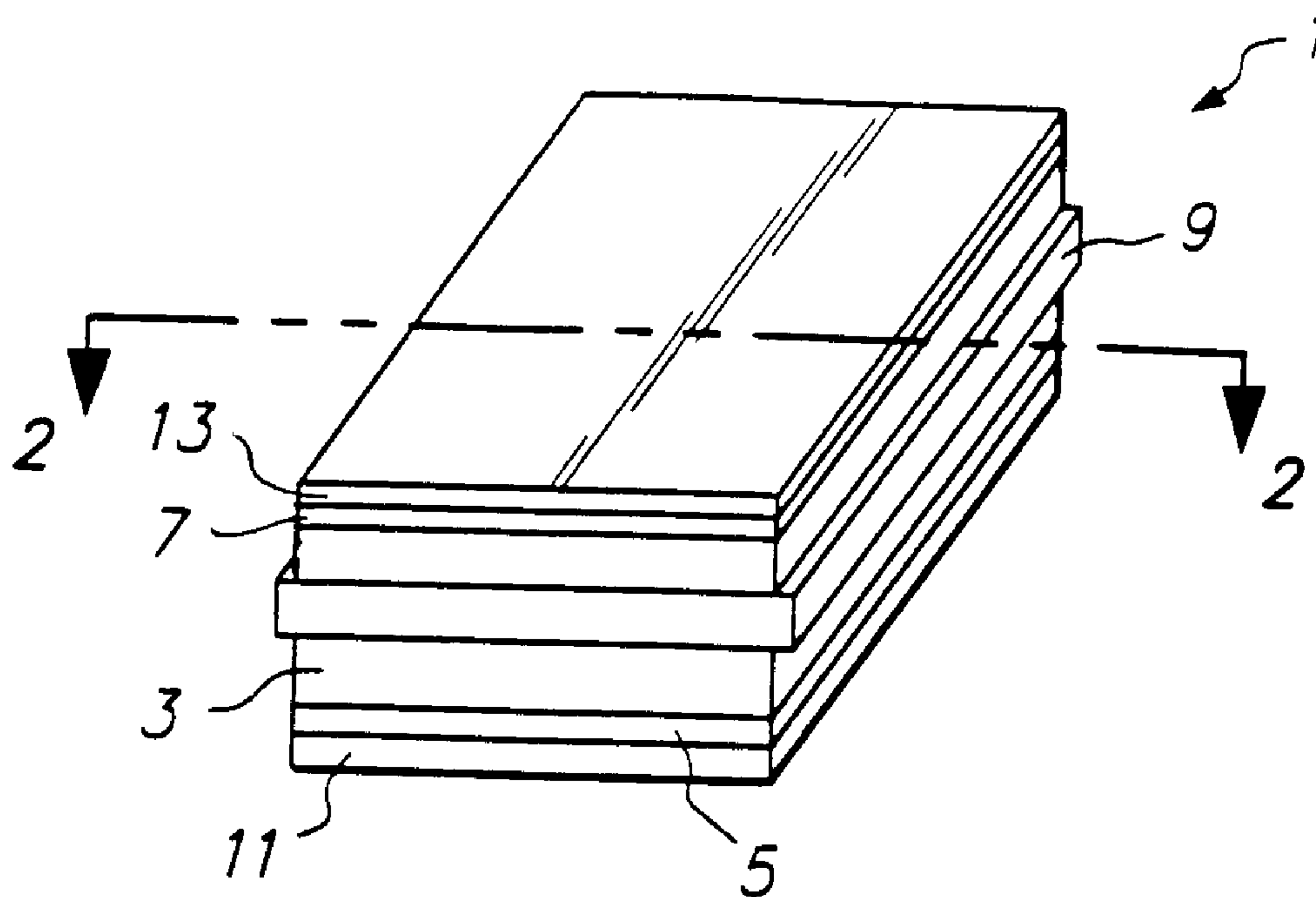




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An electrical device (1) in which a laminar PTC element (3) composed of a conductive polymer composition is sandwiched between two metal foil electrodes (5, 7). A first insulating layer (9) which is composed of an electrically insulating flexible material conforms to at least part of the perimeter of the PTC element, but is substantially free of contact with the two electrodes. Such devices are suitable for use as circuit protection devices in high voltage applications and can be surface-mounted onto a substrate such as a printed circuit board.



