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(54) ARTICLES HAVING A POSITIVE TEMPERATURE COEFFICIENT OF RESISTANCE

(71) We, RAYCHEM CORPORATION, a Corporation organized under the laws of the State of California, United States of America, of 300, Constitution Drive, Menlo Park, California 94025, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to shaped structures of electrically conductive compositions, preferably polymeric, the structures having a positive temperature coefficient of resistance (PTC), especially to heating elements comprising PTC materials.

An improvement in electrical heating devices in recent years has been the provision of self-regulating heating devices which utilize materials exhibiting certain types of PTC characteristics, namely that upon attaining a certain temperature a substantial rise in resistance occurs. Heaters utilizing such PTC materials reportedly exhibit more or less sharp rises in resistance within a narrow temperature range but below that temperature range exhibit only relatively small changes in resistance with temperature. The temperature at which the resistance commences to increase sharply is often designated the switching or anomaly temperature (T_s) since on reaching that temperature the heater exhibits an anomalous change in resistance and, for practical purposes, switches off. Self regulating heaters utilizing PTC materials have advantages over conventional heating apparatus in that they generally eliminate the need for separate thermostats, fuses or in-line electrical resistors.

The most widely used PTC material has been doped barium titanate which has been utilized for self-regulating ceramic heaters employed in such applications as food warming trays and other small portable heating appliances. Although such ceramic PTC materials are in common use for heating applications, their rigidity severely limits the type of application for which they can be used. PTC materials comprising electrically conductive polymeric compositions are also known, some of which are stated to possess the special characteristics described herein-above. However, the use of such polymeric PTC materials has been relatively limited, primarily due to their low heating capacity. Such materials generally comprise one or more conductive fillers, for example carbon black or powdered metal, dispersed in a crystalline thermoplastic polymer. PTC compositions prepared from highly crystalline polymers generally exhibit a steep rise in resistance commencing a few degrees below their crystalline melting point similar to the behaviour of their ceramic counterparts at the Curie temperature (the T_c for ceramics). PTC compositions derived from homopolymers and copolymers of lower crystallinity, for example, less than about 50%, exhibit somewhat less steep increases in resistance which increase commences at a less well defined temperature in a range often considerably below the polymer's crystalline melting point. In the extreme case the resistance of some polymers of low crystallinity increase more rapidly with temperature as the temperature rises. Other types of thermoplastic polymers yield resistances which increase fairly smoothly and more or less

steeply but continuously with temperature. Figure 1 of the accompanying drawings illustrates characteristic curves for the aforementioned different types of PTC compositions. In Figure 1 curve I exhibits the sharp virtually instantaneous increase in resistance (hereinafter known as type I behaviour) generally characteristic of *inter alia* polymers having high crystallinity; curve II shows the more gradual increase at lower temperatures (relative to the polymer melting point) hereinafter known as type II behavior generally characteristic of lower crystallinity polymers. Curve III illustrates the concave (from above) curve characteristic (Type III behavior) of many very low crystallinity polymers while curve IV illustrates the behavior of a PTC material above its T_s , and shows a large increase in resistance without a region of more or less constant resistance (Type IV behavior) at least in the temperature range above about 10°C. Curve V illustrates the gently increasing resistance temperature characteristic (Type V behavior) shown by many "normal" electrical resistors. Although the above types of behavior have been illustrated mostly by reference to specific types of polymeric material it will be realized by those skilled in the art that the particular type of behavior manifested is also very dependent on the type and amount of conductive filler and, particularly in the case of carbon black, on its particle size and shape, surface characteristics, tendency to agglomerate and the shape of the particle agglomerates, i.e., its tendency to structure).

It should be noted that the preferred PTC compositions disclosed in the prior art are all stated to manifest essentially Type I behavior. In fact, the prior art does not specifically recognize Types II to IV behavior notwithstanding the fact that many of the PTC compositions disclosed in the prior art in fact exhibit not Type I, but rather Type II, III or IV behavior.

With type I resistance temperature characteristics, the increase in resistance above T_s is rapid so that T_s may be regarded as the temperature at which the device switches off. However, with type II or type III PTC materials the transition from a resistance relatively stable as temperature is increased to a resistance rising steeply with temperature is much less well defined, and the anomaly temperature or T_s is frequently not an exact temperature.

Previously disclosed self-regulating thermal devices utilizing a PTC material are described as having extremely steep (Type I) $R=f(T)$ curves so that above a certain temperature the device will in effect shut off, while below that temperature a relatively constant wattage output at constant voltage is achieved. At temperatures below T_s the resistance is at a relatively low and constant level and thus the

current flow is relatively high for any given applied voltage. The power generated by this current flow is dissipated as heat, i.e. heat is generated by electrical resistance and warms up the PTC material. As the temperature rises, the resistance stays at this relatively low level until about the T_s temperature, at which point a rapid increase in resistance occurs. With the increase in resistance there is a concomitant decrease in power, thereby limiting the amount of heat generated so that when T_s is reached heating is essentially stopped. Then, upon a lowering of the temperature of the device below T_s by dissipation of heat to the surroundings, the resistance drops, thereby increasing the power output.

At a steady state, the heat generated will essentially balance the heat dissipated. Thus, when an applied voltage is directed across a PTC heating element, the Joule heat causes heating of the PTC element up to about its T_s , the rapidity of such heating depending on the applied voltage and type of PTC element, after which little additional temperature rise will occur because of the increase in resistance. Because of the resistance rise, a PTC heating element will ordinarily reach a steady state at approximately T_s thereby self-regulating the heat output of the element without resort to fuses or thermostats. The advantages of such a self contained heat regulating element in many applications will be apparent.

Kohler, U.S. Patent 3,243,753 discloses carbon filled polyethylene wherein the conductive carbon particles are in substantial contact with one another. Kohler describes a product containing 40% polyethylene and 60% carbon particles so as to give a resistance at room temperature of about 0.4 ohm/cm. As is typical of the alleged performance of the prior art materials, Kohler's PTC product is described as having a relatively flat curve of electrical resistance versus temperature below the switching temperature, followed by a sharp rise in resistivity of at least 250% over a 14°C range. The mechanism suggested by Kohler for the sharp rise in resistivity is that such a change is a function of the difference in thermal expansion of the materials, i.e. polyethylene and particulate carbon. It is suggested that the composition's high level of conductive filler forms a conductive network through the polyethylene polymer matrix, thereby giving an initial constant resistivity at lower temperatures. However, at about its crystalline melt point, the polyethylene matrix rapidly expands, such expansion causing a breakup of many of the conductive networks, which in turn results in a sharp increase in the resistance of the composition.

Other theories proposed to account for the PTC phenomenon in conductive particle filled polymer compositions include complex

mechanisms based upon electron tunnelling through inter-grain gaps between particles of conductive filler or some mechanism based upon a phase change from crystalline to amorphous regions in the polymer matrix. A background discussion of a number of proposed alternative mechanisms for the PTC phenomenon is found in "Glass Transition Temperature as a Guide to the Selection of Polymers Suitable for PTC Materials", J. Meyer, Polymer Engineering and Science, November, 1973, 13, No. 6. In U.S. Patent 3,673,121 Meyer suggests that, based upon a phase change theory, to attain a steeply sloped PTC of resistance with a sharp cutoff (Type I) the polymer matrix should comprise a crystalline polymer having a narrow molecular weight distribution. Kawashima *et al*, in U.S. Patent 3,591,526, disclose a PTC molding composition in which the conductive particles, such as carbon black, are first dispersed in a thermoplastic material, and thereafter this dispersed mixture is blended into a molding resin. Kawashima *et al* likewise suggest the desirability of an extremely steep temperature-resistance curve (that is $R=f(T)$) curve at a T_s of about 100°—130°C.

Because of their flexibility, comparatively low cost, and ease of installation, PTC strip heaters comprising conductive particles dispersed in a crystalline polymer have recently found wide use as pipe tracing heaters on industrial piping and in related apparatus. For example, such polymeric PTC heaters, because of their self-regulating features, have been used for wrapping pipes in chemical plants to protect against freezing, or for maintaining a constant temperature which in turn permits aqueous or other solutions to flow through the pipes without "salting out".

In such applications, heaters ideally attain and are maintained at a temperature at which the energy lost through heat transfer to the surroundings equals that gained from the current. Such heaters ordinarily consist of relatively narrow and thin ribbon or strip of carbon filled polymeric material having electrodes (such as embedded copper wires) at opposite edges along the long axis of the strip. Thus an electrical potential gradient along the plane of, and transverse to the long axis of, the strip has generally been contemplated, an applied voltage between the opposite electrodes resulting in heating of the entire strip, usually to approximately its T_s .

Obviously, from the preceding discussion it is apparent that Type I materials have significant advantages over the other types of PTC material enumerated hereinbefore in most applications. Types II and III have a disadvantage in that because of the much less sharp transition the steady state temperature of the heater is more dependent on the thermal load placed on it. Such compositions also suffer from a current inrush

problem as described in greater detail herein-after. Types IV and V materials, because they lack a useful temperature range in which the power output changes from being independent of temperature to being dependent on temperature, have not so far been considered as suitable materials for practical heaters under ordinary circumstances.

In such uses as have been described above and in others there exists a need for flexible strip heaters with much higher power output densities and/or higher operating temperatures than are contemplated by the prior art. It does not appear possible to operate heaters, particularly strip heaters fabricated from prior art compositions and according to prior art designs, at higher power outputs, i.e., higher wattage levels (above 1.5 watts/sq. in.) and/or higher temperatures (above about 100°C). The actual wattage delivered by prior art heaters is far less than that which would be expected based on the heater area and heat transfer considerations apparently because the heat is produced in a very thin band down the longitudinal axis of the strip between the two electrodes. Such a phenomenon is herein termed a hotline. This hotline results in an inadequate and nonuniform heating performance and renders the entire heating device useless for most of the heating cycle in applications where high wattage outputs, especially at temperatures above 100°C, are desired. More specifically, because the heat output is confined to a narrow band or line transverse to a current path, the high resistance of this line prevents the flow of current across the path, in effect causing the entire heater to shut off until the temperature of the hotline drops below T_s again.

It has now been discovered that this hotline condition occurs in most if not all prior art design polymeric PTC strip heaters where a voltage is applied, and the current flows, transversely across the strip, the extent of such condition being generally dependent upon the amount of applied voltage as well as the thermal conductivity of the polymer and the extent of non-uniform heat dissipation. The hot-line along the longitudinal axis of the strip, between the electrodes, effectively shuts down the heating device even though only a small portion of the surface area of the film, i.e. the hot line, has achieved T_s . This, in many cases, will destroy the heater or at the very least render it so inefficient that it appears to exhibit the very low heating capability found to be generally associated with the PTC polymeric strip heaters of the prior art.

