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(54) **Radiation cross-linking of PTC conductive polymers.**

(57) The higher the voltage applied to an electrical device comprising a PTC conductive polymer, the more likely it is that intermittent application of the voltage will cause the device to fail. According to the invention, the likelihood of such failure is substantially reduced by irradiating the PTC conductive polymer (1) so that it is very highly cross-linked, for example to a dosage of at least 50 Mrads, preferably at least 80 Mrads, especially at least 120 Mrads. In this way, for example, it is possible to make a circuit protection device which will continue to provide effective protection even after repeated exposure to a voltage of 200 volts.

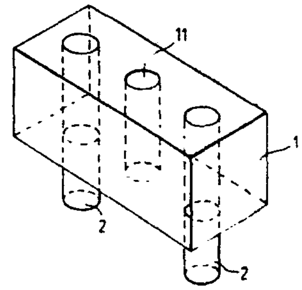

Fig.2

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This invention relates to the radiation cross-linking of PTC conductive polymers.

Conductive polymer compositions exhibiting PTC behavior, and electrical devices comprising them, have been described in published documents and in our earlier specifications. Reference may be made, for example, to U. S. Patents Nos. 2,952,761, 2,978,665, 3,243,753, 3,351,882, 3,571,777, 3,757,086, 3,793,716, 3,823,217, 3,858,144, 3,861,029, 4,017,715, 4,072,848, 4,085,286, 4,117,312, 4,177,376, 4,177,446, 4,188,276, 4,237,441, 4,242,573, 4,246,468, 4,250,400, 4,255,698, 4,272,471, 4,276,466 and 4,314,230; J. Applied Polymer Science 19, 813-815 (1975), Klason and Kubat; Polymer Engineering and Science 18, 649-653 (1978), Narkis et al; German OLS 2,634,999, 2,746,602, 2,755,076, 2,755,077, 2,821,799 and 3,030,799; European Published Applications Nos. 0028142, 0030479, 0038713, 0038714, 0038715 and 0038718; pending European Applications No. 81,301,767.0, 81,301,768.8 and 81,302,201.9; and pending U.S. Applications Nos. 176,300, 184,647, 254,352, 272,854 and 300,709. The disclosures of these patents, publications and applications are incorporated herein by reference.

It is known to cross-link PTC conductive polymers by radiation, and in practice the dosages employed have been relatively low, e.g. 10-20 Mrads. Higher dosages have, however, been proposed for some purposes. Thus OLS 2,634,999 recommends a dose of 20-45 Mrads; U.K. Specification No. 1,071,032 describes irradiated compositions comprising a copolymer of ethylene and a vinyl ester or an acrylate monomer and 50-400% by weight of a filler, e.g. carbon black, the radiation dose being about 2 to about 100 Mrads, preferably about 2 to about 20 Mrads, and the use of such compositions as tapes for grading the insulation on cables; and U.S. Patent No. 3,351,882 discloses the preparation of electrical devices by embedding planar electrodes in a PTC conductive polymer element, and then cross-linking the conductive polymer by irradiating it to a dosage of 50 to 100 Mrads.

The higher the voltage applied to an electrical device comprising a PTC conductive polymer, the more likely it is that intermittent application of the voltage will cause the device to fail. This has been a serious problem, for example, in the use of circuit protection devices where the voltage dropped over the device in the "tripped" (i.e. high resistance) condition is more than about 200 volts. [Voltages given herein are DC values or RMS values for AC power sources.] We have now discovered that the likelihood of such failure can be substantially reduced by irradiating the conductive polymer so that it is very highly cross-linked.

In its first aspect, the invention provides a process for the preparation of an electrical device comprising (a) a cross-linked PTC conductive polymer element and (b) two electrodes which can be connected to a power source to cause current to flow through the PTC element, which process comprises cross-linking the PTC element by irradiating it to a dosage of at least 50 Mrads, subject to the proviso that if each of the electrodes has a substantially planar configuration, then either (a) the element is irradiated to a dosage of at least 120 Mrads, or

(b) the electrodes are metal foil electrodes which are secured to the PTC element after it has been cross-linked.