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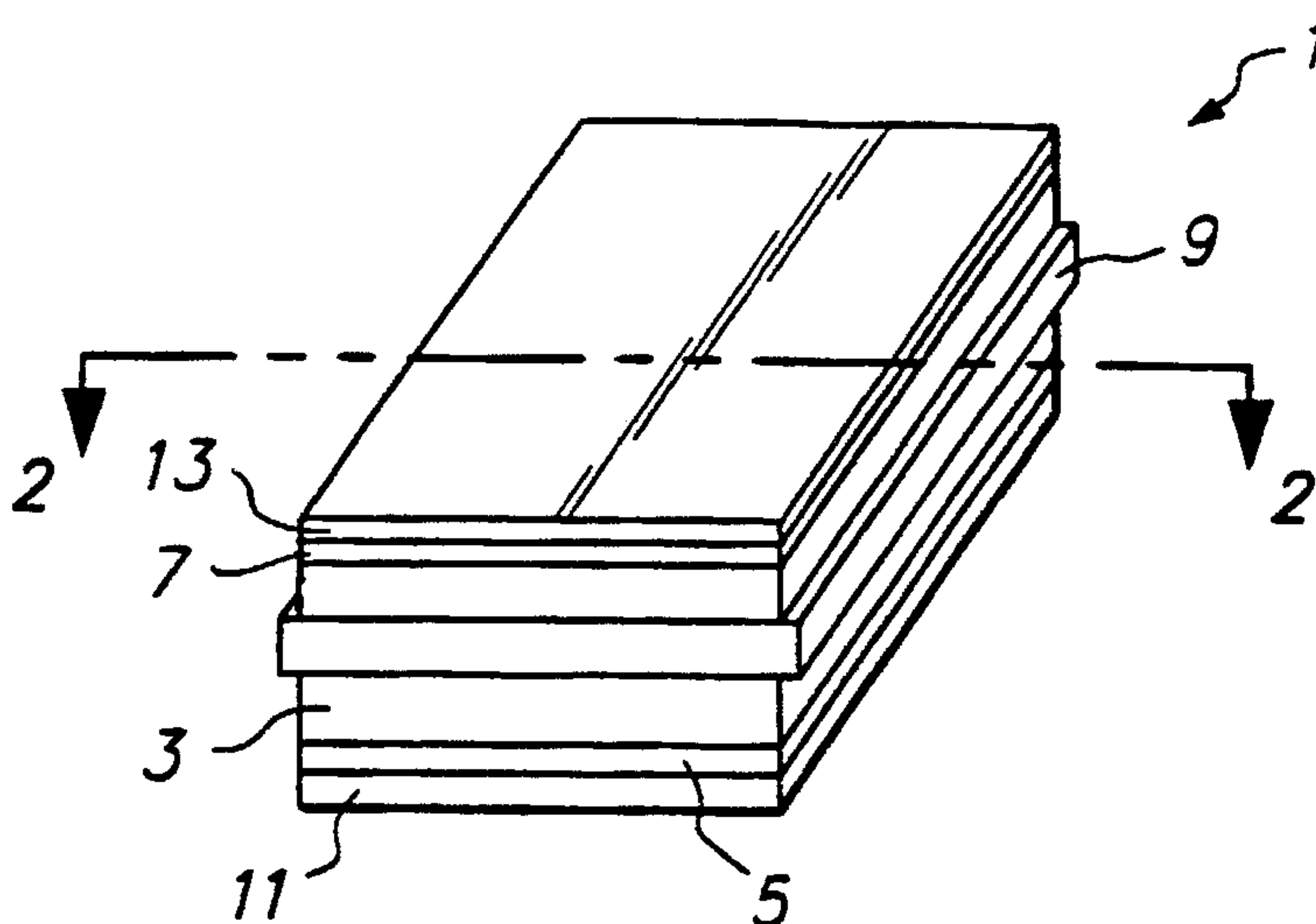
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(57) Abstract: An electrical device (1) in which a laminar PTC element (3) composed of a conductive polymer composition is sandwiched between two metal foil electrodes (5, 7). A first insulating layer (9) which is composed of an electrically insulating flexible material conforms to at least part of the perimeter of the PTC element, but is substantially free of contact with the two electrodes. Such devices are suitable for use as circuit protection devices in high voltage applications and can be surface-mounted onto a substrate such as a printed circuit board.

