is transported from the mixing apparatus through a die. The term "die" is used in this specification to mean any element which has an orifice through which the molten material can pass. Thus a die may be a mold, a nozzle, or an article with an opening or gap of a particular shape through which the molten material passes. The die can be attached directly to an exit port of the mixing apparatus, e.g. by means of an adapter, or it may be separated from the mixing apparatus by one or more pieces of equipment, e.g. a gear pump or a vacuum apparatus. When the mixing apparatus is an extruder, the "transporting" of the molten mixture occurs during the normal operation of the extruder. Other means of transporting the molten mixture may be required if other types of mixing apparatus are used.

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In step (D), the molten mixture is formed into a polymeric sheet. This can be achieved easily by extrusion through a sheet die or by calendering the molten mixture, i.e. passing the molten mixture between rollers or plates to thin it into a sheet. The thickness of the calendered sheet is determined by the distance between the plates or rollers, as well as the rate at which the rollers are rotating. Generally the polymeric sheet has a thickness of 0.025 to 3.8 mm (0.001 to 0.150 inch), preferably 0.051 to 2.5 mm (0.002 to 0.100 inch). The

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polymeric sheet may have any width. The width is determined by the shape and width of the die or the volume of material and rate of calendering, and is often 0.15 to 0.31 m (6 to 12 inches).

5 In step (E), a laminate is formed by attaching metal foil to at least one side, preferably to both sides, of the polymeric sheet. When the laminate is cut into an electrical device, the metal foil layer(s) act(s) as an electrode. The metal foil generally has a thickness of at most 0.13 mm (0.005 inch), preferably at most 0.076 mm (0.003 inch), particularly at most 0.051 mm (0.002 inch), e.g. 0.025 mm (0.001 inch). The width of the metal foil is generally  
10 approximately the same as that of the polymeric sheet, but for some applications, it may be desirable to apply the metal foil in the form of two or more narrow ribbons, each having a width much less than that of the polymeric sheet. Suitable metal foils include nickel, copper, brass, aluminum, molybdenum, and alloys, or foils which comprise two or more of these materials in the same or different layers. Particularly suitable metal foils have at least one  
15 surface that is electrodeposited, preferably electrodeposited nickel or copper. Appropriate metal foils are disclosed in U.S. Patents Nos. 4,689,475 (Matthiesen), and 4,800,253 (Kleiner et al), and in International Publication No. WO95/34081 (Raychem Corporation, published December 14, 1995). In a preferred embodiment, the metal foil contacts the polymeric sheet and is then passed through rollers, e.g. via a roll stack, to promote good lamination of the foil  
20 to the polymer. In addition, to minimize cooling of the sheet as it exits the die, it is preferred that the distance between the die and the roll stack be relatively small, e.g. less than 0.61 m (2 feet), preferably less than 0.31 m (1 foot). For some applications, an adhesive composition (i.e. a tie layer) may be applied to the polymeric sheet, e.g. by spraying or brushing, before contact with the metal foil. The laminate resulting from step (E) may be wound onto a reel or  
25 sliced into discrete pieces for further processing or storage. The thickness of the laminate is generally 0.076 to 4.1 mm (0.003 to 0.160 inch).

The method of the invention can be used to produce a laminate with more than one polymeric sheet by using two or more mixing apparatus/transporting/forming set-ups which  
30 produce polymeric sheets based on the same or different polymeric components and conductive fillers.

When the laminate comprises two metal foils, it can be used to form an electrical device, particularly a circuit protection device. The device may be cut from the laminate in  
35 step (F). In this application, the term "cut" is used to include any method of isolating or separating the device from the laminate, e.g. dicing, punching, shearing, cutting, etching and/or breaking as described in International Publication No. WO95/34084 (Raychem

Corporation, published December 4, 1995), or any other suitable means. Step (F) may, but need not, be part of the single continuous procedure of steps (A) to (E). Additional metal leads, e.g. in the form of wires or straps, can be attached to the foil electrodes to allow electrical connection to a circuit. In addition, elements to control the thermal output of the device, e.g. one or more conductive terminals, can be used. These terminals can be in the form of metal plates, e.g. steel, copper, or brass, or fins, that are attached either directly or by means of an intermediate layer such as solder or a conductive adhesive, to the electrodes. See, for example, U.S. Patent Nos. 5,089,801 (Chan et al) and 5,436,609 (Chan et al). For some applications, it is preferred to attach the devices directly to a circuit board. Examples of such attachment techniques are shown in International Publications Nos. WO94/01876 (Raychem Corporation, published January 20, 1994) and WO95/31816 (Raychem Corporation, published November 23, 1995).

