

PATENT SPECIFICATION (11)

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- (21) Application No. 51229/76 (22) Filed 8 Dec. 1976 (19)
 (31) Convention Application No. 638 440 (32) Filed 8 Dec. 1975 in
 (33) United States of America (US)
 (44) Complete Specification published 11 June 1980
 (51) INT. CL.³ H05B 3/34 3/10
 (52) Index at acceptance

H5H 105 107 113 140 142 144 155 170 176 211 224 230
 231 232 233 250 251 260 AF BA1 BA2 CA

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(54) EXPANSIBLE HEATER

(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 heating elements comprising conductive polymers; and to articles in which such heating elements form components.

It is well known that polymers can be made electrically conductive by dispersing therein suitable amounts of finely divided conductive fillers. It is also well known that certain polymeric articles can be rendered heat-recoverable. It has been proposed (see British Patent No. 1,265,194) to make a heat-recoverable article comprising a first heat-recoverable member composed of a conductive polymer and a second heat-recoverable member which is not electrically conductive, and to cause such an article to recover by passing an electric current through the first member. However, our researches have shown that such articles suffer from certain disadvantages. In particular we have found that the electrical characteristics of the conductive polymer member are liable to change excessively if any of the dimensions of the member are changed by more than 30%, which is less than is generally desirable for heat-recoverable articles. Furthermore, the presence of the conductive polymer layer increases the force needed to deform the article and can adversely affect recovery. We have also found that if the current is passed from end to end of the conductive polymer member, as suggested by British Patent No. 1,265,194, the member is often not heated as uniformly as is desirable to achieve satisfactory shrinkage and to avoid local over-heating.

We have now discovered that if a laminar conductive polymer member is sandwiched between a pair of laminar flexible electrodes, and suitable apertures are formed in the resulting laminate, it is possible to obtain an easily expansible and/or contractable product having greatly improved electrical characteristics.

Thus in its first aspect, the invention provides a heating element which comprises:

(A) a laminar member composed of a material which comprises an organic polymer and electrically conductive particles dispersed in the polymer in amount sufficient to render the member electrically conductive, and which preferably has a resistivity greater than 10 ohm.cm at room temperature; and

(B) a pair of laminar flexible electrodes which are connected (directly or indirectly) to opposite faces of said laminar member and are capable of being connected to an external source of power to cause current to pass through said laminar member;

said laminar member and laminar electrodes having a plurality of elongate, overlapping apertures through the thickness thereof, the apertures being of a size, shape and distribution which permit at least one of the dimensions of the element in the plane thereof to be changed without complete rupture of the electrode at any point (as hereinafter defined), the dimensional change being accommodated by a change in the shape of the apertures.

The term "without complete rupture of the electrode at any point" means that each electrode maintains an electrical pathway completely surrounding each aperture; thus the electrode may tear partially but not completely at any point.

The apertures in the heating element generally are (or in the case of an element which has been deformed in the plane thereof, preferably correspond to) apertures

which are capable of changing in shape so as to accommodate a change in a planar dimension of the element at the melting point of the polymer, without complete rupture of the electrode at any point, of at least 30%, often at least 50%, e.g. at least 70%, especially at least 100%, and for some purposes at least 250%. However, it is to be understood that if the element is deformed by an amount greater than can readily be accommodated by a change in the shape of the apertures, the possibility of some stretching or contraction of the element material itself is not excluded.

The "melting point of the polymer" referred to above is for crystalline thermoplastic polymers the temperature at which melting of crystalline material begins, and for other polymers, e.g. elastomers and non-crystalline thermoplastic polymers, is the softening point of the polymer.

These heating elements are useful in situations in which it is desirable to have a heater which can readily change at least one of its planar dimensions. In many cases it is possible to design the heating element so that even when it is deformed by a relatively high percentage, its resistance does not increase by more than 20%, which is a very valuable property.

The term "apertures" is used herein to include slits which open up into, for example, diamond-shaped openings when the element is extended. In general it will be convenient for the apertures in the undeformed element to be such that substantial planar deformation of the element is possible only by stretching, i.e. the element is expansible; and the invention will be chiefly so described. However, the invention includes, for example, elements which in the undeformed state are expansible or contractable in one direction, and elements having apertures such that the element can be stretched simultaneously in two directions.