From the foregoing discussion, it is apparent that the elimination of hotline is important for the efficient operation of a PTC self-regulating heater, especially one with a high power output and/or high operating temperature.

It would also be most advantageous if a

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PTC self-regulating heater could be fabricated wherein the heating surface was of a shape other than a relatively long, narrow strip, e.g., a square or round heating pad. Also desirable would be a PTC self-regulating heater which could be fabricated into relatively complex three-dimensional configurations, e.g., one capable of making effective contact with essentially the entire outside surface of a chemical process vessel. Unfortunately, the tendency to hotline is particularly prevalent when the current path distance, i.e. the distance between electrodes, is large relative to the thickness of PTC material through which the current must flow. For example, in the case of a heating strip with electrodes at the strip edges, a relatively wide short strip has a greater tendency to hotline than a narrow strip of the same length, composition and thickness. Likewise, for the same length and width, the thinner the strip the greater the tendency to hotline. Increasing the strip length while holding the width and thickness constant, has no significant effect on hotlining tendency. The problem of hotlining has apparently not previously been properly recognized, and certainly no suggestion for a composition or construction to reduce it has been proposed.

Polymeric PTC compositions have also been suggested for heat shrinkable articles. For example, Day in U.S. Patent Office Defensive Publication T905,001 teaches the use of a PTC heat shrinkable plastic film. However, the Day shrinkable film suffers from the rather serious shortcoming that since T_s is no greater than the crystalline melting point of the film, very little recovery force can be generated. Buiting *et al*, in U.S. Patent No. 3,413,442, suggest a heater construction involving sandwiching a PTC polymeric layer between silver electrodes. A significant shortcoming of the Buiting *et al* construction is its lack of flexibility. Additionally, neither Buiting *et al* nor any of the other previously discussed prior art teachings even addresses, much less solves, certain additional problems inherent in all prior art PTC heaters.

First is the problem of current inrush. This problem is particularly severe when it is desired to provide a heater having a T_s in excess of about 100°C. Many applications could advantageously utilize self-regulating heaters having a T_s of 200°C or even more. Unfortunately, as heretofore indicated, previously proposed PTC heater constructions are essentially unsuitable for such high T_s applications.

With materials having a T_s substantially above 100°C, the resistance of such material at or just below T_s may be as much as 10 times its resistance at ambient temperature. Since the PTC heater ordinarily functions at or slightly below its T_s , its effective heat

output is determined by its resistance at slightly below T_s . Therefore, a PTC heater drawing, for example, 15 amps at 200°C could easily draw 150 amps at ambient temperature. Such a heat system would require a current carrying capacity vastly in excess of that required for steady state operation or, alternatively, require the installation of complex and generally fragile or expensive control circuitry to prevent the 150 amp initial current inrush from burning out the heater or lead wires thereto when the heater is first connected to an electrical source.

Referring to Figure 2 of the accompanying drawings, which is a graph of resistance v temperature, the preferred type of heater characteristic (line ABC) in its ideal form has a constant resistance (denoted by the line AB) up to T_s and a resistance which increases rapidly (denoted by the line BC) above the T_s . Thus, the operating range, say from its maximum rate to ~ 0 current drawn, is as shown by the dotted lines intersecting the resistance temperature curve at B and D. The power output of the ideal heater is unaffected by changes in temperature below T_s but changes over its whole range in a very small range of temperatures above T_s . Unfortunately, as hereinbefore described, very few, if any PTC materials actually display this ideal characteristic. The nearest one can usually get with practical heaters is shown by the lines AB'C'. If the maximum permissible power drawn from the electrical circuit is given by the resistance at A, then the operating range for self limiting or "controlling" is given by the portion of the line B'C' lying between the dotted lines. Obviously, the heater temperature, when operating under "controlling" conditions, varies much more in this latter instance and the available power range in the "controlled" region is less than that in the ideal case. If a power range equal to that of the ideal case is desired, then a resistance characteristic such as A'B''C'' is necessary.

Referring again to Figure 2, curve AEF represents a portion of the resistance characteristic of a PTC material of type II. If, as in the previous instance, the operating power range is set by the dotted resistance lines, it can be readily appreciated that the temperature of the heater will vary over quite wide limits in operation depending on the thermal load.

Although, as hereinabove mentioned, the prior art recognizes the considerable advantage of having a heater composition which possesses a resistance temperature characteristic of Type I, many of the compositions alluded to in the prior art show behavior more closely resembling Type II, or even Type III behavior. The optimum (Type I) characteristic is shown only by a limited selection of compositions and there has been a long felt need for a means of modifying compositions showing

Type II or III behavior so that the behavior becomes or at least more closely approaches that of Type I.

An additional problem inherent in all prior art PTC strip heaters is that when it is desired to heat an irregularly shaped substrate the heater must be wrapped around the substrate, generally resulting in certain portions of the strip fully or partially overlapping other portions. This overlap can cause irregular heating.

It is thus apparent that while a variety of PTC compositions and constructions are well-known to the prior art, all such compositions and constructions and indeed, any apparent combination thereof, possess serious shortcomings which severely limit the use of self-regulating PTC heating articles.

The present invention provides an article comprising at least one first electrically resistive layer and at least one second electrically resistive layer at least a part of a surface of a first layer being contiguous with at least part of a surface of a second layer along an interface which provides direct electrical and thermal contact between them, the first layer exhibiting a positive temperature coefficient (hereinafter PTC as hereinafter defined) of resistance and having an anomaly temperature (T_s as hereinafter defined), above which it is substantially non-conducting, and second layer having a substantially constant resistance (hereinafter CW as hereinafter defined) below the anomaly temperature of the first layer.

The present invention also provides a self regulating heating article comprising a laminate of the said first and second layers and at least a pair of electrodes so positioned that, when there is a potential difference between the electrodes, at ambient temperature current will pass between the electrodes through at least a portion of at least one first layer and of at least one second layer.

When, however, the temperature of the article, or heating article, reaches the higher of (A) the temperature at which the resistance of the first layer exceeds that of the second layer (i.e., the resistances of their respective portions of current path between the electrodes) and

(B) the anomaly temperature of the first layer, the predominant current flow between the electrodes will be along a line which minimizes the path length through the first layer.

The present invention also provides a self-regulating heating article comprising a first layer of material which exhibits a positive temperature coefficient of resistance (PTC as hereinafter defined) and a second layer of constant resistance (CW) material as hereinafter defined, at least a part of a surface of the first layer being contiguous with at least a part of a surface of the second layer along an interface which provides direct electrical and thermal contact between them, and said

first layer being connectable to an electric power input source such that current flow is through at least a portion of said first layer and through at least a portion of said second layer, the article being such that at the higher of the temperature at which the resistance of said first layer exceeds the resistance of said second layer and the anomaly temperature (T_s , as hereinafter defined) of said first layer current flow predominantly follows a path the length of which through the first layer is as short as possible.

Preferably, the length of path through the PTC layer does not exceed its thickness (measured perpendicularly to the line between the electrodes) by more than 50%, preferably not by more than 20%.

Advantageously, the PTC layer has two substantially planar surfaces, which may be parallel, each of which is in at least partial contact with a surface of a CW layer.

In one series of embodiments the conductivity of the CW layer or layers is so chosen that the material, while being sufficiently resistive to generate heat when connected to the appropriate electrical source, is sufficiently conductive to act as electrode material also.

Alternatively, the electrode may be a metal, which may be embedded in or in contact with a surface of either the PCT layer, the CW layer, or in contact with a surface of either (i.e., at a surface remote from the contiguous surface) or both, at an interface between them. The electrode may be a fabric, braid, a grid (e.g., a series of parallel electrodes, or a mesh or network), and in the form of wire, strip or sheet. It may also be a conductive fiber. Electrodes of two or more different types may be included in a single article. Where the article is to be positioned over a conductive substrate, e.g. a metallic pipe, the substrate may itself form one electrode.

The article may comprise a plurality of electrodes intended for connexion to each of the terminals of the electrical power source, the plurality being referred to herein as a set. The electrodes in a given set are preferably parallel and equispaced. The two sets may be positioned parallel to each other, or transverse, especially perpendicular, preferably lying in parallel planes. Where the sets are parallel an electrode in one set may be positioned opposite an electrode in the other set, or it may be positioned opposite a space between two electrodes in the other set. The distance between adjacent electrodes in a given set, and that between the electrodes in one set and those in the other, together with the positioning of the sets relative to the CW or the PTC layers, and the interface between them, may all influence the performance of the heater, as described in more detail below.

The article may comprise a single electrode of one polarity, and a set of electrodes of the other. Similarly, the CW material may

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serve as at least one set, or may act as a single electrode for one polarity.

5 The article of the present invention may have any of a large number of configurations, some of which are described and illustrated below. For example, it may comprise a laminate of two layers or sheets, one CW and the other PTC material, or a sandwich of a
10 single layer of one of the materials between two layers of the other. The layer of one material may be completely surrounded by the other; the PTC material may be in the form of a layer only immediately surrounding one or both of a pair of elongate electrodes;
15 or the PTC material may be in the form of a single layer surrounding the elongate electrodes and forming a web between them.

20 In a further embodiment, the article has a generally rectangular cross-section, having a diagonal layer of one material, preferably the PTC material, one electrode being in each of the remaining substantially triangular regions. In a material of similar overall cross-section, one triangular region may be
25 of each material. It will be appreciated that many configurations of one or more CW layers and one or more PTC layers may be used, with the electrode positioning taking into account the requirements for appropriate current flow.

30 The article may be covered on one, or more, of all sides with an insulating layer. There may alternatively or also be provided on at least one surface preferably, a heat-activated adhesive, or sealant. In some embodiments, the CW layer may serve this purpose.

35 Advantageously, the first and second layers are polymeric materials having conductive particles, for example, carbon black, metal powders, or conductive fibers or fibrils dispersed therein. The CW layer may in a preferred embodiment have the fibers or fibrils as well as carbon particles. One layer may, on the other hand, comprise barium titanate.

40 Advantageously, the article is heat recoverable. Preferably, the whole of the article is heat recoverable, i.e., all the layers are individually capable of returning to or towards a heat-stable configuration, but in some embodiments some layers may simply be passive, and allow the recovery of the article as a unit. Preferably the recovery temperature of the article is within the operating range of the article as a heater. The article may be
45 laminated to heat recoverable articles, when preferably the article is itself heat recoverable.