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ELECTRICAL DEVICE

BACKGROUND OF THE INVENTION

5 Field of the Invention

This invention relates to an electrical device and a method of making such a device.

10 Introduction to the Invention

Circuit protection devices are well known. Those circuit protection devices which are particularly useful in some applications, e.g. to protect telecommunications circuits, exhibit positive temperature coefficient of resistance (PTC) behavior, i.e. the resistance
15 increases anomalously from a low resistance, low temperature state to a high resistance, high temperature state at a particular temperature, i.e. the switching temperature T_s . Under normal operating conditions, a circuit protection device which is placed in series with a load in an electrical circuit has a relatively low resistance and low temperature. If, however, a fault occurs, e.g. due to excessive current in the circuit or a condition which
20 induces excessive heat generation within the device, the device "trips", i.e. is converted to its high resistance, high temperature state. As a result, the current in the circuit is reduced and other components are protected. When the fault condition is removed, the device resets, i.e. returns to its low resistance, low temperature condition. Fault conditions may be the result of a short circuit, the introduction of additional power to the circuit, or
25 overheating of the device by an external heat source, among other reasons. When the device comprises a conductive polymer composition, during the tripping event the device expands as the polymer melts.

Devices intended for use in protecting telecommunications circuits and equipment
30 have special requirements. For example, it is important that the device be tripped by the fault conditions which occur when a power line, i.e. an electrical cable which carries high voltages (e.g. 250 to 600 volts), comes into contact with a telephone line. These fault conditions are often referred to as "power cross". An accepted test for devices which will provide such protection is described in Underwriter's Laboratory Standard 1459 (June 5,
35 1990 and December 13, 1991), the disclosure of which is incorporated herein by reference. In this test, a device is subjected to a cycle consisting of 600 volts AC and 40 A (short circuit) conditions. The device must survive one cycle in order to pass the test.

Under such test conditions, it is possible for the device to arc or flashover at the edge from one electrode to the other due to the high power levels. Simultaneously, the device is expanding rapidly in order to absorb the energy associated with the fault condition.

5 Use of electrically insulating coatings or housings to surround circuit protection devices and other electrical components is known. See, for example, U.S. Patent Nos. 4,223,177 (Nakamura), 4,315,237 (Middleman et al), 4,481,498 (McTavish et al), 4,873,507 (Antonas), and 5,210,517 (Abe), the disclosures of which are incorporated herein by reference. Such coatings provide electrical insulation and mechanical
10 protection, and are particularly important for use with devices exposed to high voltage conditions in which arcing from one electrode to the other may occur. However, many conventional coatings, e.g. epoxies, are rigid, and will restrict the expansion of the PTC element, causing the device to fail. Other flexible or conformable coatings may crack or pull away from the device as a result of the expansion during tripping, leaving the device
15 edges exposed and subject to further arcing.

One additional issue with many conventional circuit protection devices for high voltage applications is that they are not surface-mountable, i.e. they must be mounted onto a printed circuit board or other substrate by means of wires or leads protruding
20 through the circuit board, rather than directly onto traces on the circuit board. For example, devices sold by Raychem Corporation under the tradename PolySwitch[®] TR600-160 devices, meet the UL1459 test but contain wire leads, which require that the device stand up off the circuit board. If, however, the device is made surface-mountable, it is necessary that the insulating coating be able to withstand the temperatures generated
25 by solder reflow, i.e. the attachment of the device directly onto the printed circuit board by means of solder. During that process, the solder must be heated sufficiently to melt it, typically resulting in exposure of the device to temperatures of 240 to 260°C for 3 to 5 seconds. Exposure to such high temperatures causes most conductive polymer devices to expand, putting additional stress on the coating and providing a situation under which the
30 coating will lift off from the device. In addition, a device which is completely encapsulated will be subject to solder-bridging because the solder will flow when the PTC device expands.

BRIEF SUMMARY OF THE INVENTION

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We have now found that is possible to make a surface-mountable device which is capable of passing the high voltage tests required for telecommunications equipment

protection. The device withstands solder-reflow onto a substrate such as a printed circuit board without destroying the integrity of the insulating coating on expansion.

Furthermore, the device is able to withstand multiple high voltage/high current cycles.