The choice of apertures will be dependent on the degree of expandability required and the ductility of the electrodes and member A. The apertures must be elongate and must overlap each other, but a wide variety of apertures fulfilling these requirements can be used. Thus the apertures may be regular or irregular and may for example be straight or wave-form slits or slots, oval holes or diamond-shaped holes. It will generally be convenient that the apertures should be regularly spaced and of the same size and shape. It is generally desirable that the apertures should be such that the element responds symmetrically through the thickness thereof to extensions in the plane of the element, in order to avoid buckling of the element. We have obtained

good results with elements in which the distance between the edges of adjacent apertures is 1/10 to 1/2 inch (0.25 to 1.25 cm). Preferably the apertures are a plurality of identical straight slits in parallel equally-spaced rows with the slits in adjacent rows overlapping each other; the slits are preferably at least 1/2 inch (1.25 cm) long, especially 5 to 20 times the distance between adjacent rows of slits. Elements which can be stretched to at least three times their original length can be obtained in this way.

In a preferred embodiment, the member A is composed of a material which is one of the small proportion of conductive polymers which exhibits what is known as PTC (positive temperature coefficient) behavior, i.e. a rapid increase in resistivity at a particular temperature or over a particular temperature range. The term "switching temperature" (usually abbreviated to T_s) is used to denote the temperature at which the rapid increase takes place. When the increase takes place over a temperature range (as is often the case) then T_s can conveniently be designated as the temperature at which extensions of the substantially straight portions of the plot of the log of the resistance against the temperature (above and below the range) cross.

PTC materials used in member A will generally have a T_s above 50°C, often above 100°C, and a resistivity at temperatures below T_s from about 25 to about 10⁵ ohm.cm. It is also desirable that the increase in resistance above T_s should be sufficiently high that member A is effectively converted from an electrical conductor to an electrical insulator by a relatively limited increase in temperature. A convenient expression of this requirement is that the material should have an R_{14} value of at least 2.5 or an R_{100} value of at least 10, and preferably an R_{30} value of at least 6, where R_{14} is the ratio of the resistivities at the end and beginning of the 14°C range showing the sharpest increase in resistivity; R_{100} is the ratio of the resistivities at the end and beginning of the 100°C range showing the sharpest increase in resistivity; and R_{30} is the ratio of the resistivities at the end and beginning of the 30°C range showing the sharpest increase in resistivity.

For a general survey of conductive polymers, reference may be made to "Conductive Rubbers and Plastics" by R. H. Norman, published in 1970 by Elsevier Publishing Company. PTC compositions are disclosed in Polymer Engineering and Science, November 1973, 13 No. 6, pages 462-468, and United States Patents Nos. 2,978,665; 3,243,753; 3,412,358; 3,591,526; 3,793,716; 3,823,217; and 3,914,363. For details of recent developments in this field, reference may be made to British Patent 130

Specifications Nos. 1,528,622, 1,529,353, 1,529,354, 1,529,355, 1,529,356 and 32,275/76; and 32,378/76 (Serial Nos. 1,562,085 and 1,562,086).

5 The use of a PTC material for member A prevents the member from being electrically heated to a temperature above its T_s . The T_s of PTC materials is usually very much dependent upon the tensile stress thereof, and in the absence of the apertures, 10 the T_s of member A would alter considerably when its planar dimensions were changed. However, we have found that, although parts of member A are under 15 considerable stress, the overall T_s of member A is not substantially changed by expansion or contraction.

The electrodes will usually have a resistivity of less than 10 ohm.cm, preferably 20 less than 1 ohm.cm, and may be of any suitable material, for example of metal or a highly conductive polymer, and may comprise peripheral bussing sections which do not contain apertures and which run at 25 right angles to the direction of major dimensional change. Metals are generally preferred because they have high conductivity coupled with elongations which are generally high enough for most uses; metals 30 having a ductility at least as high as aluminium are preferred. The tendency of metal foil electrodes to tear can be decreased (and at the same time flexibility increased) by corrugating the foil, for example by an amount which shortens it by 35 about 15%. Suitable metals include copper, lead and aluminium. Each of the electrodes will generally be in a plane substantially parallel to the plane of member A.