In order to improve the electrical stability of the device, it is often desirable to subject the device to various processing techniques, e.g. crosslinking and/or heat-treatment. Crosslinking can be accomplished by chemical means or by irradiation, e.g. using an electron beam or a  $\text{Co}^{60}$   $\gamma$  irradiation source. The level of crosslinking depends on the required application for the composition, but is generally less than the equivalent of 200 Mrads, and is preferably substantially less, i.e. from 1 to 20 Mrads, preferably from 1 to 15 Mrads, particularly from 2 to 10 Mrads for low voltage (i.e. less than 60 volts) circuit protection applications. Generally devices are crosslinked to the equivalent of at least 2 Mrads. Various processing procedures for devices are described in International Publication No. WO96/29711 (published September 26, 1996).

Devices of the invention are preferably circuit protection devices that generally have a resistance at 20°C,  $R_{20}$ , of less than 100 ohms, preferably less than 50 ohms, particularly less than 20 ohms, more particularly less than 10 ohms, especially less than 5 ohms, most especially less than 1 ohm. Because laminate prepared by the method of the invention comprises a conductive polymer composition which can have a low resistivity, it can be used to produce devices with very low resistances, e.g. 0.001 to 0.100 ohm. Devices which are heaters generally have a resistance of at least 100 ohms, preferably at least 250 ohms, particularly at least 500 ohms.

It is to be understood that the laminate made by the method of this invention can be used for any type of electrical device, e.g. heaters or sensors, as well as circuit protection devices.

The invention is illustrated by the following Examples in which Examples 1, 2, 4, 6, 8, and 10 are Comparative Examples.

#### Examples 1 to 7

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For each Example, the following ingredients, in the weight percentages based on the weight of the total composition listed in Table I, were mixed at 1500 rpm for three minutes using a Henschel™ mixer: PVDF (KF™ 1000W, polyvinylidene fluoride in powder form with a melting temperature of about 177°C, available from Kureha), ETFE (Tefzel™ HT 10 2163, ethylene/ tetrafluoroethylene/perfluorinated butyl ethylene terpolymer with a melting temperature of about 235°C, available from DuPont), CB (Raven™ 430, carbon black, available from Columbian Chemicals), TAIC (triallyl isocyanurate), and CaCO<sub>3</sub> (Atomite™ powder, calcium carbonate, available from John K. Bice Co.) The mixed dry ingredients were then subjected to either a two-step process (comparative) or a one-step process of the 15 invention.

#### Two-Step Process

For Comparative Examples 1, 2, 4, and 6, the mixed dry ingredients were introduced 20 into a corotating twin screw extruder using a screw with an L/D ratio of 40:1 (ZSK-40, available from Werner-Pfleiderer), mixed, extruded into strands, and cut into pellets.

For Example 1, the pellets were dried at 80°C (175°F) for at least 24 hours and then were extruded through a 25 mm (1 inch) single screw extruder fitted with a nozzle with a 25 diameter of 9.5 mm (0.375 inch). The molten material was extruded from the nozzle and fed onto a roll stack positioned about 25 mm (1 inch) from the nozzle end. The roll stack was used to both calender the material into a sheet with a thickness of about 0.250 mm (0.010 inch) and a width of about 114 to 152 mm (4.5 to 6.0 inches) and to attach electrodeposited 30 nickel/copper foil (Type 31, 1-oz foil having a thickness of about 0.044 mm (0.0017 inch) available from Fukuda) to both sides of the calendered sheet. The resulting laminate had a thickness of about 0.34 mm (0.0135 inch).

For Examples 2, 4, and 6, the pellets were extruded through a counter-rotating/co-rotating twin-screw extruder (ZSE-27, available from Leistritz) in a corotation mode using a 35 screw with no kneading elements and having an L/D ratio of 40:1. The extruder was fitted with a gear pump having a capacity of 10 cm<sup>3</sup>/revolution (Pep II, available from Zenith) and

then with a nozzle as above. The material was extruded, calendered, and laminated following the same procedure as for Example 1.

#### One-Step Process

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The mixed dry ingredients were introduced into a ZSE-27 extruder used in a corotation mode, and having a screw configuration in which 11% of the total screw length was kneading elements. The screw had an L:D ratio of 40:1. The extruder was fitted with a gear pump and nozzle as in Examples 2, 4, and 6. The material was mixed, and the mixed  
10 material was extruded through the gear pump and nozzle, calendered, and laminated following the same procedure as for Examples 2, 4, and 6.

#### Device Preparation

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For Examples 2 to 7, the laminate was irradiated in a continuous process using a 3.5 MeV electron beam to a total of 7.5 Mrad. The laminate was then coated in a continuous process with solder (using a solder temperature of about 250°C), and devices with dimensions of 11 x 15 mm (0.43 x 0.59 inch) were punched from the laminate. Two 20 AWG tin-coated copper leads about 25 mm (1 inch) long were attached to the device and the device was  
20 temperature cycled at a rate of 10°C/minute from 40°C to 160°C to 40°C for six cycles, with a 30 minute dwell time at the temperature extremes for each cycle.