50 The article may be of any of a number of configurations, advantageously being an elongate flexible strip with current passing, in operation, in a direction substantially transverse to the longitudinal axis, rather than along it.

55 Advantageously, the article has an effective T_s above 90°C , which is greater than the inherent T_s of the first layer; this layer is

advantageously a polymeric layer, preferably a cross-linked polymeric layer, and its crystalline melting point is less than the effective T_s .

At ambient temperatures, i.e., about 24°C , the resistivity of the first and second layers may be in the ratio 0.1:1.0 to 20.0:1.0.

70 The invention also provides a method of heating a substrate which comprises positioning the article of the invention which has electrodes in thermal contact with the substrate, and energizing the article by connecting the electrodes to an electrical power source.

75 The invention also provides a process for supplying heat and automatically controlling the maximum temperature reached which comprises passing electrical current through an article which comprises a first electrically resistive layer and a second electrically resistive layer, at least a part of a surface of the first layer being contiguous with at least a part of a surface of the second layer along
80 an interface which provides direct electrical and thermal contact between the layers, the first layer being composed of a material which exhibits a positive temperature coefficient of resistance (hereinafter PTC as hereinbefore defined) and having an anomaly temperature (T_s as hereinafter defined) above which it is substantially non-conducting, and the second layer being composed of a constant resistance (CW as hereinbefore defined) material, the current passing sequentially through the two layers, the resistance of the first layer being greater than the resistance of the second layer, and the predominant current path through the first layer being as short as possible at the higher of the temperature at which the resistance of the first layer exceeds the resistance of the second layer and the anomaly temperature (T_s).

85 Preferably, the current path through the first layer is predominantly perpendicular to the interface between the first and second layers.

90 The invention also provides an article constructed in accordance with the invention, through which an electric current is passing.

95 The invention further provides a method of recovering an article according to the invention that is heat recoverable and which has electrodes by connecting the electrodes to a power source for a time sufficient to effect heat-recovery.

100 The invention also provides a method of covering a substrate which comprises applying a heat recoverable article of the invention over a substrate, and heating the article by connecting it to an electrical power source to cause recovery thereof to cover the substrate, and a substrate covered thereby.

105 The configuration and positional relationship of the PTC and CW layers and the electrodes are subject to certain limitations, and the following requirements should be met:

1. At any temperature at least some of the

current flow between electrodes of opposite polarity is through at least a portion of at least one PTC layer and also through at least a portion of at least one CW layer.

2. There is both electrical and thermal contact (and hence coupling) between PTC and CW layers. The electrical and thermal gradients may be parallel or non-parallel to each other.

As hereinafter described in greater detail, certain articles constructed in accordance with the invention manifest an anomaly temperature higher than the intrinsic T_s of the PTC layer itself. The T_s of the article is termed the effective T_s .

Advantageously, the thermal and electrical gradients in the PTC layer are predominantly along the same line or axis at or above the T_s of the PTC layer or the effective T_s if the latter is greater.

3. At or above T_s of the effective T_s , if the latter is greater, the line of maximum current flow is the line with the minimum path length through the PTC layer or layers, even though a longer path length through the CW layer or layers is occasioned thereby.

The configuration of the article will in certain instances preferably be such that the directionally shortest current path through the PTC layer does not dimensionally exceed the maximum thickness of the PTC layer in a plane perpendicular to the plane joining the electrodes and perpendicular to the current flow by more than about 50%, preferably by more than about 20%.

The term thickness as used herein is intended to connote the dimension between any two surfaces (interior and exterior) of the PTC layer which is the dimension of least measure. In most heater designs in accordance with the present invention current flow through the PTC material at or above T_s will be predominantly perpendicular to the interface between the PTC and CW layers.

Among other advantages of the present invention, hotlining may be substantially reduced, or even eliminated, even at extremely high wattage outputs and/or operating temperatures, by providing current flow through the thickness of the PTC layer as opposed to along its length or width.

Other unexpected advantages of forming a laminate of the PTC material with at least one CW material, are that the heaters may be used at outputs and for applications not only contemplated but indeed virtually unattainable by previously proposed designs.

The CW layer or layers, if sufficiently conductive, may be connected directly to a power source so as to function as and be considered to be an electrode. Alternatively, the CW layer may have impregnated therein or applied to a surface thereof electrodes to conduct current therethrough. Such CW layer-electrode combinations differ critically from previously

proposed electrode-PTC sandwiches since with such prior art designs the electrode layers served only as conductors and not as additional resistive heating elements. In contradistinction, in the structures of the present invention, the CW layer, which is in direct contact with the PTC layer, acts both as an electrode and also as an efficient heat output source.

In accordance with the present invention, thermoplastic polymer compositions having PTC characteristics can suitably be employed as a heating element that approaches more nearly Type I characteristics than does the PTC material *per se*, which would ordinarily manifest Type II, III, or IV characteristics. In particular, virtually all of the previously proposed polymeric PTC materials may be used as the PTC layer in a heating element constructed according to the present invention. Additionally, the novel PTC materials described in co-pending Application No. 39518/75 (Serial No. 1,528,622) are suitable for use in the present invention.

Suitable conductive fillers for the polymeric PTC composition useful in the present invention in addition to particulate carbon black include graphite, metal powders, conductive metal salts and oxides, and boron or phosphorus doped silicon or germanium.

By PTC material is meant one that exhibits an increase in resistivity of at least a factor of six for a temperature increase of 30 deg. C starting at T_s , or exhibits an increase of a factor of six for a temperature increase of less than 30 deg. C starting at T_s .

The anomaly temperature of a PTC material, herein designated T_s , is the lowest temperature at which the material exhibits an increase of resistivity of at least a factor of six for a temperature increase of 30 deg. C starting at T_s , or exhibits an increase of a factor of six for a temperature increase of less than 30 deg. C starting at T_s . The transition of a material from a superconductive state to a normal conductive state is not regarded in this specification as an anomaly.

In the present specification, although a device may be described as shutting off at a given T_s , it will be understood by those skilled in the art that in many practical instances T_s may be understood as the lowest temperature of a range over which the device switches off.

As mentioned herein, although prior art disclosures stress the practical advantages and importance of providing resistive compositions manifesting a type I resistivity temperature characteristic, the number of such compositions available is relatively small notwithstanding the claims of the prior art. Most of the hitherto disclosed compositions in fact possess type II and type III resistance characteristics. Thus a method of enabling a PTC material compositions having inherent type II or III resistance characteristics to manifest more closely type I behaviour very greatly increases

the number of compositions available for use in heating or other resistive devices. Thus, one can select a PTC material on the basis of its T_s and/or other desirable physical and/or chemical properties and by using the present invention provide a heating article more clearly manifesting type I behaviour.

The electrical resistivity of most electrically conductive materials, both PTC and non PTC, is found to increase or decrease more or less markedly with temperature. The magnitude of this variation ranges from the less than $\pm 0.5\%$ per deg. C characteristic of most metals to the ± 1 to 5% or higher per deg. C changes exhibited by most conductive thermoplastic polymer compositions. With most materials, however, the direction and magnitude of the change is such that when operated as an electric resistance heater the temperature attained by the heater is predominantly determined by the rate of thermal conduction or radiation to its surrounding environment and not predominantly by the switching mechanism heretofore described for commercially useful PTC heater materials. Thus, the term CW material or CW output material as used herein denotes a material whose resistance does not increase by more than a factor of six in any 30 deg. C segment below the T_s of the PTC material it is in contact with. Preferably, the CW material has a resistivity of at least 1 ohm-cm at 25°C . It should, of course, also be noted that when combined with a PTC material the CW layer or layers can yield a heater which, below its T_s , will show changes in resistivity within the above indicated limits although such layer or layers comprise materials, which if their intrinsic resistivity is measured independently, will show resistivity changes outside these limits. Additionally, since many PTC materials are constant wattage materials up to about their T_s , the term constant wattage as used herein encompasses materials which manifest PTC characteristics, provided, however, that they are used in conjunction with a PTC material having a lower T_s . Under these circumstances, the PTC material of higher T_s will not reach its T_s and hence in use will manifest only essentially constant wattage characteristics.

Constant wattage materials suitable for use in the instant invention are well known to the prior art. Suitable in this respect are polymers, especially thermoplastic polymers, containing high loadings of conductive particulate materials, for example, carbon black or metals. Where the thermoplastic material undergoes a large change in volume at its melting or softening point so as to tend to decrease the number of conductive paths between the particles at or about that temperature and thereby cause its resistance to increase, such increases may be avoided by multiplying the number of alternative conductive paths, for

example, by increasing the loading of conductive material and/or using a more structured form of the conductive material. Structured as used herein connotes both the shape of the individual particles (for example spherical, lenticular or fibrillar) and the tendency of such particles to agglomerate when incorporated into the polymeric matrix. Also suitable are essentially inorganic, flexible constant wattage materials including carbon coated asbestos paper as taught for example in Smith-Johanssen, U.S. Patent 2,952,761. Of course, in some applications it is not necessary for a high degree of flexibility to be present and resistive metal wires supported by inorganic insulating materials may be utilized as the constant wattage layer. In such a case one end of the resistive metal wire may be electrically connected to the PTC layer via an electrode coplanar with the PTC layer surface but not necessarily coextensive with the PTC layer. In yet other applications a high degree of flexibility may only be advantageous or desired in the process of forming the article, for example, by vacuum or thermoforming. In such instances the PTC layer may be formed over a layer or sandwiched between layers of relatively rigid constant wattage material in the configuration of the desired article so as to maintain good thermal coupling between the layers, the current flow being either directly across the interfacing contiguous plane or by means of an intervening electrode on the surface of the PTC layer interleaved between the PTC layer and the constant wattage layer or layers. In these types of embodiments almost any type of constant wattage material contemplated by the prior art relating to electrical heaters may suitably be used.

In certain embodiments of this invention the constant wattage layer can serve as an electrode by being conductively connected directly to the electric power source. If the constant wattage heating layer is not sufficiently conductive to act as an electrode, a metal or other highly conductive material electrode, for example, a metal grid may be embedded therein, such electrode being conductively to an outside power source. In certain embodiments it may be advantageous to disperse in the constant wattage layer (which may already contain a conductive filler) an additional quantity of highly conductive (preferably metal) filler in the form of fibers or fibrils. This embodiment is particularly advantageous when the electrodes are not coextensive with the whole planar surface of the constant wattage layer but are contiguous either with said surface or with the interface between the constant wattage and PTC layer or are embedded in said constant wattage layer.