40 One of the problems which we have found can arise, especially when using metal electrodes and/or when the apertures are diamond-shaped, is that short circuits can occur between electrodes of opposite 45 polarity at the edges of the element, or if the element is partially broken. This problem can be alleviated by coating the exposed surfaces of the electrodes with an insulating material; for example a polymer, 50 especially a cross-linked polymer, which has a softening temperature above the highest temperature likely to be reached by the electrode. It is desirable that the edges as well as the planar surfaces of the electrodes 55 should be coated, and slit apertures should therefore be opened out by expanding the element prior to coating. Suitable coating techniques include electroplating, electrostatic spraying, and dipping into a suitable 60 powdered insulator, followed by curing of the coating by heat. An alternative way of reducing the likelihood of shorting is to use apertures such as slots or ovals which have substantial width even when the element 65 is completely contracted. Another

solution is to use two electrodes which are coextensive with member A and which are composed of a material which has a resistivity of less than 10 ohm.cm at 25°C and which comprises an organic polymer and electrically conductive particles dispersed therein; such electrodes are less likely to short than a metal electrode. If necessary or desirable to provide satisfactory 70 electrical characteristics when using such electrodes, there may also be used a pair of laminar flexible metal electrodes which 75 contact the coextensive conductive polymer electrodes on the faces thereof remote from member A in selected areas which do not overlap; such an arrangement also gives rise to changed electrical characteristics because of non-uniform current flow. Areas are said to overlap if a straight line 80 perpendicular to the plane of the element intersects both of them. 85

Generally speaking the electrodes will be coextensive with member A. However, this is not essential provided that in use 90 current is passed through substantially the whole of the member A so as to provide satisfactory heating thereof.

Particularly useful heating elements are those in which member A exhibits PTC characteristics and which also comprise at 95 least one intermediate layer which (a) exhibits constant wattage (CW) behaviour (as hereinafter defined) at temperatures below the T_s of member A; (b) is composed of a material which comprises an organic 100 polymer and electrically conductive particles dispersed in the polymer in amount sufficient to render the member electrically conductive; (c) has a resistivity greater than 10 ohm.cm; and (d) is interposed between the 105 member A and an electrode. Preferably there is one such intermediate layer each side of member A. The term "constant wattage behaviour" means that the layer undergoes an increase in resistance of less than six-fold in any 30°C range below the T_s of member A and preferably between room temperature and T_s of the member A.

It is preferred that the constant wattage 115 layers have resistances at room temperature which are higher than the resistance of member A, in order that they can control the level of current inrush when the heating element is initially connected to a power supply. It is also preferred that the intermediate CW layers should exhibit PTC behaviour at temperatures above the T_s of member A, i.e. with a higher T_s . This is useful in preventing the overheating of the intermediate layer which would otherwise 125 take place if the electrode was completely ruptured at any point, thus causing current to pass through the intermediate layer to bridge the rupture; this can cause severe 130 overheating if the intermediate layer does

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not shut itself off at some suitable temperature.

The conductive particles in member A and any intermediate layers are preferably of carbon black, particularly when PTC characteristics are needed. In electrode layers comprising conductive polymers, the conductive particles are preferably of carbon black or a metal. The particles may be of any shape, including fibres. Examples of suitable compositions are to be found in the prior publications and patent specifications referred to above. The PTC compositions are preferably based on crystalline polymers, which compositions have a T_g at or near the crystalline melting point of the polymer, which may be cross-linked to give the composition improved stability about T_g . A preferred composition for member A is a mixture comprising high density polyethylene (45% by weight) an ethylene-propylene rubber (5% by weight) and carbon black (50% by weight), which has a T_g of about 120°C. A preferred composition for a constant wattage intermediate layer comprises an ethylene/vinyl acetate copolymer (61% by weight) and carbon black (39% by weight).

In formulating the compositions for the different layers, it is, of course, necessary to consider the physical, as well as the electrical, properties thereof, for example flexibility, adhesion to adjacent layers and resistance to flow at operating temperatures. Having regard to the disclosure herein, the selection of suitable compositions will present no difficulties to those skilled in the art. Preferably the element is of symmetrical construction.

The heating elements of the invention can be prepared by assembling the various layers; bonding them together with the aid of heat and pressure; and then creating the apertures in the bonded assembly. Suitable conductive adhesives, e.g. carbon-loaded hot melt adhesives, can be placed between the layers, especially between metal electrodes and adjacent polymeric layers, to ensure adequate adhesion between the layers. A suitable adhesive comprises about 65% by weight of an ethylene/acrylic acid copolymer and about 35% carbon.