For Example 1, devices with dimensions as above were cut from laminate that had been irradiated as discrete pieces and had not been solder-coated. Leads were attached and  
25 the devices were temperature cycled as above.

TABLE I

Example	1*	2*	3	4*	5	6*	7
Composition in weight% (density in g/cm <sup>3</sup> )							
PVDF (1.76)	52.90	52.90	52.90	58.20	58.20	56.43	56.43
ETFE (1.70)	5.89	5.89	5.89	6.47	6.47	6.27	6.27
CB (1.8)	37.23	37.23	37.23	31.35	31.35	33.32	33.32
TAIC (1.158)	2.00	2.00	2.00	2.00	2.00	2.00	2.00
CaCO <sub>3</sub> (2.71)	1.98	1.98	1.98	1.98	1.98	1.98	1.98
Process Steps	2	2	1	2	1	2	1

\*Comparative Examples

## 5 Device Testing

The device resistance at 20°C was measured and the resistivity calculated. The resistance versus temperature properties of the device were determined by positioning the device in an oven and measuring the resistance at intervals over the temperature range 20 to 200 to 20°C. The height of the PTC anomaly, PTC, was determined after the first temperature cycle as log(resistance at 175°C/resistance at 20°C).

The results, shown in Table II, indicate that the devices made by the method of the invention had lower initial resistances than devices made by the conventional process. In addition, the method of the invention produced devices which had PTC anomalies similar to those made by the conventional method even though the composition for the devices of the invention contained less conductive filler (compare Example 5 with Example 6 and Example 7 with Example 2).

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TABLE II

Example	1*	2*	3	4*	5	6*	7
R <sub>0</sub> (mohm)	17.9	14.6	10.9	38.3	23.7	26.1	15.6
ρ <sub>20</sub> (ohm-cm)	1.11	0.95	0.71	2.49	1.54	1.69	1.01
PTC (decades)	4.1	4.4	3.9	5.5	5.5	5.3	4.5

\*Comparative Examples

### Examples 8 to 11

The following ingredients, in the weight percentages listed in Table III, were mixed in a Henschel mixer: HDPE (Petrothene™ LB832, high density polyethylene having a melting temperature of about 135°C, available from Quantum Chemical), EBA (Enathene™ 705-009, ethylene/n-butyl acrylate copolymer having a melting temperature of about 105°C, available from Quantum Chemical), and CB (Raven 430). The mixed dry ingredients were then subjected to either a two-step process or a one-step process.

#### 10 Two-Step Process

For Comparative Examples 8 and 10, the mixed dry ingredients were introduced into a 70 mm (2.75 inch) Buss kneader (a reciprocating single screw extruder), mixed, extruded into strands, and cut into pellets. A ZSE-27 extruder in a corotation mode with a screw having no kneading elements and an L:D ratio of 40:1 was fitted with a gear pump at the exit port of the extruder as in Example 2. The gear pump was attached to a sheet die having an opening 152 mm (6 inch) wide and 0.038 mm (0.0015 inch) thick. The pellets were extruded through the sheet die to form a polymeric sheet and the polymeric sheet was drawn from the die onto a roll stack spaced about 12.7 mm (0.5 inch) from the die lip and having rubber-coated rollers heated to about 155°C. Nickel/copper foil as described in Example 1 was laminated onto the polymeric sheet. The resulting laminate had a thickness of about 0.127 mm (0.005 inch).

#### One Step Process

For Examples 9 and 11, the mixed dry ingredients were introduced into a ZSE-27 extruder used in a corotation mode, and having a screw configuration in which 11% of the total screw length was kneading elements and the L:D ratio was 40:1. The material was mixed in the extruder, and continuously extruded and laminated using the gear pump, die, and lamination process described for Example 8.

#### 30 Device Preparation

Laminate was solder coated in a continuous (using a solder temperature of about 220°C), and devices with dimensions of 5 x 12 mm (0.20 x 0.47 inch) were punched from the laminate. The devices were heat-treated in a process that exposed them to a temperature of 185 to 215°C for about 4 seconds. The devices were then crosslinked to 10 Mrad using a Co<sup>60</sup> gamma irradiation source. Nickel leads with dimensions of 0.13 x 5 x 13.5 mm (0.005 x

0.2 x 0.5 inch) were attached to the electrodes on both sides of the device by solder reflow and the devices were temperature cycled six cycles from -40°C to 85°C with a 30 minute dwell time at the temperature extremes.