It should be noted that the structure constructed in accordance with the invention may have any of a wide variety of electrode con-

figurations, types, positioning, and materials. For example, metal fabric mesh or grid, flexible metal strip, convoluted wires, conductive paint, solid carbon e.g., carbon fibers, graphite impregnated fiber, metal coated fiber e.g., copper or stainless steel, solid metal conductor of various geometries and other electrodes as known in the art are all suitable. An electrode, whether connected to the constant wattage layer or the PTC layer or both, can be fully or partially coplanar with the outer surface thereof. By outer surface of the PTC layer is meant a surface thereof not contiguous with a constant wattage layer and, conversely, for the constant wattage layer, the outer surface thereof is a surface not contiguous with the PTC layer. Alternatively, the electrode may be embedded in the PTC or in a constant wattage layer. Yet another construction involves one electrode being embedded in or on the outer surface of the PTC layer and the other electrode being located at the interface between the PTC and constant wattage layers. Of course, if desired a plurality of electrodes which are shunt connected for each polarity can be utilized with the same variety of placements being suitable.

As herein above indicated, with prior art PTC compositions and also with the novel PTC compositions of the above-mentioned Application No. 39518/75 (Serial No. 1,528,622) certain embodiments of the present invention significantly affect the operating characteristics of a heater utilizing the PTC composition. More particularly, when embedded or abutting electrodes whose surface is not coextensive with that of the CW or PTC layer are used, the placement of the electrodes having an opposite polarity with respect to each other can significantly modify the operating characteristics of the apparatus. Thus, if strip electrodes of opposite polarity, coplanar but not coextensive with, the outer surfaces of the CW and PTC layers, are placed directly opposite and parallel with each other different operating characteristics are obtained from those which result when the electrodes are parallel but laterally displaced with respect to one another or when perpendicular projections of the electrodes on one another intersect. Although the invention is not to be limited by any particular theoretical interpretation it is believed that electrode placement has an effect on the favored current paths at different temperatures. Thus for the case of electrodes directly opposite to one another current flow is predominantly normal to the plane of the PTC layer. However, if electrodes are displaced in some manner from this arrangement and the resistance for the CW layer is initially (i.e., at lower temperatures) greater than that of the PTC layer, the predominant conduction path at lower temperatures may be normal to the plane of

and through the thickness of the CW layer and diagonally through the thickness of the PTC layer. At some higher temperature, where the resistances of the CW and PTC layers become equal, conduction occurs predominantly diagonally through the thickness of both layers while at yet higher temperatures the preferred conductive path may be normal to the plane of and through the thickness of the PTC layer but diagonally through the thickness of the CW layer.

In general, opposing the electrodes will yield an apparatus having a resistance-temperature curve similar but not identical to that obtained by having electrodes contiguous with the whole surface of each outer layer. As the lateral and/or angular displacement of the electrodes from an opposing parallel configuration is increased the electrical characteristics tend to deviate more from that expected for a simple series connection, as described in greater detail in the examples.

More specifically, where pairs of electrodes are opposed (i.e., their centres are on a line perpendicular to the interface between PTC and CW layers, and the current path is perpendicular through the PTC and CW layers, the effective T_s will be that characteristic of the particular combination of layered materials. However, if one electrode (or the electrodes of one polarity) is shifted in the plane i.e., parallel to the interface of the layers such that the current path is diagonal, the effective T_s is increased. Generally, the more diagonal (the more displaced from transverse to the interface) the current path between electrodes, the higher the effective T_s . Indeed, where the resistance of the CW exceeds that of the PTC layer at the latter's intrinsic T_s and where such electrode placement is utilized the effective T_s may be substantially above the crystalline melting point of the PTC material. Thus, regardless of the relative positions of opposed electrodes as the resistivity of the constant wattage layer relative to that of the PTC layer is raised, the effective T_s also tends to increase.

The electrodes may have a variety of shapes; for example, their cross-sections may be square, rectangular, or circular, they may be rectilinear, planar or curved strips, spiral (with the pitch of the spiral for each electrode being the same or different) or rectilinear spiral and, as hereinbefore mentioned, the electrodes may be directly opposite or laterally or otherwise displaced with respect to one another and either or both electrodes may be monolithic or multiple in nature. It is thus apparent that the heat output and T_s characteristics of the article of the instant invention can be varied by an appropriate choice of electrode shape and/or position, that selected being dependent upon the use to which the

structure is to be put and a suitable arrangement being ascertainable by routine experimentation.

Although in most embodiments the PTC layer and the CW layer or layers will be fully contiguous (i.e., the whole of one face of one layer will be in contact with the whole of the corresponding face of the other) in some circumstances it is advantageous for the PTC and CW layers not to be fully contiguous over the entire respective opposing surfaces. Particularly where high Joule outputs at high temperature are desired, it is advantageous to generate the major portion of the heat output in the constant wattage layer. In many such instances the PTC layer will preferably be contiguous with only a portion of the opposing surface of the CW layer. Such arrangements tend to reduce the effective T_s . When the PTC layer is contiguous with only a part of the surface of the constant wattage layer, said PTC layer can experience wide variations in power generation. Therefore, good thermal coupling and balancing of the relative power levels is desirable.

The articles provided by the present invention have utility in a wide variety of applications. For example, they may be used as heaters for causing heat recoverable articles to recover on to a substrate whether by being an integral part of the heat recoverable article or by being placed in substantially abutting heat transferring relation thereto. In applications where heat activation of an adhesive is required, the high temperatures and high outputs attainable by heaters constructed according to the present invention render them particularly suitable. The articles are also useful where uniform heating of a substantial area is required as, for example, in heated ducts for fluid flow or as enclosure walls or panels as in ovens, residences or transportation vehicles. Other uses include heaters for industrial process pipes and vessels requiring uniform heating and/or temperature control, and de-icing heaters on roads and aircraft wings. The laminar form and uniform heating characteristics of many of these articles render them particularly useful as heaters for waterbeds, warming trays and bowls and medical heating pads while their capacity for high wattage output at high temperatures in addition renders them particularly attractive as heaters for cooking appliances such as griddles and frying pans.

Most PTC materials comprise a crystalline thermoplastic matrix having a conductive, usually particulate, filler dispersed therein. For example, the previously mentioned Kohler, U.S. Patent 3,243,753 discloses a polyethylene or polypropylene carbon black composition, in which the polyolefin has been polymerized *in situ*, such materials exhibiting the PTC anomaly temperature close to the melt temperature of the polymers, i.e., about 110°C—

120°C. Likewise, Kohler *et al*, in U.S. Patent 3,351,882, disclose carbon particles dispersed in polyethylene in which the composition may be crosslinked, or may contain thermosetting resins to add strength or rigidity to the system. However, the T_s temperature still remains just below the crystalline melting point of the thermoplastic polyolefin. Hummel *et al*, in U.S. Patent 3,412,358, disclose a PTC polymeric material comprising carbon black or other conductive particles previously dispersed in an insulating material, the homogeneous mixture in turn being dispersed in a thermoplastic resin binder. The PTC characteristics are apparently achieved by the interaction of the carbon black and the insulating material and it is suggested by Hummel *et al* that the insulating material must have a specific electrical resistance and a coefficient of thermal expansion higher than that of the conductive particle.

U.S. Patent 3,823,217 to Kampe discloses a wide range of conductive particle filled crystalline polymers which exhibit PTC characteristics. These polymers include polyolefins, for example, low, medium and high density polyethylenes and polypropylenes, pol(butene-1), poly(dodecamethylene pyromellitimide), ethylenepropylene copolymers and terpolymers with non-conjugated dienes, poly(vinylidene fluoride) and vinylidene fluoride-tetrafluoroethylene copolymers. It is also suggested that blends of polymers containing carbon black can suitably be employed, for example polyethylene with an ethylene-ethyl acrylate copolymer. Kampe achieves lower resistance levels by cycling his products above and below the melt temperature of the polymers. Changes in resistance caused by the thermal history of the sample have also been found to be minimized by thermal cycling. U.S. Patent 3,793,716 to Smith-Johannsen discloses conductive polymer compositions exhibiting PTC characteristics in which a crystalline polymer having carbon black dispersed therein is dissolved in a suitable solvent and the solution impregnated into a substrate followed by evaporation of the solvent yielding articles having decreased room temperature resistivities for a given level of conductive filler. However, T_s still occurs just below the crystalline melting point of the polymer. Similarly, Kawashima *et al*, in U.S. Patent 3,591,526, disclose carbon black containing polymer blends exhibiting PTC characteristics with the T_s temperature occurring at about the crystalline melting point of a thermoplastic material added to a second material for the purpose of molding the mixture.

A particularly unexpected feature of the present invention is that when compositions of the type described in the prior art as being useful for PTC or for CW heaters are used in multi-layer heaters designed in accordance with certain embodiments of the present

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invention they manifest resistance/temperature characteristics which would in no way be expected from a consideration of the resistance/temperature characteristics of the individual layers or indeed that expected to result when such layers are connected together in series to form an electrical circuit. Fabrication of a multilayer heater in accordance with the present invention utilizing layers having appropriately chosen specific resistivities may substantially alter the T_s of the article containing the PTC layer to a temperature at or in excess of the melting or softening point of the polymeric constituent of the PTC layer.

Thus, though the prior art suggests that T_s is independent of the geometrical configuration of the heater, it has most unexpectedly been discovered that certain of the geometrical arrangements contemplated herein can result in substantial increases in T_s , even to above the polymer melting point, thus greatly increasing the utility and versatility of both previously proposed and other compositions.

In a preferred embodiment, a layered article of this invention comprises a middle layer of conductive polymeric PTC material interleaved or sandwiched between two CW layers. The CW layers may have embedded therein or deposited thereover electrodes (ordinarily metal) such that upon application of a voltage across the electrodes the current will flow through the PTC layer and thereby cause heating of both the PTC layer and the CW layers.

In another preferred embodiment, the heating element may be bonded to a heat recoverable material or be itself rendered heat recoverable, to provide a heat recoverable article which can be made to recover by means of internally generated as opposed to externally applied heat. Such an article thus advantageously avoids the requirement of an outside heating source to effect recovery, requiring only attachment to an electrical power source.