When it is desired that the polymer in member A and in any other polymeric layers should be cross-linked, as may be preferred, the polymers initially employed must, of course be cross-linkable. Cross-linking is preferably carried out after the bonding step but before the apertures are created, for example by use of ionising radiation of sufficient dosage, e.g. 5 to 20 megarads. Alternatively a chemical cross-linking agent can be incorporated in the polymers, and cross-linking effected during the bonding step, or in a separate heating

step after the bonding step but before the apertures are created.

Slits are in general easier to create in the element than openings such as slots or ovals. Slits can be simply cut by means of a sharp blade, for example a plurality of blades operating in staggered formation so that in effect the slits are made one row at a time; a stripper pad may be used to prevent the blade from tearing the element as it is withdrawn. Openings, on the other hand, must be punched out.

The heating elements of the invention are particularly useful as components of articles which comprise a heat-responsive (as hereinafter defined) sheet material having the heating element secured to one face. The heating element may be in direct contact with the sheet material, for example secured thereto by an adhesive, or may be separated therefrom by an intermediate layer provided that there is adequate heat transfer between the heating element and the sheet material. The article is preferably flexible, at least at the temperature at which the sheet material becomes responsive.

The term "heat-responsive" is used herein to mean that when the sheet material is heated to a suitable temperature it either (a) undergoes a spontaneous change in at least one dimension in the plane thereof; and/or (b) undergoes some other change, e.g. it softens (including flows), which substantially reduces the external forces (e.g. manual forces) required to change at least one dimension of the sheet material in the plane thereof. The sheet material preferably comprises an organic polymer, for example a polymeric film which is heat-recoverable or can be rendered heat-recoverable, an adhesive (for example a hot-melt or heat-activatable adhesive) or a mastic.

It will, of course, be apparent that in such articles the heating element should be placed adjacent the sheet material in such a way that it is capable of changing its dimensions in the required way when the article is heated.

The articles of the invention will generally have one heater element and one sheet material, but may contain more than one element and/or more than one sheet material; for example they may comprise an element sandwiched between two sheet materials or one sheet material sandwiched between two elements.

When the sheet material is a polymeric film which is heat-recoverable or can be rendered heat-recoverable, it preferably comprises a crystalline cross-linked polymer. Suitable polymers for heat-recoverable sheet materials are well known in the art (see for example U.S. Patent No. 3,086,242) and include polymers of one or more olefins and/or one or more ethyleni-

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cally, unsaturated monomers containing polar groups.

Articles comprising a heat-recoverable polymeric film can be made by deforming an article which comprises (a) a film which can be rendered heat-recoverable and (b), attached to one face of the film, a heating element (preferably one which has not been substantially deformed in the plane thereof), the deformation being carried out at a temperature above the crystalline melting point of the polymer in the sheet material, followed by cooling the article while it is in the deformed state. Suitable techniques are well known in the art (see for example U.S. Patent No. 3,086,242). Such articles can also be made by assembling a heat-recoverable sheet material and a heating element, preferably one that has been deformed in the plane thereof in the direction opposite to the direction of heat recovery of the sheet material.

As noted above, the sheet material will generally be secured to the heating element by means of an adhesive. The adhesive need not be a very powerful one since the dimensions of the heating element are easily changed. This is an important advantage over similar articles comprising a heating element without apertures, which generally require a powerful adhesive to ensure that the element satisfactorily follows dimensional change of the sheet material. The adhesive is preferably one which at the operating temperature, e.g. the recovery temperature of the article, permits slippage between the heating element and the sheet material, but does not flow into the apertures of the heating element and thus interfere with dimensional change thereof. Suitable adhesives are, for example, included in the disclosure of British Specification No. 1,440,810, and other adhesives containing labile ionic bonds. Preferably the adhesive is one whose Vicat melting point is below the operating temperature and whose ring and ball softening point is below the operating temperature. Particularly preferred adhesives are thixotropic at the operating temperature, e.g. the recovery temperature.