This is desirable for certain applications, e.g. circuit breaker reset conditions. Thus, in a

5 first aspect this invention provides an electrical device, said device comprising

(1) a laminar PTC element which (a) is composed of a conductive polymer composition which exhibits PTC behavior, (b) has first and second major surfaces, (c) has a thickness t mm, and (d) has a perimeter p mm;

10

(2) a first metal foil electrode which is attached to the first surface of the PTC element;

(3) a second metal foil electrode which is attached to the second surface of the PTC element; and

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(4) a first insulating layer which (a) comprises an electrically insulating flexible material which conforms to at least part of the perimeter of the PTC element, and (b) is substantially free of contact with the first and second electrodes.

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In a second aspect, the invention provides an assembly which comprises

(1) an electrical device according to the first aspect of the invention; and

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(2) a substrate to which the device is electrically attached, e.g. by surface-mounting.

BRIEF DESCRIPTION OF THE DRAWINGS

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The invention is illustrated by the drawings in which Figure 1 is a plan view of a device of the invention;

Figure 2 is a cross-sectional view of Figure 1 along line 2-2;

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Figure 3 is a perspective view of an insulating ring for use with the device of the invention; and

Figure 4 is a plan view of a device of the invention mounted on a printed circuit board.

5 DETAILED DESCRIPTION OF THE INVENTION

The electrical device of the invention comprises a laminar PTC element composed of a conductive polymer composition which exhibits PTC behavior. The conductive polymer composition comprises a polymeric component, and dispersed therein, a
10 particulate conductive filler. The polymeric component comprises one or more polymers, one of which is preferably a crystalline polymer having a crystallinity of at least 10% as measured in its unfilled state 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
15 copolymerisable therewith such as ethylene/acrylic acid, ethylene/ethyl acrylate, ethylene/vinyl acetate, and ethylene/butyl acrylate copolymers; melt-shapeable fluoropolymers such as polyvinylidene fluoride (PVDF) and ethylene/tetrafluoroethylene copolymers (ETFE, including terpolymers); and blends of two or more such polymers. For some applications it may be desirable to blend one crystalline polymer with another
20 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 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.

25 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. The quantity of conductive filler needed is based on the
30 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.

35 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. CaCO_3), or other components. These components generally comprise at most 20% by volume of the total composition.

The conductive polymer composition exhibits positive temperature coefficient (PTC) behavior, i.e. it shows a sharp increase in resistivity with temperature over a relatively small temperature range. In this application, the term "PTC" is used to mean a composition 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 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°C range, R_{100} is the ratio of the resistivities at the end and the beginning of a 100°C range, and R_{30} is the ratio of the resistivities at the end and the beginning of a 30°C range. Generally the compositions used in devices of the invention show increases in resistivity which are much greater than those minimum values.

Suitable conductive polymer compositions for use in devices of the invention are disclosed in U.S. Patent Nos. 4,237,441 (van Konynenburg et al), 4,545,926 (Fouts et al), 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), 5,250,228 (Baigrie et al), 5,378,407 (Chandler et al), 5,451,919 (Chu et al), 5,582,770 (Chu et al), and 5,747,147 (Wartenberg et al), and in International Publication No. WO96/29711 (Raychem Corporation, published September 26, 1996). The disclosure of each of these patents and applications is incorporated herein by reference.

The conductive polymer is in the form of a laminar element having first and second parallel major surfaces. The element is sandwiched between first and second metal electrodes, the first of which is attached to the first surface of the PTC element and the second of which is attached to the second major surface. Preferably, the electrodes are in the form of metal foils, although a conductive ink, or a metal layer which has been applied by plating or other means can be used. Particularly suitable foil electrodes are microrough metal foil electrodes, including electrodeposited nickel foils and nickel-plated electrodeposited copper foil electrodes, in particular as 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), the disclosure of each of which is incorporated herein by reference.

The PTC element has a thickness t mm, generally 1 to 5 mm (0.040 to 0.200 inch), as measured between the first and second electrodes. This is a thickness which is

particularly suitable for use in high voltage, e.g. 250 or 600 volt, applications. The element also has a perimeter p mm, generally 20 to 80 mm (0.79 to 3.1 inch). This perimeter is the smaller of (1) the smallest circumference around the device and (2) the circumference measured at a distance halfway between the first and second electrodes.

- 5 The measurement of the perimeter preferably includes any noticeable depressions, cracks, or inclusions.