In a particularly preferred embodiment of the present invention of great utility to the manufacture of heat recoverable devices, PTC compositions disclosed in Application No. 39518/75 (Serial No. 1,528,622) referenced above are used. Such compositions comprise blends of thermoplastic and elastomeric materials having conductive materials dispersed therein. As pointed out in the above specification such blends exhibit a steep rise in resistance at about the melting point of the thermoplastic component, the resistance continuing to rise with temperature thereafter. Because of the increased safety margin given by the further increases of resistance above the melting point such heaters can be designed to control at temperatures above T_s and at resistances well in excess of that at T_s , but yet avoid the risk of thermal runaway and/or burn out which occurs when prior art PTC

compositions are used in such designs. Such preferred heaters, especially when the increase in resistance with temperatures above T_s is very steep, are very demand insensitive, that is, the operating temperature of the PTC material varies very little with thermal load. They can also be designed to generate very high powers up to T_s when electrically connected to a power source. Because of their excellent temperature control, they can be employed to activate adhesives and cause heat recoverable devices to recover around substrates e.g., thermoplastic telephone cable jackets without fear of melting or deforming the substrate even if left connected for considerable periods of time.

In this preferred embodiment, a heater PTC core in accordance with the teaching of Application No. 39518/75 (Serial No. 1,528,622) is combined with a constant wattage outer layer whose thermoplastic polymer ingredients, if any, have a melting point not greater than that of the thermoplastic polymer component of the PTC composition. The constant wattage layer, if comprising thermoplastic polymers, can be made heat recoverable. Additionally, or alternatively, but preferably additionally a member comprising a layer of a heat recoverable polymer composition having a recovery temperature less than the melting point of the thermoplastic component of the PTC composition is provided. An additional layer of a hot melt adhesive or mastic may also be provided, the hot melt, if used, having a melting point similar to that of the heat recoverable member and an activation temperature less than the melting point of the thermoplastic component of the PTC composition. The electrodes are advantageously formed from flattened braided wires which are produced by extruding a braid over a thermoplastic core, and flattening the product while the thermoplastic is soft. Such an embodiment has been found to be particularly advantageous as hereinabove mentioned, where the substrate is heat sensitive i.e., if warmed above its melting point will deform or flow. Such applications include telephone splice cases and many other applications in the communication industry.

The invention will now be described in greater detail, by way of example only, with reference to the accompanying drawings, in which:

Figures 1 and 2 which have already been discussed, illustrate the resistance temperature characteristics of various PTC materials;

Figures 3 to 5 are perspectives of prior art structures utilizing PTC compositions;

Figures 6 to 12, 13b and 15 to 34 are perspectives of or serve to illustrate and explain various articles constructed in accordance with the invention;

Figure 13a is a cross section of the embodiment shown in Figure 13b, while Figure 14

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is a cross section of the embodiment shown in Figure 15;

Figure 35 illustrates an embodiment in which electrodes, which are in effect point electrodes, are provided at intervals along the length of the article;

Figures 36 and 37 illustrate the power-temperature relationship for products described in certain of the examples.

Referring now more especially to Figures 3 to 5, there are shown various prior art structures utilizing PTC compositions. Figure 3 shows a strip heater similar to that disclosed by Buiting *et al* in U.S. Patent 3,413,442, wherein thin sheets of silver, 1 and 3, are positioned on each side of a PTC material layer 2. This is not in accordance with the present invention, even though a laminated configuration is disclosed, since material contiguous with a PTC layer is so conductive that it will not itself act as a heater.

Figure 4 depicts a strip heater according to Kohler, U.S. Patent 3,243,753, wherein a PTC material 6 has on each edge thereof conductive grid electrodes 5 and 7.

Figure 5 represents a previously proposed strip heater, in which a PTC material 10 having a cross section in the shape of a dumb-bell has conductive wire electrodes, 8, 9, positioned along its length.

Turning now to configurations constructed in accordance with the invention, Figure 6 depicts a PTC layer 11 having contiguous, or partially contiguous, therewith a CW heating layer 12. Overlying the surface of the constant wattage layer is a grid electrode 13 while the second grid electrode 14 is contiguous with the surface of the PTC layer remote from constant wattage layer 12.

In Figure 7, a plurality of strip electrodes 16, connected in parallel, are embedded in a CW layer 15. The opposite electrode 18 is a continuous sheet, applied to the remote surface of the PTC material 17.

Figure 8 depicts a further variation in which electrodes 20 and 22 are strip electrodes (electrodes 20 being parallel, or shunt, connected, electrodes 22 likewise), the electrodes 20 being sandwiched between a PTC layer 21 and a CW layer 19. In this configuration a low resistance CW layer is desirable because the gradient potential along the interface between layers 21 and 19 is thereby reduced.

Figure 9 depicts a configuration similar to Figure 6, with a grid electrode 23 overlying the CW layer 24 which in turn is contiguous with a PTC layer 25. However, the other electrode is grid electrode 26, sandwiched within the PTC layer.

Turning to Figure 10, a CW layer 27 has embedded therein a first set of electrodes 28, while a PTC layer 29 has embedded therein a second electrode 30.

It will be understood that the various embodiments depicted in Figures 6 to 10

may be utilized in accordance with this invention, in any combination. More specifically, grid electrodes, as shown in Figures 6 and 9, film or sheet electrodes as shown in Figure 7 or strip electrodes as shown in Figure 8 may be utilized in any of the embodiments, and combination of two or more different type electrodes may be utilized in a given configuration. A first electrode may be positioned over the CW layer, embedded in the CW layer or be positioned between the CW layer and the PTC layer. A second electrode may be positioned on the opposite side of the PTC layer over, within or between a second CW layer or beneath or embedded in the PTC layer.

Figure 11 shows strip electrodes 32 and 34 embedded in two CW layers 31 and 35, the electrode CW layers sandwiching a PTC layer 33 therebetween. Of course, as previously discussed, the electrode may have a grid, film or other construction.

Figure 12 represents a particular embodiment of the present invention which has been found useful for increasing T_s . As previously discussed, by staggering the electrodes, so that the current path has a component across the layers as opposed to being perpendicular through, then the effective T_s may be increased. Thus, in Figure 12 strip electrodes 37 are staggered between the geometrical perpendicular projections of strip electrodes 39, the sets of electrodes 37 and 39 being embedded in CW layers 36 and 40, a PTC layer 38 being sandwiched therebetween.

Figures 13a and 13b are a cross section and perspective view of a preferred embodiment. A plurality of wire electrodes, 42, shunt connected, is embedded within a CW layer 41 and similarly a plurality 45 in the layer 44, a PTC layer 43 being sandwiched between the layers 41 and 44. Wires 42 are preferably substantially all in one direction, with wires 45 being in a second direction substantially perpendicular to that of the first. Further, the overall layer configuration may take the form of a disk, such form being particularly well suited for a number of heating applications.

Turning to Figures 14 and 15, a layered configuration particularly suited for the making of heat recoverable encapsulating articles, as described fully in Applications No. 39516/75, 9805/78 and 10294/78 (Serial Nos. 1,529,353, 1,529,355, 1,529,356) is shown. For this purpose, the layers are generally of a flexible, polymeric material, with any or all of the layers being rendered heat recoverable. For a more detailed description of heat recoverable articles, and their applications, see the hereinabove referred to application. If the article is to be used for sealing an electrical splice, utilizing the layer composite of this invention, an outer layer 46 is provided, which may be insulating material, which may or may not be heat recoverable. Next in the

lamine is a CW material layer 47 having embedded therein electrodes 48 which may be of a braided, serrated or convoluted configuration, and which are shunt connected to a power source. A PTC material layer 49 follows, with a second set of electrodes 51 embedded within a second CW layer 50. A second insulating material layer 53, which may be heat recoverable, is placed adjacent the heating layers, and on the face surface of this layer 53 is an adhesive layer 54, which is heat activated by the heating element of this invention.

Referring now to Figures 16 to 34, the electrodes, of whatever form, are denoted by reference numerals 55 and 56, CW layers are denoted by 57 and 58, PTC layers by 59 and 60 and a conductive substrate, e.g., a pipe by 61.

Figure 16 represents an embodiment in which the dimensions (for example thickness) of a particular layer and, as a result, the relative thicknesses, of the CW and PTC layers, are varied across the width of the heater, the power output density and/or the effective T_s varying continuously across the width as a result. Figure 17 represents an embodiment in which the PTC and/or CW layer have different compositions in different areas to alter the watt density and/or effective T_s .

Figure 18 is a cross section of an embodiment in which the substrate, for example, a metal pipe, is part of the electrical circuit, that is, it forms one of the electrodes. Figure 19 represents an embodiment where the individual layers are wrapped consecutively around an object that is required to be heated so as to form a layered heater *in situ*. The layers can be caused to adhere together by heating either externally or by passage of an electric current or the layers can be formed from materials which adhere together at the temperature at which the article is applied. This is an example of an embodiment in which it may be especially useful to have the substrate form part of the electrical circuit. Figures 20 to 26 show another group of embodiments. In a modification of the construction shown in Figure 20, the electrode 56 may also have a coaxial layer 60 of PTC material as shown for the electrode 55. The constructions shown in Figures 23 to 25 are examples of heaters in which conduction below the effective T_s (depending on the relative resistivities of the PTC and CW layers) may be predominantly across the PTC material between the electrodes. However, when the PTC layer heats up to a temperature above its T_s , conduction then occurs predominantly or almost entirely from one electrode through the thickness of the PTC layer by way of the shortest possible path from that electrode to the constant wattage layer then through the constant wattage layer to the

other electrode (again through the minimum thickness of any PTC material which may be intervening).

It will be appreciated that the "predominant" current flow referred to herein relates to the path along which the greatest current 'flux' exists. Although theoretically this path will not always be exactly the shortest path in the PTC layer, because even at or above T_s there will be some portion of the current that is carried by the rest of the PTC material, this portion may be ignored for practical purposes e.g., in a configuration such that as in Figure 24, as shown in the drawing, current will for practical purposes predominantly flow perpendicularly upward and downward through the PTC layer 59, and along the layers 57 and 58, although there must be a very slight component toward the other electrode in the path of the predominant current flow in the PTC layer. This is small enough to be ignored for practical purposes.

In a variation of the construction illustrated in Figure 25, the layer 58 may be omitted, and the electrode 56 positioned in contact with the layers 57 and 59, spaced apart from the electrode 55.

Figures 26 and 27 illustrate embodiments in which the PTC layer is contiguous with only a part of the CW layer. We have found that as the fraction of the total CW surface area in contact with the PTC surface area is reduced the ambient temperature at which for a given applied voltage the heater limits its power output is also reduced.

Figure 28 shows another variant of the embodiment shown in Figure 21. In a variant of Figure 28, there may be a single CW layer 57 which is positioned where the layer 59 is illustrated and a pair of PTC layers 59, 60 which replace the illustrated CW layers 57, 58.