Our experiments indicate that the higher the radiation dose, the greater the number of "trips" (i.e. conversions to the tripped state) a device will withstand without failure. The radiation dose is, therefore, preferably at least 60 Mrads, particularly at least 80 Mrads, with yet higher dosages, e.g. at least 120 Mrads or at least 160 Mrads, being preferred when satisfactory PTC characteristics are maintained and the desire for improved performance outweighs the cost of radiation.

We have further discovered a method of determining the likelihood that a device will withstand a substantial number of trips at a voltage of 200 volts. This method involves the use of a scanning electron microscope (SEM) to measure the maximum rate at which the voltage changes in the PTC element when the device is in the tripped state. This maximum rate occurs in the so-called "hot zone" of the PTC element. The lower the maximum rate, the greater the number of trips that the device will withstand. Accordingly, the present invention provides, in a second aspect, an electrical device which comprises (a) a radiation cross-linked PTC conductive polymer element and (b) two electrodes which can be connected to a power source to cause current to flow through the PTC element, said device, when subjected to SEM scanning (as hereinafter defined), showing a maximum difference in voltage between two points separated by 10 microns which is less than 4.2 volts, e.g. less than 4.0 volts, preferably less than 3.0 volts, particularly less than 2.0 volts, especially less than 1.0 volt, subject to the proviso that if each of the electrodes has a substantially planar configuration, the maximum difference is less than 3 volts.

The term "SEM scanning" is used herein to denote the following procedure. The device is inspected to see whether the PTC element has an exposed clean surface which is suitable for scanning in an SEM and which lies between the electrodes. If there is no such surface, then one is created, keeping the alteration of the device to a minimum. The device (or a portion of it if the device is too large, e.g. if it is an elongate heater) is then mounted in a scanning electron microscope so that the electron beam can be traversed from one electrode to the other and directed obliquely at the clean exposed surface. A slowly increasing current is passed through the device, using a DC power source of 200 volts, until the device has been "tripped" and the whole of the potential dropped across it. The electron beam is then traversed across the surface and, using voltage contrast techniques known to those skilled in the art, there is obtained a photomicrograph in which the trace is a measure of the brightness (and hence the potential) of the surface between the electrodes; such a photomicrograph is often known as a line scan.
A diagrammatic representation of a typical photomicrograph is shown in Figure 1. It will be seen that the trace has numerous small peaks and valleys and it is believed that these are due mainly or exclusively to surface imperfections. A single "best line" is drawn through

the trace (the broken line in Figure 1) in order to average out small variations, and from this "best line", the maximum difference in voltage between two points separated by 10 microns is determined.

When reference is made herein to an electrode "having a substantially planar configuration", we mean an electrode whose shape and position in the device are such that substantially all the current enters (or leaves) the electrode through a surface which is substantially planar.

The present invention is particularly useful for circuit protection devices, but is also applicable to heaters, particularly laminar heaters. In one class of devices, each of the electrodes has a columnar shape. Such a device is shown in isometric view in Figure 2, in which wire electrodes 2 are embedded in PTC conductive polymer element 1 having a hole through its centre portion.

In a second class of devices, usually circuit protection devices,

(A) the PTC element is in the form of a strip with substantially planar parallel ends, the length of the strip being greater than the largest cross-sectional dimension of the strip; and

(B) each of the electrodes is in the form of a cap having (i) a substantially planar end which contacts and has substantially the same cross-section as one end of the PTC element and (ii) a side wall which contacts the side of the PTC element.

Such a device is shown in cross-section in Figure 3, in which cap electrodes 2 contact either end of cylindrical PTC conductive polymer element 1 having a hole 11 thorugh its centre portion.

In a third class of devices, usually heaters,

(A) the PTC element is laminar; and
(B) the electrodes are displaced from each other so that current flow between them is along one of the large dimensions of the element.

In a fourth class of devices, each of the electrodes has a substantially planar configuration. Meshed planar electrodes can be used, but metal foil electrodes are preferred. If metal foil electrodes are applied to the PTC element before it is irradiated, there is a danger that gases evolved during irradiation will be trapped. It is preferred, therefore, that metal foil electrodes be applied after the radiation cross-linking step. Thus a preferred process comprises the

(1) irradiating a laminar PTC conductive polymer element in the absence of electrodes;
(2) contacting the cross-linked PTC element from step (1) with metal foil electrodes under conditions of heat and pressure, and
(3) cooling the PTC element and the metal foil electrodes while continuing to press them together.