Attached to the laminar element is a first insulating layer which comprises an electrically insulating flexible material which conforms to at least part of the perimeter of the PTC element. Preferably, the first insulating layer conforms to at least 10% of the thickness around the perimeter of the PTC element, particularly at least 30% of the thickness, especially at least 50% of the thickness, more especially at least 70% of the thickness. In some embodiments it is preferred that the first insulating layer conform to substantially all of the thickness around the perimeter of the PTC element, wherein
15 “substantially all” means at least 90% is covered by the first insulating layer. It is preferred that the first insulating layer be positioned to cover the width of any “hotline” or “hotzone” region of the device, i.e. the part of the device with the highest voltage drop. The first insulating layer is substantially free of contact with the first and second electrodes, wherein “substantially free” means that at most only 10% of the total surface
20 area of the first and second electrodes is covered by the first insulating layer.

The first insulating layer may comprise any flexible, conformable coating material, but is preferably polymeric. Suitable materials include polyethylenes, ethylene copolymers, fluoropolymers, silicones, elastomers, rubbers, hot-melt adhesives, mastics,
25 and gels. It is important that the layer conform and adhere to the conductive polymer composition of the PTC element, and that it maintain its conformance and adhesion during expansion of the conductive polymer during assembly and operation. Thus, it is preferred that the material have similar thermal expansion properties to the PTC element. In order to enhance its performance under high voltage conditions, the insulating layer
30 may comprise one or more fillers which are arc-suppressing materials, stress-grading materials, flame-retarding materials, or track-resistant materials.

The first insulating layer may be applied by any appropriate technique, e.g. it may be painted or sprayed on, or applied by pressure (as with a tape) or melting. One
35 particularly preferred technique is to apply a ring which is preferably a self-supporting component prior to attachment onto the PTC element. The ring may be prepared from a heat-recoverable article, e.g. heat-recoverable tubing or a heat-recoverable strip formed

into a ring. A heat-recoverable article is an article the dimensional configuration of which may be changed by subjecting the article to heat treatment. In their most common form, such articles comprise a heat-shrinkable sleeve or tube made from a polymeric material exhibiting the property of elastic or plastic memory as described, for example, in U.S. Patents Nos. 2,027,962 (Currie); 3,086,242 (Cook et al); and 3,597,372 (Cook), the disclosures of which are incorporated herein by reference. The polymeric material has been crosslinked during the production process so as to enhance the desired dimensional recovery. One method of producing a heat-recoverable article comprises shaping the polymeric material into the desired heat-stable form, subsequently crosslinking the polymeric material, heating the article to a temperature above the crystalline melting point (or, for amorphous materials the softening point of the polymer), deforming the article, and cooling the article while in the deformed state so that the deformed state of the article is retained. In use, because the deformed state of the article is heat-unstable, application of heat will cause the article to assume its original heat-stable shape. The heat-recoverable article, when recovered into contact with the PTC element, may act as the first insulating layer. Alternatively, the inner surface of the heat-recoverable article may be coated with a hot-melt adhesive or mastic which, when the article is heated and recovered, melts and/or flows into contact with the PTC element, providing a conformal coating and filling small voids or irregularities on the perimeter of the element. In this configuration, the heat-recoverable article may comprise a carrier member (generally the outer layer) and an inner adhesive member. The carrier member may remain after installation or it may be removed. The adhesive or mastic may itself contain a filler of the type described above to enhance its high voltage performance. When a heat-recoverable article is used, it is preferred that the inner perimeter of a fully recovered article (without a PTC element present) is somewhat less than the perimeter of the PTC element. This allows the recovered article to maintain excellent contact with the PTC element even after the expansion resulting from tripping the device into a high temperature state. Preferably the inner perimeter of the heat-recoverable article is at most 95% (i.e. 0.95p), particularly at most 90% (i.e. 0.9p), especially at most 85% (i.e. 0.85p), more especially at most 80% (i.e. 0.8p) that of the perimeter of the PTC element. The perimeter of the ring or the heat-recoverable article is preferably the same shape as the PTC element.

For some applications, it is preferred that the first insulating layer comprise an material which has a relatively low melting temperature, e.g. a melting temperature below the switching temperature of the device. If an arc occurs, the material, e.g. an adhesive, will melt and act to quench the arc.