Figures 29 and 30 show further variants of the basic layered heater having the same general form and manner of function as Figures 23 to 25.

Figures 31 and 32 illustrate other forms of the heater wherein the effective T_s of the heater may be advantageously different from that of the PTC material alone as hereinbefore described.

Figures 33 and 34 show how useful layered heaters can be formed by combined extrusion coated wires wherein the coatings have PTC or CW characteristics.

Referring now to Figure 35, there is shown an additional article constructed in accordance with the invention wherein conductors 55 and 56, which in operation are of different polarity, have a concentric layer of insulation 62 around them. Reference numeral 59 represents the PTC material and 57 and 58 the CW material. The layer 62 is discontinuous over the surface of the conductor in that as shown in an article of substantially linear elongate

configuration, segments of the insulation are removed intermittently along the length of the conductors. As can be seen, where the insulation has been removed each conductor is in direct conductive contact with the CW material. Such areas of contact for each electrode are not opposite each other but in fact diagonally opposed along the long axis of the article. The advantage of the present embodiment is that of necessity current flow between the electrodes of opposite polarity is not merely across the width of the article, i.e., distance X but in fact current must flow distance Y so that the current path is down a portion of the length of the article. A long current path is desirable in that it enables one to utilize a CW material of low resistivity (enabling higher voltages to be used) without manifesting a tendency to burn out. Of course, alternative configurations which ensure that the current flow is at least partially down the length of the article are readily constructed. For example, in a construction in which a PTC layer is sandwiched between two CW layers with strip electrodes disposed on the outer surface of the CW layers; an intermittent insulating layer may be positioned between each constant wattage layer and the electrode disposed on the surface thereof. Or, where a continuous insulating layer is disposed on the outer surface, the electrodes may alternatively pass at intervals through the insulating layer and contact the CW layer.

The following examples illustrate the invention: Articles constructed in accordance with the invention may be made in a variety of ways known *per se*. For polymer heaters the individual layers may be extruded separately and thereafter laminated, bonded or otherwise affixed together, the electrodes being inserted during extrusion or lamination as desired. The layers may otherwise be made by calendering or coextrusion, the electrodes, as previously indicated, being inserted at any suitable stage in the operation. A preferred method of fabricating a particular embodiment of a heater in accordance with the present invention is described in the hereinabove mentioned Applications Nos. 39516/75, 9805/78 and 10294/78 (Serial Nos. 1,529,353, 1,529,355, 1,529,356).

Methods of construction of nonpolymeric conductive compositions suitable for utilization in the present invention, for example ceramics or carbon loaded asbestos paper, are well known in the art. The layers may be affixed to other layers by bonding, welding, gluing and other well known processes which preserve or maintain conductive contact between the layers.

"Templace", "Epsyn", "Profax", "Cabot", "Sterling", "Black Pearls", "Elvax", "Marlex" and "Silastic" are trade marks.

Parts are parts by weight unless otherwise indicated. 65

Example 1.

A laminate was constructed as generally shown in Fig. 14 having a PTC layer as described in Example 5, Sample 5-2 and a constant wattage layer as described in Example 3, with the insulating layers (46, 53) comprising a blend of polyethylene and a low structure, low conductivity black. The adhesive layer was a hot melt adhesive with a ring and ball softening temperature of 110° C. The laminate was irradiated to effect cross-linking prior to coating with the adhesive, hot stretched perpendicular to the convoluted wire electrodes and cooled. The expanded sheet was wrapped around a polyethylene jacketed telephone cable and the opposing ends held together. On connecting the electrode wires to a 12 volt lead-acid battery, the laminate shrank smoothly and uniformly onto the telephone cable. 70 75 80 85

Example 2.

A $2.5 \times 15.2 \times 0.05$ cm strip to which was attached on opposite edges along its length copper electrodes and having the composition 70% of a medium density polyethylene, 18% ethylene/ethyl acrylate copolymer and 12% XC72 carbon black from Cabot Corp. was annealed at 150°C in vacuum for 16 hours and then irradiated to a dose of 20 Mrads and coated with a temperature indicating paint (Templace 76°C indicating paint). The electrodes were connected to a 110 volt A.C. supply. Within less than a minute the white paint had melted in a thin region approximately one tenth of an inch wide and roughly equidistant between the electrodes a "hotline". The surface temperature in the middle of the hotline was estimated to be close to 85°C which is just above T_g for this particular composition. Regions only 0.5 cm away from the hotline were below 50°C. In this condition the element was generating substantially all its power from the hotline area. In a similar experiment in which the element was insulated, placed in water and connected to a power source a similar "hotline" was noted. Then the composition of this example was fabricated into a laminated core sandwiched between CW layers of carbon black filled silicone rubber, each CW layer carrying a 20 AWG (about 0.081 cm diameter) multi strand copper bus in its center. The element heated smoothly to a uniform surface temperature of about 65°C in air, the core temperature being about 80°C. Thus, layering of the PTC layer between constant wattage layers eliminated the hotline for this PTC composition. 90 95 100 105 110 115 120

Example 3.

A series of laminated heaters was constructed using a constant wattage layer consisting of ethylene-propylene rubber, 35 parts, ethylene-vinyl acetate copolymer, 30

parts and carbon black, 35 parts and a PTC core composition as described in Table I below in which the carbon black was dispersed in the polypropylene before the TPR 1900 rubber was blended in.

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TABLE I

Sample No.	1	2	3	4	5	6
TPR 1900 (thermo-plastic ethylene-propylene rubber from Uniroyal Corporation)	72.5	70.0	68.75	67.5	66.25	65.0
Profax 6524 (polypropylene from Hercules Corporation)	16.5	18.0	18.75	19.5	20.25	21.0
CX72 (carbon black from Cabot Corporation)	11.0	12.0	12.5	13.0	13.5	14.0

15 The CW and PTC materials were hydraulically pressed at 200°C into 15.2 × 15.2 × 0.05 cm slabs for one minute and the heater constructions comprising a PTC layer sandwiched between two CW layers laminated at 200°C for two minutes and then annealed at 200°C for 10 minutes and irradiated. Heater segments 2.5 × 3.75 cm were cut from each specimen and 2.5 × 0.635 cm

electrodes of conductive silver paint were painted adjacent to diagonally opposite 2.5 edges of the CW layers, one electrode to each CW layer. The effect of varying the composition of the layers on the inrush/operating current ratio and self regulating temperature can be seen from the inrush ratio and T_s in Table II below:

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TABLE II

Composition	Carbon Black level in core %	Room Temp. resistance of laminate (ohms)	Inrush Ratio*	T_s (°C)**
PTF Core Alone	12.5	—	8	85
1	11	21,000	8	90
2	12	260	5	105
3	12.5	245	4.4	125
4	13	230	3.9	165
5	13.5	220	3.7	185
6	14	205	not measured	

* Defined as the ratio of resistance at T_s to resistance at room temperature

** Melting point of PTC approximately 165°C.

30 As is apparent, minor alteration of composition of the PTC material with the CW material being held constant can significantly alter the T_s and the inrush ratio when used in a heater constructed according to the

invention. Specifically, T_s can be varied to above the melting point of the PTC. Furthermore; when a PTC material having a T_s of 85°C and containing 12.5% of carbon black was sandwiched between CW layers,

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the effective T_s was raised to 125°C, the resistance temperature characteristic of the latter as shown by the inrush ratio being much closer to Type I behavior (which by definition has an inrush ratio of 1).

Example 4.

A 0.063 cm thick slab of PTC material having the composition described in Example 2 was laminated between two 0.063 cm thick CW layers having the composition of the CW layers of Example 3. The laminate was annealed at 150°C for 16 hours and then irradiated to a dose of about 10 megarads. A 2.5 cm square piece cut from the laminate and painted with conductive silver paint over the entire outer surfaces of the CW layers was found to have a T_s of 70°C. A similar sample in which two 2.5 × 0.63 cm strip

electrodes were affixed to diagonally opposite planar surfaces of the constant wattage layer (one to each layer) was found to have a T_s in excess of 90°C. It is thus apparent that electrode placement can significantly alter the T_s of constructions in accordance with the present invention.

Example 5.

PTC compositions having the formulation and characteristics shown in Table III were prepared by mill blending, then hydraulically pressed into slabs of 0.025 cm thickness and irradiated to effect cross-linking. Layers heaters were constructed by sandwiching the PTC slab between two CW layers of resistivity 7 ohm-cm prepared from a conductive silicone rubber (R1515) either 0.025 or 0.10 cm thick.

TABLE III

PTC "core" Material Nos.	Marlex 6003* %	Sterling SRFNS** %	dose Mrads.	Resistivity at room temp. of 0.025 cm film ohm-cm
5-1	65	35	12	200
5-2	61	39	12	20
5-3	58	42	12	1.5

* Ethylene-propylene modified rubber

** Carbon black

Electrodes were applied to the outer surfaces of the CW layers. The heater was then placed on and in good thermal contact with a stainless steel block equipped with a thermometer mounted on a temperature controlled hot plate whereby the temperature of the block could be varied. The heater was connected to a voltage source of such a magnitude that it generated about 0.31 watts/sq. cm at about ambient room temperature. The power output of the heater was monitored as the temperature of the metal block was raised. For results see Figure 36.

Figure 37 shows how the power/temperature curve of a heater constructed from a 0.025 cm layer of compositions 5-2 sandwiched between unirradiated 0.025 cm layers of constant wattage carbon black-containing silicone rubber varies with the electrode configuration. Unirradiated silicone constant wattage layers were chosen because their resistance changes very little with temperature and thus the observed changes can be ascribed to geometrical effects and changes in the PTC layer resistance. Three configurations were compared: A) in which the electrodes covered the whole of the upper and lower surfaces of the specimen (i.e. similar to Figure 6 except that two CW layers were employed

and the electrodes were silver paint, not mesh), B) in which opposed silver paint electrodes 0.63 × 2.5 cm were disposed across the upper and lower surfaces (two on each side, the electrodes on each side being spaced 2.5 cm apart), and C) in which one upper and one lower electrode 0.63 × 2.5 cm were arranged 2.5 cm apart in a staggered configuration. The power density/temperature relations for these three configurations as shown in Figure 37 demonstrate that the power/temperature curve can be changed dramatically and unexpectedly by changes in electrode configuration. For many applications the power curve denoted C is preferred and Figure 37 shows that with the compositions and resistance chosen this can be obtained with an alternating or laterally displaced electrode configuration. However, even when the electrodes cover the whole upper and lower surfaces of the CW layer, a curve of the C type can be obtained by appropriate selection of the resistivity of the PTC and CW layer as shown in Figure 36 which indicates that to obtain a type C power curve the room temperature resistivity of the PTC layer should be less than that of the CW layer. However, with alternating, laterally displaced electrodes, type C power curves are

obtained by choosing a PTC layer with a resistivity higher than that of the CW layers.