PTC conductive polymers suitable for use in this invention are disclosed in the patents and applications referenced above. Their resistivity at 23°C is preferably less than 1250 ohm.cm, eg. less than 750 ohm.cm, particularly less than 500 ohm.cm, with values less than 50 ohm.cm being preferred for circuit protection devices. The polymeric component should be one which is cross-linked and not significantly degraded by radiation. The polymeric component is preferably free of thermosetting polymers and often consists essentially of one or more crystalline polymers. Suitable polymers include polyolefins, eg. polyethylene, and copolymers of at least one olefin and at least one olefinically unsaturated monomer containing a polar group. The conductive filler is preferably carbon black. The composition may also contain a non-conductive filler, eg. alumina trihydrate. The composition can, but preferably does not, contain a radiation cross-linking aid. The presence of a cross-linking aid can substantially reduce the radiation dose required to produce a particular degree of cross-linking, but its residue generally has an adverse effect on electrical characteristics.

Shaping of the conductive polymer will generally be effected by a melt-shaping technique, eg. by melt-extrusion or molding.

The invention is illustrated by the following Example

EXAMPLE

The ingredients and amounts thereof given in the Table below were used in the Example.

TABLE

	Masterbatch			Final Mix		
	g	wt%	vol%	g	wt%	vol%
Carbon black (Statex G)	1440	46.8	32.0	1141.5	33.7	26.7
Polyethylene (Marlex 6003)	1584	51.5	66.0	1256.2	37.1	55.2
Filler (Hydral 705)				948.3	28.0	16.5
Antioxidant	52.5	1.7	2.0	41.5	1.2	1.6

Notes:

Statex G, available from Columbian Chemicals, has a density of 1.8 g/cc, a surface area (S) of 35 m^2/g, and an average particle size (D) of 60 millimicrons.

Marlex 6003 is a high density polyethylene with a melt index of 0.3 which is available from Phillips Petroleum.

Hydral 705 is alumina trihydrate available from Aluminum Co. of America.

The antioxidant used was an oligomer of 4,4-thio bis (3-methyl-6-5-butyl phenol) with an average degree of polymerization of 3-4, as described in U.S. Patent Number 3,986,981.

After drying the polymer at 70°C and the carbon black at 150°C for 16 hours in a vacuum oven, the ingredients for the masterbatch were dry blended and then mixed for 12 minutes in a Banbury mixer turning at high gear. The mixture was dumped, cooled, and granulated. The final mix was prepared by dry blending 948.3 g. of Hydral 705 with 2439.2 g. of the masterbatch, and then mixing the dry blend for 7 minutes in a Banbury mixer turning at high gear. The mixture was dumped, cooled, granulated, and then dried at 70°C and 1 torr for 16 hours.

Using a cross-head die, the granulated final mix was melt extruded as a strip 1 cm. wide and 0.25 cm. thick, around three wires. Two of the wires were pre-heated 20 AWG (0.095 cm. diameter) 19/32 stranded nickel-plated copper wires whose centers were 0.76 cm. apart, and the third wire, a 24 AWG (0.064 cm. diameter) solid nickel-plated copper wire, was centered between the other two. Portions 1 cm. long were cut from the extruded product and from each portion the polymeric composition was removed from about half the length, and the whole of the center 24 AWG wire was removed, leaving a hole running through the polymeric element. The products were heat treated in nitrogen at 150°C for 30 minutes and then in air at 110°C for 60 minutes, and were then irradiated. Samples were irradiated to dosages of 20 Mrads, 80 Mrads or 160 Mrads. These samples, when subjected to SEM scanning, were found to have a maximum difference in voltage between two points separated by 10 microns of about 5.2, about 4.0 and about 2.0 respectively. Some of these samples were then sealed inside a metal can, with a polypropylene envelope between the conductive element and the can.