Devices of the invention may be crosslinked, e.g. by irradiation or chemical means, to enhance their voltage withstand performance. See, for example, U.S. Patents Nos. 4,724,417 (Au et al) and 4,845,838 (Jacobs et al), the disclosures of which are incorporated herein by reference. Crosslinking the device with the first insulating layer in place may serve to enhance the adhesion of the first insulating layer.

Devices of the invention are particularly useful when the device is to be solder-reflowed onto a substrate, e.g. a printed circuit board. Such devices may comprise a solder layer on either or both of the first and second electrodes. When such a solder layer is present, it is substantially free of contact with the first insulating layer. Because most solder reflow operations require exposure of a device to a temperature of 240 to 260°C for at least 3 to 5 seconds, it is important that first insulating layer be capable of withstanding such conditions without degradation.

In addition to a first insulating layer, devices of the invention may also comprise a second insulating layer. This second insulating layer preferably surrounds the PTC element and first and second electrodes, as well as the first insulating layer. It may be in the form of a self-supporting element, e.g. a box, which is positioned away from direct contact with the PTC element, an overmolded layer, e.g. silicone or rubber, or another coating layer, e.g. an encapsulant such as an epoxy, a silicone, a polyimide, a polyurethane, a polyester, a liquid crystal polymer, or a rubber.

Devices of the invention may be made by providing a laminar PTC element, positioning a heat-recoverable article around the perimeter, and heating the article to cause it to recover.

An assembly of the invention can be made by attaching a device of the invention onto a substrate, e.g. a printed circuit board. It is preferred that the device be surface-mounted onto the substrate.

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The invention is illustrated by the drawings in which Figure 1 is a plan view of device 1 of the invention and Figure 2 is a cross-sectional view along line 2-2 of Figure 1. PTC element 3 is sandwiched between first and second metal foil electrodes 5,7 which are coated with first and second solder layers 11,13, respectively. First insulating layer 9 surrounds the perimeter of resistive element 3 and conforms to the shape of the resistive element.

35

Figure 3 is a perspective view of insulating ring 15 which may be a heat-recoverable article. Ring 15 contains carrier member 17 in contact with adhesive member 19. When heated and shrunk around the perimeter of a resistive element, adhesive member 19 acts as the first insulating layer.

Figure 4 shows a plan view of a device 1 mounted on substrate 25 to form an assembly of the invention 29. First and second electrical leads 21,23 are attached to first and second solder layers 11,13. First and second electrical leads 21,23 are then attached, e.g. by a solder reflow operation, onto traces 27 of substrate 25.

The invention is illustrated by the following Examples, in which Example 1 is a comparative example.

Preparation of Devices

A first conductive polymer composition was prepared by mixing high density polyethylene (Petrothene™ LB832, available from Equistar), carbon black (Raven™ 430, available from Columbian Chemicals), and magnesium hydroxide (Kisuma™ 5A, available from Kisuma). The mixed compound was then extruded to produce a first sheet with a thickness of 0.76 mm (0.030 inch). A second conductive polymer composition from the same ingredients but a lower carbon black loading and thus a higher resistivity was prepared and a second sheet having a thickness of 0.51 mm (0.020 inch) was extruded. A laminate was prepared by stacking two pieces of the first sheet, one piece of the second sheet, and two additional pieces of the first sheet between two sheets of 0.0025 cm (0.001 inch) thick electrodeposited nickel foil (available from Fukuda), and heating under pressure. The resulting plaque had a thickness of about 3.6 mm (0.140 inch). Chips with dimensions of 8.0 x 15.0 mm (0.315 x 0.592 inch) were cut from the plaque.

Example 1 (Comparative)

Chips were irradiated to a total of 100 Mrad using a 4.5 MeV electron beam. Electrical leads were attached by solder to the metal foil electrodes to form devices. The devices were then tested according to the Overvoltage Test below. All devices tested failed. The results are reported in Table I, which shows the number of devices tested (for Examples 2 to 5), whether an adhesive layer was present, whether the device was crosslinked after the insulating layer was applied, and what percentage of devices survived after each cycle of the test.

Example 2

For each device, a ring with a length of 3.05 mm (0.120 inch) was cut from a
5 length of expanded heat-recoverable tubing composed of high density polyethylene. The
expanded ring was installed around the perimeter of a chip irradiated to 100 Mrads using
a 4.5 MeV electron beam, and the device was then heated at 150°C for 5 minutes to heat
and recover the ring into conforming contact with the conductive polymer of the chip. No
10 part of the electrode was in contact with the ring. Electrical leads were applied as in
Example 1. The devices were tested according to the Overvoltage Test below and the
results are shown in Table I.