Example 6.

Heaters were constructed according to configuration A of Example 5 and of the same compositions as in Example 5. However, in certain specimens as shown below, the CW layer was 0.10 cm thick. The heaters were tested while mounted on a stainless steel block as described in Example 5. The block temperature at which the power generated by the heater commenced to drop is shown in

Table IV. The results show that by varying the relative resistances of the PTC and CW layers the drop off temperature and hence T_s can be varied quite significantly. Likewise, the degree of change of power with temperature is significantly affected. As is apparent, resistance for the CW layer is altered by increasing its thickness. In the last two experiments shown in Table IV the size of the PTC core layer was reduced while keeping the CW layers constant. Depending upon the ratio of interface area of the PTC layers to the CW layers, the drop-off temperature can be varied quite significantly.

TABLE IV

Heater PTC "core"	CW layer thickness cm	Power drop-off temperature °C	Power at 23.9°C
			Power at 85°C
5-3	0.025	124	1.31
	0.1	127	1.15
5-2	0.025	110	1.06
	0.1	113	1.06
5-1	0.025	77	1.27
	0.1	80	1.30
5-2*	0.025	93	—
**	0.1	80	—

* PTC layer covers 1/3 of CW layer

** PTC layer covers 1/6 of CW layer

A particular advantage of the thicker, i.e. higher resistance CW layers is that resistance variations in the PTC layer do not have such a great impact on the power output, i.e. there is a higher temperature at which the power output falls, about 3 deg. C in the samples in Table IV. In this way, one can use a highly crystalline, high molecular weight polymer with a highly structured carbon black for the PTC layer (such combinations yield the desired behavior, approximately Type I, but show extreme sensitivity of the resistance obtained to processing and thermal history). By combining such compositions with CW layers of much higher resistivity as may be prepared from blends of low crystallinity or amorphous polymers with blends of low crystallinity or amorphous polymers with medium or high structure blacks (which give resistivities of lower sensitivity to processing or thermal history), one can provide a heater of much greater uniformity (i.e., consistency of output at different regions in its area) reproducibility and functional usefulness than has hitherto been available.

As mentioned hereinabove, an important feature of a functional heater is the ratio of resistance at room temperature to that at the desired operating temperature. This ratio is related to but not identical with the inrush ratio. Furthermore, lower values of this resistance ratio also indicate a closer approach to a Type I resistance characteristic. For the heaters described in this example, an operating range in the neighbourhood of 85°C is considered optimum. PTC to CW volume resistivity ratios (at 24°C) between about 0.1:1 and 20:1 (the exact ratio depending on the relative thickness of the layers) are preferred, those between 1:1 and 10:1 being particularly preferred, to obtain low ratios of resistance at room temperature to that at operating temperature.

Example 7.

PTC materials were made up as in the previous examples having the compositions given in Table V. 0.05 cm thick slabs of these compositions were laminated between two 0.05 cm slabs of a mixture of 20%

Black Pearls carbon black in Silastic 437 (resistivity 400 ohm-cm) and the laminates then irradiated with 12 Mrads of ionizing radiation to effect cross-linking throughout.

TABLE V

Sample Nos.	Marlex 6003 (%)	SRF-NS (%)	PTC layer resistivity ohm-cm	Power curve Type (Fig. 37)
7-1	58	42	100	B
7-2	60	40	240	C but some drop off near room temp.
7-3	62	38	400	Very good C type

This example demonstrates how the shape of the power curve can be modified by the selection of appropriate resistivity ratios for the PTC and CW layers. The power temperature relation is, of course, equatable with the temperature resistance relationship according to the formula

$$P = I^2 R \text{ or } P = \frac{E^2}{R}$$

The curve labelled C is close to the ideal expected from a heater having a resistance temperature characteristic of Type I.

Example 8.

Two 30 cm long sections of flat strip heater constructed in accordance with U.S. Patent Number 3,861,029 and having a PTC core of composition similar to that used in Example 1, and shaped like Figure 5 (0.8 cm wide) were affixed to an aluminium block maintained at 18°C by circulating water. The other side of each of the heater sections was painted with temperature indicating paint. The voltage applied to the sections was varied so as slowly to increase their power output. Attempts to operate either of these sections (which had different initial resistances) at power levels greater than about 0.08 watts per square cm resulted in hotlining.

Example 9.

A layered heater, was constructed in which a PTC layer (0.075 cm thick) had the composition 47% Marlex 6003, 5% Epsyn 5508 (ethylene-propylenediene modified rubber) and 48% Sterling SRF-NS (carbon black). Two CW layers 0.15 cm thick having the composition 60% Elvax 250 (ethylene-vinyl acetate copolymer) and 40% Cabot XC72 (carbon black) and having embedded therein flattened wire braid electrodes 0.95 cm wide and 0.95 cm apart (three in all to each CW layer) were applied to each side of the PTC layer so that the electrodes were opposed to

one another i.e., similarly to Figure 11 except that the electrodes were braided rather than strips. The dimensions of the heater were 7.5 cm by 15 cm with the electrodes running along the long dimension with electrodes of opposite polarity extending beyond the polymeric layers at opposite ends of the heater. The layers were carefully laminated together and the article then heated at 200°C for 10 minutes to anneal out any stress, then cooled and irradiated to 12 Mrads dose using Cobalt-60 gamma rays whilst enclosed in a container containing nitrogen. The heater was sandwiched between 0.025 cm thick insulating layers comprising crosslinked low density polyethylene and pressed firmly to a cooled aluminium block as in the previous example and temperature indicating paint applied to the upper surface of the heater. Electrodes of opposite polarity were connected to a 12 volt battery. The heater consumed more than 70 amps while warming up, i.e., more than 5.4 watts/cm². For a period of several minutes the heater stabilized at a current of over 20 amps, i.e. greater than 1.55 watts/cm². Finally, the aluminium block started to warm up despite the applied cooling and the heater PTC layer warmed up to its T_s (about 120°C). The temperature indicating paint melted during this last stage starting in the center and proceeding rapidly and smoothly to the edges. In this final condition the heater maintained itself at a temperature very close to its T_s and was consuming about 10 amps, i.e., a heat output of about 0.7 watts/cm². When the aluminium block was replaced by a slab of thermally insulating material, the current fell to much less than one amp, i.e., less than 0.07 watts/cm² at a heater temperature still very close to T_s, the whole surface of the heater being at about this temperature. It is thus apparent that a heater in accordance with the present invention can operate at high power outputs at T_s temperatures well in excess of 100°C without hotlining.

It will be appreciated that references herein

to a PTC layer being or becoming substantially non-conducting are relative to the electrical properties of the CW layer. It is not appropriate to give absolute values for such properties since these depend, among other factors, on the relative configurations of the various layers, but in a simple laminate as illustrated for example in Figure 23, as soon as the PTC layer exceeds its anomaly temperature the current through the CW layer is many times that through the PTC layer in any portion of the laminate where the two layers are electrically in parallel.

Advantageously, where the two types of layers are electrically in parallel, the proportion of current passing through a CW layer is at least 10, preferably at least 25 times that passing through a PTC layer at temperatures above its anomaly temperature, although in certain cases, for example if the article is in proximity to a relatively large heat sink, lower ratios, of 5 or less, may be adequate.

WHAT WE CLAIM IS:—

1. An article comprising at least one first electrically resistive layer and at least one second electrically resistive layer at least a part of a surface of a first layer being contiguous with at least part of a surface of a second layer along an interface which provides direct electrical and thermal contact between them, the first layer exhibiting a positive temperature coefficient (hereinafter PTC as hereinbefore defined) of resistance and having an anomaly temperature (T_a as hereinbefore defined), above which it is substantially non-conducting, and the second layer having a substantially constant resistance (hereinafter CW as hereinbefore defined) below the anomaly temperature (T_s) of the first layer.

2. An article as claimed in claim 1, comprising a laminate of the said first and second layers, and at least a pair of electrodes so positioned that, when there is a potential difference between the two electrodes, at ambient temperatures current will pass between the electrodes through at least a portion of at least one first layer and of at least one second layer.

3. A self-regulating heating article comprising a first layer of material which exhibits a positive temperature coefficient of resistance (PTC as hereinbefore defined) and a second layer of constant resistance (CW) material as hereinbefore defined, at least a part of a surface of the first layer being contiguous with at least a part of a surface of the second layer along an interface which provides direct electrical and thermal contact between them and said first layer being connectable to an electric power input source such that current flow is through at least a portion of said first layer and through at least a portion of said second layer, the article being such that at the higher of the temperature at which the resistance

of said first layer exceeds the resistance of said second layer and the anomaly temperature (T_a , as hereinbefore defined) of said first layer current flow predominantly follows a path the length of which through the first layer is as short as possible.

4. An article as claimed in claim 2 or claim 3, wherein the length of path through the first layer does not exceed the thickness thereof by more than 50%.

5. An article as claimed in any one of claims 1 to 4, wherein the PTC layer has two substantially planar surfaces and has a CW layer at least partially contiguous with each of the planar surface.

6. An article as claimed in any one of claims 1 to 5, wherein the CW layer serves, or the CW layers serve, as electrodes.

7. An article as claimed in any one of claims 2 to 5, which comprises, or as claimed in claim 1 or 6 which also comprises, a conductive fiber electrode.

8. An article as claimed in any one of claims, 1, 3, 4 or 5, which comprises, or as claimed in claims 2, 6 or 7, which also comprises, a metal electrode.

9. An article as claimed in claim 8, wherein the metal electrode is a fabric, braid or grid and/or the material of the electrodes is in the form of a wire, strip or sheet.

10. An article as claimed in any one of claims 1 to 9, wherein at least one electrode is embedded in a CW layer.

11. An article as claimed in any one of claims 1 to 10, wherein at least one electrode is positioned on a face of a CW layer remote from the face in contact with a PTC layer.

12. An article as claimed in any one of claims 1 to 11, wherein at least one electrode is embedded in a PTC layer.

13. An article as claimed in any one of Claims 1 to 12, wherein the first layer and the second layer are each disposed around an electrode or electrodes.

14. An article as claimed in any one of claims 1 to 13, wherein at least one electrode is positioned at an interface between a CW layer and a PTC layer.

15. An article as claimed in any one of claims 1 to 14 which comprises at least one set of electrodes connected together in parallel.