The sheet material and heating element can, for example, be secured to each other by assembling them with a layer of a suitable hot melt or heat-activatable adhesive between them, and heating the assembly under pressure, e.g. from a pair of rollers. If the sheet material has been rendered heat-recoverable prior to assembly and preparation of the assembly involves use of a temperature above the recovery temperature, then steps must be taken to prevent complete recovery of the sheet material.

When the heating element provides one face of the article, it may be desirable that

at least some of the apertures therein contain a composition which flows at the operating temperature of the article, for example a solder or a mastic or a hot melt adhesive. This is particularly useful when the article is heat-recoverable, for example a heat-shrinkable sleeve having the heating element on the inside, and recovery of the article brings the heating element into contact with a substrate to be covered and thus causes the composition to be squeezed from the apertures. Presence of the composition can also improve heat transfer from the heater element to the sheet material.

The articles of the invention may be of any suitable shape, and can be part of a larger object. Thus the invention includes objects having one or more sections which are articles according to the invention. Particular useful articles are sleeves, i.e. hollow articles of closed cross-section having at least one open end, e.g. tubular articles of circular or other cross-section, especially such sleeves which contract to a smaller diameter on heating. When the heating element is on the inside, such sleeves can conveniently be made by expanding a heating element sleeve by placing it over a mandrel, surrounding the exterior of the element with a suitable adhesive (e.g. a preformed tube thereof); surrounding the exterior of the adhesive with a sleeve of sheet material which is heat-shrinkable to a diameter less than the external diameter of the element; heating the assembly to cause the sleeve to shrink down and bond to the element via the adhesive; cooling the assembly; and removing the mandrel. When the heating element is on the outside, such sleeves can conveniently be made by assembling a potentially heat-recoverable sleeve inside a heating element with an intermediate layer of adhesive; heating the assembly and pneumatically expanding it against an external die; and cooling the assembly while maintaining the assembly in expanded condition.

A tubular heating element can conveniently be made by joining opposite edges of a sheet material through a strip of insulating material, e.g. of an organic polymer, to which the edges can be bonded by a suitable adhesive.

A particularly valuable use of the heating elements of the invention is in the splice cases described in our copending Application No. 51230/76.

The article of the invention may be employed in useful processes by connecting the electrodes to an external source of power which causes current to pass through the laminar member A and to provide at least part of the heat needed to heat the sheet material to a temperature at which it becomes responsive; and allowing or forcing

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the sheet material at said temperature to undergo dimensional change in the plane thereof. The process is particularly useful when a substrate is covered by positioning the article adjacent to the substrate and connecting the electrodes so that the heated sheet material undergoes dimensional change such that the article conforms to the surface of the substrate. If desired the article can surround the substrate or can cooperate with another covering member to surround the substrate. The external source of power used in these processes is conveniently DC of about 12 volts from a battery or AC of about 115 or about 220 volts from a mains source. It may be desirable to continue heating the article (by continuing to pass current through the heating element or otherwise) after the planar dimensions thereof have changed, for example to heat a substrate brought into contact therewith to ensure adequate adhesion between the article and the substrate, by heat-activatable adhesive or otherwise.

The invention is illustrated in the accompanying drawing, in which the Figure is an isometric view of a part of a heating element of the invention. The element comprises a layer 12 composed of a conductive polymer which exhibits PTC behavior. Adherent to layer 12 are constant wattage layers 13a and 13b which are composed of a conductive polymer and preferably exhibit PTC behavior with a T_s higher than layer 12. Layer 13a and 13b are secured to corrugated metal foil layers 15a and 15b via layers of adhesive 14a and 14b, to form a laminated sheet. There are a plurality of apertures in the form of slits formed in parallel staggered rows 17. The slits, which extend through the sheet from one surface to the other, will generally be somewhat longer than is shown in the drawing. The edge portions of the sheet parallel to the slits do not contain slits. When these edge portions are separated, the apertures become diamond-shaped.

The invention is further illustrated by the following Example in which the percentages are by weight.

Example

Laminar members of the compositions and thicknesses shown were assembled in the order shown:

(1) Lead foil electrode; 4 mils (0.01 cm) thick.

(2) A mixture of an ethylene/acrylic acid copolymer (65%) and carbon black (35%); 5 mils (0.0125 cm) thick.

(3) A mixture of an ethylene/vinyl acetate copolymer (61%) and carbon black (39%); 10 mils (0.025 cm) thick.