The resulting circuit protection devices were tested to determine how many test cycles they would withstand when tested in a circuit consisting essentially of a 240 volt AC power supply, a switch, a fixed resistor and the device. The devices had a resistance of 20-30 ohms at 23°C and the fixed resistor had a resistance of 33 ohms, so that when the power supply was first switched on, the initial current in the circuit was 4-5 amps. Each test cycle consisted of closing the switch, thus tripping the device, and after a period of about 10 seconds, opening the switch and allowing the device to cool for 1 minute before the next test cycle. The resistance of the device at 23°C was measured initially and after every fifth cycle. The Table below shows the number of cycles needed to increase the resistance to 1-1/2 times its original value.

Device irradiated to a dose of	Resistance increased to 1-1/2 times after
20 Mrads	40-45 cycles
80 Mrads	80-85 cycles
160 Mrads	90-95 cycles

CLAIMS

1. A process for the preparation of an electrical device comprising (a) a cross-linked PTC conductive polymer element and (b) two electrodes which can be connected to a power source to cause current to flow through the PTC element, which process comprises cross-linking the PTC element by radiation, characterised in that the PTC element is irradiated to a dosage of at least 50 Mrads, subject to the proviso that if each of the electrodes has a substantially planar configuration, then either (a) the element is irradiated to a dosage of at least 120 Mrads, or (b) the electrodes are metal foil electrodes which are secured to the PTC element after it has been cross-linked.

2. A process according to claim 1, characterised in that each of the electrodes has a columnar shape and the device is irradiated to a dosage of at least 60 Mrads, preferably at least 80 Mrads.

3. A process according to claim 1 characterised in that

(A) the PTC element is in the form of a strip with substantially planar parallel ends, the length of the strip being greater than the largest cross-sectional dimension of the strip;

(B) each of the electrodes is in the form of a cap having (i) a substantially planar end which contacts and has substantially the same cross-section as one end of the PTC element and (ii) a side wall which contacts the side of the PTC element; and

(C) the device is irradiated to a dosage of at least 60 Mrads, preferably at least 80 Mrads.

4. A process according to claim 1 characterised in that

(A) the PTC element is laminar;

(B) the electrodes are displaced from each other so that current flow between them is along one of the large dimensions of the element; and

(C) the device is irradiated to a dosage of at least 60 Mrads, preferably at least 80 Mrads.

5. A process according to claim 1 characterised by the steps of

(1) irradiating a laminar PTC conductive polymer element in the absence of electrodes;

(2) contacting the cross-linked PTC element from step (1) with metal foil electrodes under conditions of heat and pressure, and

(3) cooling the PTC element and the metal foil electrodes while continuing to press them together.

6. A process according to claim 5 characterised by irradiating the PTC element to a dose of at least 60 Mrads, preferably at least 80 Mrads.

7. A process according to any one of the preceding claims characterised in that the device is irradiated to a dosage of at least 120 Mrads, preferably at least 160 Mrads.

8. An electrical device which comprises (a) a radiation cross-linked PTC conductive polymer element and (b) two electrodes which can be connected to a power source to cause current to flow through the PTC element, characterised in that, when the device is subjected to SEM scanning (as hereinbefore defined), the maximum difference in voltage between two points separated by 10 microns is less than 4.2 volts, preferably less than 3 volts, particularly less than 2 volts, especially less than 1 volt, subject to the proviso that if each of the electrodes has a substantially planar configuration, the maximum difference is less than 3 volts.

9. A device according to claim 8 characterised in that each of the electrodes has columnar shape and the maximum difference is less than 4.0 volts.

10. A device according to claim 8 characterised in that

(A) the PTC element is in the form of a strip with substantially planar parallel ends, the length of the strip being greater than the largest cross-sectional dimension of the strip;

(B) each of the electrodes is in the form of a cap having (i) a substantially planar end which contacts and has substantially the same cross-section as one end of the PTC element and (ii) a side wall which contacts the side of the PTC element; and

(C) the maximum difference is less than 4.0 volts.