Example 3

15 The process of Example 2 was followed except that the ring contained a lining of
a polyamide-based hot-melt adhesive. Upon heating at 150°C to recover the ring, the
adhesive melted and contacted the conductive polymer of the chip, filling any
indentations or cracks around the perimeter. The devices were tested and the results are
shown in Table I.

20

Example 4

The process of Example 2 was followed, except that the ring was applied after the
chip had been irradiated 50 Mrad using a 4.5 MeV electron beam. Following installation
25 of the ring, the device was irradiated 50 Mrad more. The devices were tested and the
results are shown in Table I.

Example 5

30 The process of Example 3 was followed, except that the ring was applied after the
chip had been irradiated 50 Mrad using a 4.5 MeV electron beam. Following installation
of the ring, the device was irradiated 50 Mrad more. The devices were tested and the
results are shown in Table I.

Overvoltage Test

A device is inserted into a circuit in series with a switch, a 600 volt 60 Hz AC power source, a 1.6 A line simulator fuse, and a 15 ohm fixed resistor which provides 40 A in a short circuit condition. The device is in contact with a piece of cheesecloth. Each cycle of the test consists of closing the switch, thus tripping the device, and maintaining the switch closed for 1.5 seconds. The device is deemed to pass the test if the line simulator fuse is protected, the device does not burn, and if the cheese cloth is not marked. This test is similar to Underwriter's Laboratory Standard 1459. The test was conducted for five cycles. The results are shown in Table I. The devices of Example 1, which did not contain the first insulating coating, were unable to withstand even one cycle of the test.

TABLE I

<u>Example</u>	<u>Devices Tested</u>	<u>Adhesive</u>	<u>Cross-linked*</u>	<u>Percent Survival After Each Cycle</u> (Cycle Number)				
				<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
1	-	No	No	0				
2	100	No	No	99	94	79	52	42
3	100	Yes	No	99	98	97	91	89
4	70	No	Yes	100	99	89	74	71
5	70	Yes	Yes	100	93	87	81	79

*Crosslinking conducted following application of first insulating layer.

The results showed that devices having an insulating layer in contact with the conductive polymer perimeter had better performance than those with no insulating layer, and that the devices with an adhesive layer in direct contact with the conductive polymer perimeter had better performance than those without adhesive.

What is claimed is:

1. An electrical device, said device comprising
 - (1) a laminar PTC element which (a) is composed of a conductive polymer composition which exhibits PTC behavior, (b) has first and second major surfaces, (c) has a thickness t mm, and (d) has a perimeter p mm;
 - (2) a first metal foil electrode which is attached to the first surface of the PTC element;
 - (3) a second metal foil electrode which is attached to the second surface of the PTC element; and
 - (4) a first insulating layer which (a) comprises an electrically insulating flexible material which conforms to at least part of the perimeter of the PTC element, and (b) is substantially free of contact with the first and second electrodes.
2. A device according to claim 1 wherein the first insulating layer conforms to at least 10 percent of the thickness around the perimeter of the PTC element, preferably conforms to substantially all of the thickness around the perimeter of the PTC element.
3. A device according to claim 1 or 2 wherein the first insulating layer comprises a filler which is an arc-suppressing material, a stress-grading material, a flame-retarding material, or a track-resistant material.
4. A device according to claim 1 wherein the first insulating layer is in the form of a ring.
5. A device according to claim 4 wherein the ring is in the form of a heat-recoverable article.
6. A device according to claim 5 wherein the heat-recoverable article comprises (a) a carrier member and (b) an adhesive member which is in contact with the carrier member and the device perimeter.

7. A device according to claim 6 wherein the adhesive member comprises a filler which is an arc-suppressing material, a stress-grading material, a flame-retarding material, or a track-resistant material.

8. A device according to claim 1 which further comprises a solder layer which (a) is in contact with at least part of an exposed surface of the first metal foil electrode, and (b) is substantially free of contact with the first insulating layer.

9. A device according to claim 1 which further comprises a second insulating layer which surrounds the device, said second insulating layer comprising a self-supporting box or an encapsulant.

10. An assembly which comprises

- (1) an electrical device according to claim 1; and
- (2) a substrate to which the device is electrically attached by surface-mounting.