(4) A mixture of high density polyethylene (45%), an ethylene/propylene rubber (5%) and carbon black (50%); 20 mils (0.051 cm) thick.

(5) as laminar member (3).

(6) as laminar member (2).

(7) as laminar member (1).

These layers were bonded together with heat and pressure and then exposed to 6 megarads of ionising radiation. An expansible heating element was made by creating in the bonded assembly slits 0.5 inch (1.25 cm) long in parallel but offset rows 0.025 inch (0.06 cm) apart; the slits in a row were spaced apart 0.10 inch (0.25 cm). A heat-recoverable polymeric sheet was obtained as follows. A sheet 0.8 inch (0.2 cm) thick was extruded from a mixture of an ethylene/ethyl acrylate copolymer (88.4%) (DPD 6181 from Union Carbide), a dispersion of 1 part of carbon black in 3 parts of an ethylene/vinyl acetate copolymer (9%) (Colorant CC 004), finely divided silica (3%) (Cabosil) and an antioxidant (0.6%); the sheet was crosslinked with 12 megarads radiation; a sample 10 × 4 inch (25 × 10 cm) was cut from the sheet, stretched to 20 inch (50 cm), and held there until cool. A section of a heating element prepared as described above and about 10 × 4 inch (25 × 10 cm) with the slits extending parallel to the long dimension was connected to a 24 volt power source and allowed to heat, and was then stretched to 20 inch (50 cm). The heating element while hot was bonded to the sample of the heat-recoverable sheet by means of a 5 mil (0.0125 cm) thick layer of an adhesive that would soften but not flow at about 100°C. The heat produced by the heater softened the adhesive and by application of pressure the heater was fused to the recoverable sheet. The recoverable sheet was restrained to prevent its recovery. The resulting article was allowed to cool to room temperature and the restraint on the heat-recoverable member removed. The heater was then connected to a 24 volt power source. The heat-recoverable member and heating element recovered to their original dimensions within 2 min. The heater reached its control temperature of about 115°C in about 1 min. Shrinkage of the heat-recoverable member and heater occurred smoothly.

It will be appreciated that as the heating element is not necessarily flat, for example in those embodiments in which it is a sleeve, the terms "plane" and "planar" refer not only to the plane actually occupied by the element or portion thereof, but also that plane in which the element or portion thereof would lie if it were flat.

WHAT WE CLAIM IS:—

1. A heating element which comprises: 130

the sheet material at said temperature to undergo dimensional change in the plane thereof. The process is particularly useful when a substrate is covered by positioning the article adjacent to the substrate and connecting the electrodes so that the heated sheet material undergoes dimensional change such that the article conforms to the surface of the substrate. If desired the article can surround the substrate or can cooperate with another covering member to surround the substrate. The external source of power used in these processes is conveniently DC of about 12 volts from a battery or AC of about 115 or about 220 volts from a mains source. It may be desirable to continue heating the article (by continuing to pass current through the heating element or otherwise) after the planar dimensions thereof have changed, for example to heat a substrate brought into contact therewith to ensure adequate adhesion between the article and the substrate, by heat-activatable adhesive or otherwise.

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(4) A mixture of high density polyethylene (45%), an ethylene/propylene rubber (5%) and carbon black (50%); 20 mils (0.051 cm) thick.

(5) as laminar member (3).

(6) as laminar member (2).

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These layers were bonded together with heat and pressure and then exposed to 6 megarads of ionising radiation. An expansible heating element was made by creating in the bonded assembly slits 0.5 inch (1.25 cm) long in parallel but offset rows 0.025 inch (0.06 cm) apart; the slits in a row were spaced apart 0.10 inch (0.25 cm). A heat-recoverable polymeric sheet was obtained as follows. A sheet .08 inch (0.2 cm) thick was extruded from a mixture of an ethylene/ethyl acrylate copolymer (88.4%) (DPD 6181 from Union Carbide), a dispersion of 1 part of carbon black in 3 parts of an ethylene/vinyl acetate copolymer (9%) (Colorant CC 004), finely divided silica (3%) (Cabosil) and an antioxidant (0.6%); the sheet was crosslinked with 12 megarads radiation; a sample 10 × 4 inch (25 × 10 cm) was cut from the sheet, stretched to 20 inch (50 cm), and held there until cool. A section of a heating element prepared as described above and about 10 × 4 inch (25 × 10 cm) with the slits extending parallel to the long dimension was connected to a 24 volt power source and allowed to heat, and was then stretched to 20 inch (50 cm). The heating element while hot was bonded to the sample of the heat-recoverable sheet by means of a 5 mil (0.0125 cm) thick layer of an adhesive that would soften but not flow at about 100°C. The heat produced by the heater softened the adhesive and by application of pressure the heater was fused to the recoverable sheet. The recoverable sheet was restrained to prevent its recovery. The resulting article was allowed to cool to room temperature and the restraint on the heat-recoverable member removed. The heater was then connected to a 24 volt power source. The heat-recoverable member and heating element recovered to their original dimensions within 2 min. The heater reached its control temperature of about 115°C in about 1 min. Shrinkage of the heat-recoverable member and heater occurred smoothly.

