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(54) ARTICLE WITH FABRIC ELECTRODES

(71) WE, RAYCHEM CORPORATION, a Body Corporate organised according to 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 heat recoverable articles, particularly self heating heat recoverable articles.

Polymeric heat recoverable articles may be used, for example, in tubular form as sealing, insulating or protective coatings for elongate objects *e.g.* cables and pipes. A tube of heat recoverable material is slipped over the substrate and heated to its recovery temperature, when it shrinks to a smaller diameter. Since the tube is pliant and elastic at its recovery temperature it shrinks and contacts the substrate, thereby conforming to its shape.

In many cases there is not a free or conveniently accessible end to the elongate object and a heat recoverable sheet material is wrapped about the substrate and its ends joined. In position, the wrap-around sleeve is heated to cause its recovery. Examples of wrap-around devices for substrates in which there is no access to a free end are given in U.S. Patent No. 3 379 218 issued on 23rd April 1968 to Julian S. Conde, U.S. Patent No. 3 455 336 issued on 15th July 1969 to Roger H. Ellis and U.S. Patent No. 3 770 556 issued on 6th November 1973 to Joseph H. Evans and Gareth W. Will.

The heat recoverable articles described above may be conveniently obtained from a wide variety of crosslinked crystalline polymeric compositions. Suitable materials and processes for causing crosslinking, e.g. by ionizing radiation, and for rendering the articles heat recoverable are described in U.S. Patent 3 086 242 issued on 23rd April 1963 to Paul M. Cook and Richard W. Muchmore. Chemical crosslinking agents, for example, peroxides, may also be employed.

To render an article made from such a composition heat recoverable, it is dimensionally deformed above the crystalline melting point (or range) and held in the deformed state until the article is cooled below the melting point. In the cooled state the article can be said to be dimensionally unstable since it will exhibit "elastic memory" when, without restraint, it is again heated above the crystalline melting point, i.e. it will return to its original dimensions. In its recovered form, the article is frequently said to be dimensionally heat stable.

The recovery of a heat recoverable article may suitably be effected by the application of heat to the article using a torch or heat gun. However, in certain cases, for example, if the zone where the application of heat is required is inaccessible or located in an area where flames are hazardous or prohibited as in mines where large amounts of flammable gases may be present, treating by such means is undesirable or even impossible. In these circumstances, conductive polymers may be used as the heat recoverable material in heat recoverable articles. An article made from a conductive polymer is wired into an electrical circuit as a resistive heating element and when connected to a power source, for example, a 12 to 24 or even 36 volt battery or an A.C. (e.g., at 115 volts) outlet, current flows through the article. As a result of its ohmic resistance it becomes heated and this heat can be employed as a part or all of the heat required to cause recovery of the article. If heated to too high a temperature, the polymeric material will undergo decomposition. Delicate components shielded by the article may also be damaged, although the extent of this damage may not be apparent by visible inspection.

To avoid excessive temperatures, thermostats or other heat control devices may be used. However, in many instances this defeats the purpose of using self-heated recoverable articles in that bulky and expensive hardware must be employed in places that are frequently virtually inaccessible. It has previously been proposed to eliminate added hardware by using as the conductive polymeric composition a composition that exhibits a positive temperature coefficient (PTC) of resistance. These compositions may be referred to as PTC compositions.

Suitable compositions comprise an organic thermoplastic polymer, particularly a crystalline polymer, that contains carbon or another particulate conductor, for example, a finely divided metal. PTC compositions undergo a relatively small increase in resistance as the temperature increases until a certain temperature T_s (which may be a temperature range) sometimes referred to as the switching or anomaly temperature is reached. Above T_s a further increase in temperature results in a large increase in resistance. The increase in resistance may be so sharp that the current is cut down to a level which limits the temperature of the composition to its T_s temperature. For crystalline polymers, T_s is at or just below the crystalline melting point or range.

When a PTC composition is employed as a component of a self-heating, heat-recoverable article, it can affectively limit the temperature to which the article can be heated. Suitable PTC compositions are described in British Patent Specification No. 1528622 and DE-OS 2 543 346.

The types of applications of heat-recoverable articles suggested above have previously been limited because in most configurations the heat-recoverable article must be provided with a plurality of electrodes, generally pairs of substantially parallel wires. The articles can therefore only be deformed into its heat unstable state by deformation in a direction transverse to the direction in which the electrodes are arranged. This feature has significantly limited the useful shapes of self-heating heat-recoverable articles.

The present invention provides an article which comprises electrically resistive material at least part of which material is in the form of a heat-recoverable member, or a member capable of being dimensionally altered to become recoverable, or a member which has been heat-recovered, and which article also comprises at least one fabric electrode sufficiently compliant and dimensionally deformable that it does not substantially impede dimensional alteration of the member to a heat-recoverable configuration and does not substantially impede recovery of the member from that configuration to a heat-recovered configuration, and a second electrode, the electrodes being capable on connection with a source of electrical power of causing current to flow through the electrically resistive material.