## 5 Device Testing

Devices were tested as above except that the PTC anomaly was measured over a temperature range of 20 to 160 to 20°C. The height of the PTC anomaly was determined at three different temperatures, 105°C, 125°C, and 140°C as  $\log(\text{resistance at } T_y^\circ\text{C}/\text{resistance at } 20^\circ\text{C})$  for the second cycle, where y was the measurement temperature. (The measurement at 140°C was closest to the actual melting pointing of the conductive polymer composition.) The results, shown in Table III, indicated that similar PTC anomalies could be achieved, but with a much lower resistance, for a composition made with the one-step continuous process rather than a conventional two-step process (compare Examples 8 and 9).

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TABLE III

Example	8*	9	10*	11
Composition in weight % (density in g/cm <sup>3</sup> )				
HDPE (0.954)	5.0	5.0	4.8	4.8
EBA (0.922)	45.0	45.0	43.0	43.0
CB (1.8)	50.0	50.0	52.2	52.2
R <sub>0</sub> (mohm)	44.6	33.4	28.6	22.8
PTC <sub>105</sub>	5.42	4.73	4.35	3.76
PTC <sub>125</sub>	8.95	8.12	7.50	6.62
PTC <sub>140</sub>	9.35	8.28	7.64	6.73

\*Comparative Examples



What is claimed is:

1. A method of making a laminate from a conductive polymer composition which comprises (i) a polymeric component and (ii) a particulate conductive filler dispersed in the polymeric component, said method comprising

- (A) loading the polymeric component and the conductive filler into a mixing apparatus;
- (B) mixing the polymeric component and the conductive filler in the mixing apparatus to form a molten mixture;
- (C) transporting the molten mixture from the mixing apparatus through a die;
- (D) forming the molten mixture into a polymeric sheet; and
- (E) attaching metal foil to at least one side of the sheet to form a laminate,

steps (A) to (E) being conducted sequentially in a single continuous procedure.

2. A method according to claim 1 wherein the mixing apparatus is an extruder, preferably a single screw extruder, a co-rotating twin screw extruder, a counter-rotating twin screw extruder, or a reciprocating single screw extruder.

3. A method according to claim 1 wherein the die is a nozzle.

4. A method according to claim 1 wherein the die is directly attached to an exit port of the mixing apparatus.

5. A method according to claim 1 wherein step (E) comprises attaching metal foil to two sides of the sheet.

6. A method according to claim 1 wherein the conductive polymer composition in the laminate has a resistivity of less than 20 ohm-cm, preferably less than 10 ohm-cm.

7. A method according to claim 1 wherein the polymeric sheet has a thickness of 0.025 to 3.8 mm (0.001 to 0.150 inch), and is formed by extrusion or calendering.
8. An electrical device which
  - (1) comprises (a) a resistive element which is composed of a conductive polymer composition which exhibits PTC behavior and which comprises (i) a polymeric component which has a melting temperature  $T_m$ , and (ii) dispersed in the polymeric component a particulate conductive filler; and (b) two electrodes which (i) are attached to the resistive element, (ii) comprise metal foils, and (iii) can be connected to a source of electrical power;
  - (2) has a resistance at 20°C,  $R_{20}$ , of at most 50.0 ohm;
  - (3) has a resistivity at 20°C,  $\rho_{20}$ , of at most 50.0 ohm-cm; and
  - (4) has been made by a method according to claim 5 which further comprises
    - (F) cutting the laminate to form the device.
9. A device according to claim 8 wherein the polymeric component comprises a crystalline polymer which is a polyethylene, an ethylene copolymer, a fluoropolymer, or a mixture of these polymers, and the particulate filler comprises carbon black.
10. A device according to claim 8 which has a PTC anomaly of at least  $10^{4.0}$ .

# INTERNATIONAL SEARCH REPORT

In: .tional Application No  
PCT/US 97/13419

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 B32B31/30 B32B15/08 H01C7/02

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 B29C H01C B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 97 06660 A (BOURNS MULTIFUSE HONG KONG LTD) 27 February 1997 see page 4, line 12 - line 18 see page 7, line 29 - page 8, line 29 see page 14, line 8 - page 17, line 23 see figures 1,2	1-7
P,Y	---	8-10
P,X	GB 2 301 223 A (JOHNSON ELECTRIC SA) 27 November 1996 see page 2, line 17 - line 26 see page 4, line 23 - line 27 see page 5, line 11 - line 33 see figure 2	1-7
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

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Date of the actual completion of the international search

20 October 1997

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INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 97/13419

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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Y	"IN-LINE COMPOUNDING/ EXTRUSION KNOW HOW" EUROPEAN PLASTICS NEWS., vol. 10, no. 12, December 1983, LONDON GB, XP002044048 see page 36 ---	1-7
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