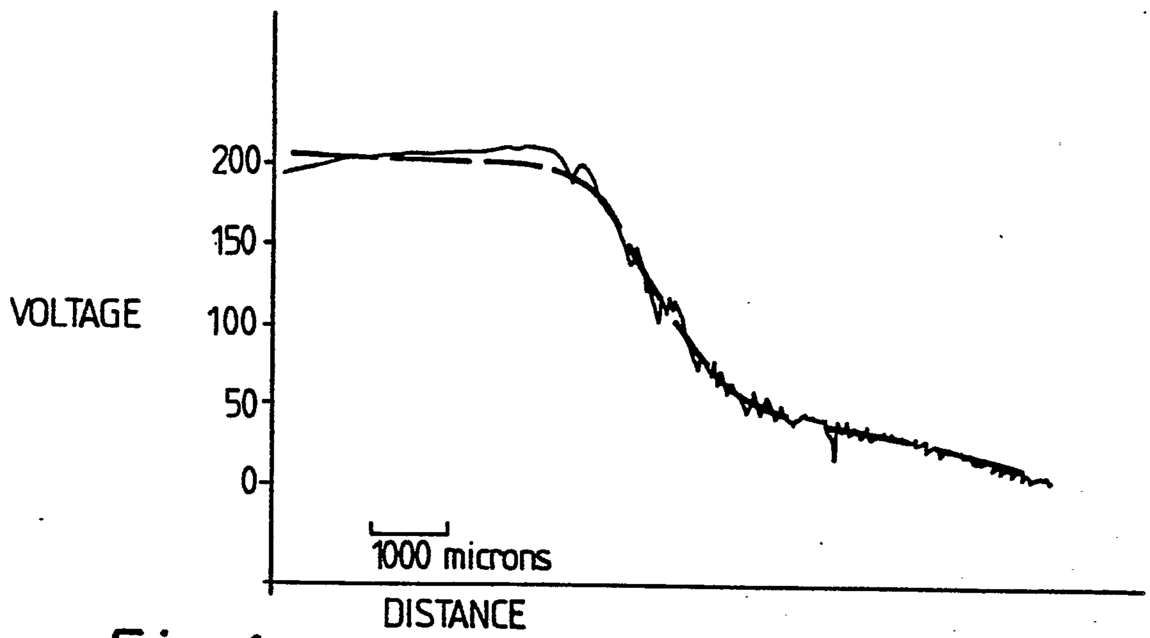

Fig.1

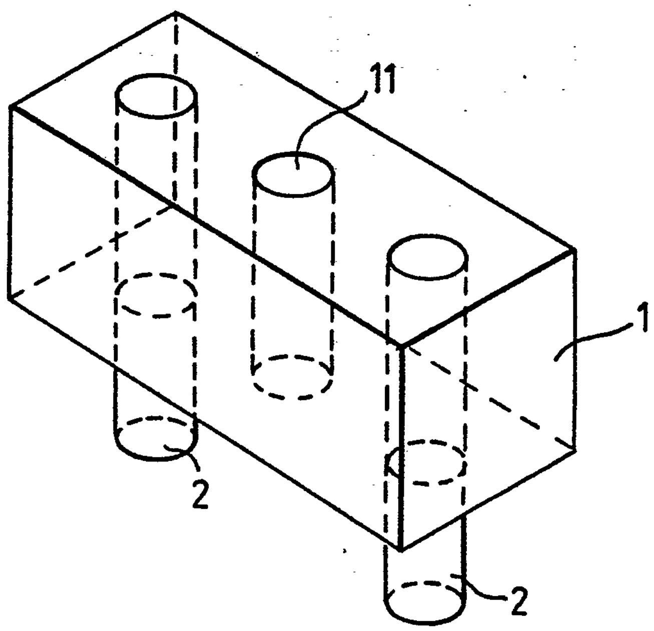

Fig.2

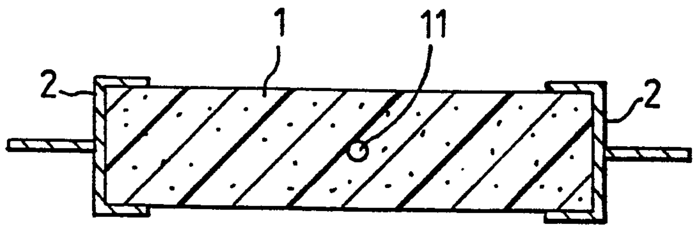

Fig.3