It will be appreciated that as the heating element is not necessarily flat, for example in those embodiments in which it is a sleeve, the terms "plane" and "planar" refer not only to the plane actually occupied by the element or portion thereof, but also that plane in which the element or portion thereof would lie if it were flat.

WHAT WE CLAIM IS:—

1. A heating element which comprises:



* C L M S *

(A) a laminar member composed of a material which comprises an organic polymer and electrically conductive particles dispersed in the polymer in amount sufficient to render the member electrically conductive; and

(B) a pair of laminar flexible electrodes which are connected to opposite faces of said laminar member and are capable of being connected to an external source of power to cause current to pass through said laminar member;

said laminar member and laminar electrodes having a plurality of elongate, overlapping apertures through the thickness thereof, the apertures being of a size, shape and distribution which permit at least one of the dimensions of the element in the plane thereof to be changed without complete rupture of the electrode at any point (as hereinbefore defined), the dimensional change being accommodated by a change in the shape of the apertures.

2. An element according to claim 1, wherein the apertures are of a size, shape and distribution which permit at least one of the dimensions of the element in the plane thereof to be changed at the melting point of the polymer by a percentage which is at least 30%, based on the original dimension, without complete rupture of the electrode at any point (as hereinbefore defined), the dimensional change being accommodated by a change in the shape of the apertures.

3. An element according to claim 1 or 2, wherein the conductive particles in member A are carbon black particles.

4. An element according to any of the preceding claims, wherein member A is composed of a material which exhibits PTC behaviour (as hereinbefore defined).

5. An element according to claim 4, wherein member A has an R_{10} value (as hereinbefore defined) of at least 2.5 or an R_{100} value (as hereinbefore defined) of at least 10.

6. An element according to claim 4, wherein member A has an R_{10} value (as hereinbefore defined) of at least 6.

7. An element according to any one of the preceding claims, wherein the organic polymer in member A is a cross-linked crystalline polymer.

8. An element according to any one of the preceding claims, wherein the electrodes are composed of a material which has a resistivity of less than 10 ohm.cm at 25°C and comprises an organic polymer and electrically conductive particles dispersed therein, and are coextensive with member A.

9. An element according to claim 8, which also comprises a pair of laminar flexible metal electrodes which contact said coextensive electrodes on the faces thereof

remote from the said member A in selected areas which do not overlap.

10. An element according to any one of the preceding claims wherein member A is composed of a material which has a resistivity greater than 10 ohm.cm at room temperature and the electrodes are composed of a material having a resistivity of less than 1 ohm.cm at room temperature.

11. An element according to claim 10, wherein the electrodes are of metal.

12. An element according to claim 11, wherein the metal is lead.

13. An element according to claim 11, wherein the metal is aluminium.

14. An element according to claim 11, wherein the metal is copper.

15. An element according to Claim 11, wherein the electrodes are composed of a metal having a ductility at least as high as aluminium.

16. An element according to any one of Claims 11 to 15, wherein the electrodes are corrugated.

17. An element according to any one of the preceding claims wherein the faces of the electrodes remote from the laminar member are coated with an insulating material.

18. An element according to any one of the preceding claims wherein the electrodes comprise peripheral bussing sections which do not contain apertures.

19. An element according to any one of the preceding claims wherein member A is as defined in any one of Claims 3 to 6 and which also comprises at least one intermediate layer which (a) exhibits constant wattage behaviour (as hereinbefore defined) at temperatures below the switching temperature of member A; (b) is composed of a material which comprises an organic polymer and electrically conductive particles dispersed in the polymer in amount sufficient to render the member electrically conductive; (c) has a resistivity greater than 10 ohm.cm; and (d) is interposed between the member A and an electrode.