16. An article as claimed in claim 15 which comprises two sets of electrodes, one set being positioned in a plane parallel to the plane of the other set.

17. An article as claimed in claim 16, wherein the electrodes in one set are transverse to the electrodes in the other set.

18. An article as claimed in claim 16, wherein the electrodes of one set are positioned in lines parallel to those of the other set.

19. An article as claimed in claim 18, wherein the electrodes of one set are opposite spaces between electrodes in the other set.

20. An article as claimed in any one of

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to a PTC layer being or becoming substantially non-conducting are relative to the electrical properties of the CW layer. It is not appropriate to give absolute values for such properties since these depend, among other factors, on the relative configurations of the various layers, but in a simple laminate as illustrated for example in Figure 23, as soon as the PTC layer exceeds its anomaly temperature the current through the CW layer is many times that through the PTC layer in any portion of the laminate where the two layers are electrically in parallel.

Advantageously, where the two types of layers are electrically in parallel, the proportion of current passing through a CW layer is at least 10, preferably at least 25 times that passing through a PTC layer at temperatures above its anomaly temperature, although in certain cases, for example if the article is in proximity to a relatively large heat sink, lower ratios, of 5 or less, may be adequate.

WHAT WE CLAIM IS:—

1. An article comprising at least one first electrically resistive layer and at least one second electrically resistive layer at least a part of a surface of a first layer being contiguous with at least part of a surface of a second layer along an interface which provides direct electrical and thermal contact between them, the first layer exhibiting a positive temperature coefficient (hereinafter PTC as hereinbefore defined) of resistance and having an anomaly temperature (T_a as hereinbefore defined), above which it is substantially non-conducting, and the second layer having a substantially constant resistance (hereinafter CW as hereinbefore defined) below the anomaly temperature (T_a) of the first layer.

2. An article as claimed in claim 1, comprising a laminate of the said first and second layers, and at least a pair of electrodes so positioned that, when there is a potential difference between the two electrodes, at ambient temperatures current will pass between the electrodes through at least a portion of at least one first layer and of at least one second layer.

3. A self-regulating heating article comprising a first layer of material which exhibits a positive temperature coefficient of resistance (PTC as hereinbefore defined) and a second layer of constant resistance (CW) material as hereinbefore defined, at least a part of a surface of the first layer being contiguous with at least a part of a surface of the second layer along an interface which provides direct electrical and thermal contact between them and said first layer being connectable to an electric power input source such that current flow is through at least a portion of said first layer and through at least a portion of said second layer, the article being such that at the higher of the temperature at which the resistance

of said first layer exceeds the resistance of said second layer and the anomaly temperature (T_a as hereinbefore defined) of said first layer current flow predominantly follows a path the length of which through the first layer is as short as possible.

4. An article as claimed in claim 2 or claim 3, wherein the length of path through the first layer does not exceed the thickness thereof by more than 50%.

5. An article as claimed in any one of claims 1 to 4, wherein the PTC layer has two substantially planar surfaces and has a CW layer at least partially contiguous with each of the planar surface.

6. An article as claimed in any one of claims 1 to 5, wherein the CW layer serves, or the CW layers serve, as electrodes.

7. An article as claimed in any one of claims 2 to 5, which comprises, or as claimed in claim 1 or 6 which also comprises, a conductive fiber electrode.

8. An article as claimed in any one of claims, 1, 3, 4 or 5, which comprises, or as claimed in claims 2, 6 or 7, which also comprises, a metal electrode.

9. An article as claimed in claim 8, wherein the metal electrode is a fabric, braid or grid and/or the material of the electrodes is in the form of a wire, strip or sheet.

10. An article as claimed in any one of claims 1 to 9, wherein at least one electrode is embedded in a CW layer.

11. An article as claimed in any one of claims 1 to 10, wherein at least one electrode is positioned on a face of a CW layer remote from the face in contact with a PTC layer.

12. An article as claimed in any one of claims 1 to 11, wherein at least one electrode is embedded in a PTC layer.

13. An article as claimed in any one of Claims 1 to 12, wherein the first layer and the second layer are each disposed around an electrode or electrodes.

14. An article as claimed in any one of claims 1 to 13, wherein at least one electrode is positioned at an interface between a CW layer and a PTC layer.

15. An article as claimed in any one of claims 1 to 14 which comprises at least one set of electrodes connected together in parallel.

16. An article as claimed in claim 15 which comprises two sets of electrodes, one set being positioned in a plane parallel to the plane of the other set.

17. An article as claimed in claim 16, wherein the electrodes in one set are transverse to the electrodes in the other set.

18. An article as claimed in claim 16, wherein the electrodes of one set are positioned in lines parallel to those of the other set.

19. An article as claimed in claim 18, wherein the electrodes of one set are opposite spaces between electrodes in the other set.

20. An article as claimed in any one of



claims 1 to 19 which comprises a layer of a CW material sandwiched between two layers of PTC material.

21. An article as claimed in any one of claims 1 to 20, which comprises a layer of a PTC material sandwiched between two layers of CW material.

22. An article as claimed in any one of claims 1 to 21, wherein the first layer is surrounded by the second, or wherein the second layer is surrounded by the first.

23. An article as claimed in claim 22, wherein the layers are coaxial.

24. An article as claimed in claim 20 or claim 21, wherein the article is of substantially rectangular cross-section and the first or second material forms a diagonal layer, the second or first material forming the remainder of the cross-section.

25. An article as claimed in any one of claims 1 to 19, wherein the article is of substantially rectangular cross-section, the boundary between the first and second materials being a diagonal of the rectangle.

26. An article is claimed in any one of claims 1 to 25, which is covered at least partially by an insulating layer.

27. An article as claimed in any one of claims 1 to 26, which also comprises a sealant or adhesive on at least one surface, the sealant or adhesive being heat-activatable at a temperature within the operating range of the article.

28. An article as claimed in claim 27, wherein the CW layer is a sealant or adhesive.

29. An article as claimed in any one of claims 1 to 28, wherein the first layer comprises a polymeric composition.

30. An article as claimed in any one of claims 1 to 29, wherein the second layer comprises a polymeric composition.

31. An article as claimed in claim 29 or claim 30, wherein the polymeric material has dispersed therein carbon black.

32. An article as claimed in any one of claims 1 to 30, wherein the second layer is polymeric and has dispersed therein carbon black and conductive fibers or fibrils.

33. An article as claimed in any one of claims 1 to 32 which is heat recoverable.

34. An article is claimed in claim 33, wherein the article is heat-recoverable at a temperature within the operating range of the article as a heater.

35. An article as claimed in claim 33 or claim 34 which comprises an electrical insulating layer, which layer is heat-recoverable.

36. An article as claimed in any one of claims 1 to 30, wherein the first layer comprises barium titanate.

37. An article as claimed in any one of claims 1 to 36 which is an elongate flexible strip.

38. An article as claimed in any one of

claims 1 to 37 which has an effective T_s (as hereinbefore defined) above 90°C , which is greater than the T_s of the first layer.

39. An article as claimed in claim 38, wherein the first layer comprises a polymer and the effective T_s is greater than its melting point.

40. An article as claimed in claim 39, wherein the said polymer is cross-linked.

41. An article as claimed in any one of claims 1 to 40, wherein the resistivity ratio of the first and second layers is in the ratio of from 0.1:1 to 20.0:1.0 at 24°C .

42. An article as claimed in claim 1, substantially as hereinbefore described with reference to, and as illustrated by, any one of Figs. 6 to 13, or Figs. 14 and 15 of the accompanying drawings.

43. An article as claimed in claim 1, substantially as hereinbefore described with reference to, and as illustrated by, any one of Figs. 16 to 35 of the accompanying drawings.

44. An article as claimed in claim 1, substantially as described with reference to any one of Examples 1 to 4 herein.

45. An article as claimed in claim 1, substantially as described with reference to any one of Examples 5 to 7 and 9 herein.

46. A method of covering a substrate which comprises applying an article, as claimed in any preceding claim, that is heat-recoverable over a substrate and heating the article by connecting it to an electrical power source to cause recovery thereof to cover the substrate.

47. A method of heating a substrate which comprises positioning an article as claimed in any one of claims 1 to 45, which has electrodes, in thermal contact with the substrate and energizing the article by connecting the electrodes to an electrical power source.

48. A method as claimed in claim 46 or claim 47, wherein the substrate forms one electrode.

49. A method of recovering an article as claimed in any one of claims 1 to 45 that is heat-recoverable and which has electrodes, which comprises connecting the electrodes to an electrical power source for a time sufficient to effect heat-recovery.

50. A substrate whenever covered by an article as claimed in any one of claims 1 to 45 or by a method as claimed in either of claims 46 or 47.

51. An article as claimed in any one of claims 1 to 45, wherein the CW material has a resistivity of at least 1 ohm-cm. at 25°C .

52. An article as claimed in any one of claims 1 to 45 or 51, wherein the CW material changes resistivity, at between $\pm 5\%$ per deg. C.

53. A process for supplying heat and automatically controlling the maximum temperature reached which comprises passing electrical current through an article which comprises a

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first electrically resistive layer and a second electrically resistive layer, at least a part of a surface of the first layer being contiguous with at least a part of a surface of the second layer along an interface which provides direct electrical and thermal contact between the layers, the first layer being composed of a material which exhibits a positive temperature coefficient (hereinafter PTC as hereinbefore defined) of resistance and having an anomaly temperature (T_s as hereinbefore defined) above which it is substantially non-conducting and the second layer being composed of a constant resistance (CW as hereinbefore defined) material, the current passing sequentially through the two layers, the resistance of the first layer being greater than the resistance of the second layer, and the predominant current path through the first layer being as short as possible at the higher of the temperature at which the resistance of the first layer exceeds the resistance of the second layer and the anomaly temperature (T_s).

54. A process as claimed in claim 53 wherein the current path through the first layer is predominantly perpendicular to the interface between the first and second layers.

55. A process as claimed in claim 53 or claim 54, wherein the article is as specified in any one of claims 2 to 45, 51, or 52.

56. A process as claimed in any one of claims 53 to 55, wherein the article is generating at least 1.5 watts per square inch.

57. A process as claimed in any one of claims 53 to 56, wherein the PTC material is at a temperature in excess of 100°C.

58. A process as claimed in any one of claims 53 to 57, wherein equilibrium is maintained between the heat supplied and the heat lost.

59. An article as claimed in any one of claims 1 to 45, and 51 through which an electric current is passing.

60. An article according to Claim 59, wherein the temperature of the article produced solely by passage of the electric current is higher than the T_s of the material of the PTC layer.

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