20. An element according to Claim 19, wherein said intermediate constant wattage layer exhibits PTC behaviour with a switching temperature which is above the switching temperature of member A.

21. An element according to any one of the preceding claims wherein the apertures are straight or wave-form slits or slots, or oval or diamond-shaped holes.

22. An element according to any one of the preceding claims in which the apertures are a plurality of identical straight slits in parallel equally-spaced rows with the slits in adjacent rows overlapping each other.

23. An element according to Claim 22, wherein each slit is at least $\frac{1}{4}$ inch long.

24. An element according to Claim 23, 130





wherein the length of each slit is 5 to 20 times the distance between adjacent rows of slits.

25. An element according to any one of Claims 21 to 24, wherein the distance between the edges of adjacent apertures is $1/10$ to $1/2$ inch.

26. An element according to any one of the preceding claims wherein the apertures are arranged in a regular pattern and give a symmetrical response through the thickness of the element to extension in the plane of the element.

27. An element according to any one of the preceding claims wherein at least one of the junctions between the electrodes, the member A) and any intermediate layer is bonded by means of a conductive adhesive.

28. An element according to any one of the preceding claims wherein the electrodes are substantially coextensive with member A.

29. An element as claimed in any one of the preceding claims wherein the apertures are of a size, shape and distribution which permit at least one of the dimensions of the element in the plane thereof to be changed at the melting point of the polymer by a percentage which is at least 50%, without complete rupture of the electrode at any point (as hereinbefore defined), the dimensional change being accommodated by a change in the shape of the apertures.

30. An element according to claim 29, wherein said percentage is at least 70%.

31. An element according to claim 30, wherein said percentage is at least 100%.

32. An element according to claim 31 wherein said percentage is at least 250%.

33. An element according to any one of claims 2 and 29 to 32 whose resistance at room temperature does not change by more than 20% as a result of extension to said percentage.

34. A heating element which has been obtained by changing at least one of the dimensions of an element as claimed in any one of claims 2 and 29 to 32, the dimensional change being in the plane of the element and being insufficient to cause complete rupture of the electrode (as hereinbefore defined) at any point.

35. An article which comprises a heat-responsive (as hereinbefore defined) sheet material and secured to one face of the sheet material a heating element as claimed in any one of the preceding claims.

36. An article according to claim 35, wherein the sheet material softens on heating.

37. An article according to Claim 36, wherein the sheet material is a polymeric material.

38. An article according to Claim 37, wherein the sheet material is an adhesive or a mastic.

39. An article according to Claim 37, wherein the sheet material is a heat-recoverable polymeric film.

40. An article according to any one of Claims 34 to 39 in the form of a heat-shrinkable sleeve.

41. An article according to Claim 37, wherein the sheet material is a polymeric film which can be rendered heat recoverable.

42. An article according to any one of Claims 36 to 41, wherein the sheet material and the element are secured to each other by an adhesive which is thixotropic at the temperature at which the sheet material softens.

43. An article according to any one of Claims 36 to 42, wherein the heating element provides a face of the article and at least some of the aperture therein contain a composition which flows at the temperature at which the sheet material softens.

44. An article according to Claim 43 which is in the form of a heat-shrinkable sleeve with the heating element on the interior surface thereof.

45. An article according to Claim 43 or 44, wherein the composition is a mastic.

46. An article according to Claim 43 or 44, wherein the composition is an adhesive.

47. A process for covering a substrate which comprises positioning an article as claimed in any one of Claims 35 to 46 adjacent the substrate; connecting the electrodes of said article to an external source of power which causes current to pass through the laminar member A and to provide at least part of the heat needed to heat the sheet material to a temperature at which it becomes heat-responsive (as hereinbefore defined); and allowing or forcing the sheet material at said temperature to undergo dimensional change in the plane thereof so that the article conforms to the surface of the substrate.

48. A process according to Claim 47, wherein the article surrounds the substrate.

49. A process according to Claim 47, wherein the article cooperates with another covering member to surround the substrate.

50. A heating element substantially as hereinbefore described with reference to and as illustrated by the accompanying drawing.

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