The second electrode may be incorporated in the electrically resistive material (which is preferred and in which case it will form part of the member), may be in contact with the heat-recoverable member, for example as a substrate, or may be incorporated in the article, but in a second member adjacent to the heat-recoverable member. The second electrode may consist of a strip or grid of metal provided that it does not hinder the deformation of the recoverable article between its initial, recoverable and recovered configurations. Advantageously the second electrode is a fabric electrode having the compliance and deformability of the first, and preferably both are incorporated in the electrically resistive material.

The heat recoverable member advantageously comprises a polymeric composition having sufficient conductive filler, for example, a particulate carbon black or metal, so that it is capable of conducting an electrical current at a constant voltage, for example, 12 to 36 volts from a battery or 115 volt A.C. The composition should also exhibit sufficient ohmic resistance so that its heat output is capable of effecting recovery of the heat recoverable member, which may be several millimetres thick. There are many suitable polymers for use in these compositions. Particularly useful are crosslinked crystalline polymers, for example, those described in U.S. Patent No. 3 086 242. An article made from such a polymer can be deformed above the crystalline melting point or range of the polymer (hereinafter crystalline m.p.) and maintained in the deformed state until cool in order to render the article heat recoverable.

Preferably the heat recoverable member comprises at least one layer of a conductive polymer as described above.

The layer or layers may exhibit either constant wattage behaviour or have a positive temperature coefficient of resistance. Preferably, a PTC material used in the heat recoverable member exhibits at least a six fold increase in resistance in a 30°C range of temperature above T_s. A constant wattage material has a resistance which may increase with temperature but which does not have a temperature at which its resistance increases so rapidly that for most purposes it becomes an insulator. Within the context of this specification, a constant wattage material is one whose resistance does not increase by a factor of more than six in any 30° range of temperature between 25°C and the melting point of the polymer or a higher temperature if the polymer has been crosslinked to give it structural stability above the melting point. Preferably the material in the form of a layer has a superficial resistivity of at least 1 ohm/square at 25°C.

Constamt wattage materials suitable for use in the present invention are known in the prior art. In many cases the polymers used in PTC compositions can be used in constant wattage compositions by incorporating in the polymer a higher proportion of conductive filler than is used in PTC compositions. If the T_s of compositions exhibiting PTC character is high enough these compositions can be used as constant wattage materials. The details that characterize PTC materials and constant wattage materials useful in the heat recoverable articles of the present invention are described in British Patent Specification No. 1 529 354 and DE-OS 2 543 314.

Advantageously, the extensible fabric electrode comprise strand material of any suitable conductive material. Preferably the strands are made from materials that have low resistivity and that are moderate in cost, for example, copper wire strands, and preferably 28-40 gauge wire strands. Strands of other metals, including alloys and bicomponent metal strands, metal and polymer fibre composites, metal plated polymer fibres or conductive carbon fibres may also be used.

The fabric electrode must be sufficiently pliable that, when incorporated into the polymer composition, it can be dimensionally deformed to the same extent as the composition when the latter is heated above the crystalline m.p. in order to render it heat recoverable as described in U.S. Patent No. 3 086 242. In addition the electrode should not substantially impede the recovery of the heat recoverable member when it is heated. Such electrodes are advantageously capable of undergoing at least a 100% change, and preferably a 300% change, in dimension, for example, of length and width or if, tubular, of diameter or length based on its dimension when the member is in a dimensionally heat stable state. However, any fabric that may be deformed with the recoverable article between its initial, i.e., heat stable, recoverable, and recovered configurations is suitable for use in the invention. It will be appreciated, therefore, that the suitability of a given material will be readily determined by simple routine experiment in any individual case.

Suitable electrode fabrics can be made by techniques well known to the art, *e.g.* weaving, knitting or braiding. Of these braiding is preferred because, using this technique, electrodes having good compliancy or flexibility are obtained. Preferably the electrode will readily undergo the elongation involved in the deformation process that renders the polymer composition heat recoverable and also will offer a minimum of resistance to recovery of the heat recoverable member. Advantageously braided electrodes comprise tubular braids preferably braided about a core of a thermoplastic material. Tubular braid having a high braid angle, relative to the axis of the tube, for example, an angle greater than approximately 50° and preferably approximately 75°, is particularly advantageous. A suitable braid is obtained using 16 carriers each of four strands of 38 American wire gauge tinned copper wire at a 75° braid angle to form a braid about a cylindrical core, which may be tubular, of a conductive or non-conductive thermoplastic material preferably a conductive material compatible with the polymer from which the heat recoverable member is made, having an outside diameter of 0.64 cm. Usually, the braided tube is heated above the softening point of the thermoplastic core and flattened, care being taken to avoid stretching the braid in the course of this deformation. For some purposes, for example, where it is desired that the tube be radially expansible rather than longitudinally extensible, lower braid angles can be employed. The braiding character of radially expansible tube is described in U.S. Patent No. 3 253 619 issued on 31st May 1966 to Paul M. Cook and F. Raymond Young.

The invention will now be described in greater detail with reference to the accompanying drawings, in which

Figure 1 is a perspective view of a braided electrode.

Figures 2, 3 and 5 to 7 are perspective views of five different embodiments of heat-recoverable articles constructed in accordance with the invention and

Figure 4 is a perspective view of an electrode assembly.

Referring to Figure 1, a braided electrode 10 comprises a tubular braid 11 wound over a tubular core member 12. Referring to Figure 2, the heat recoverable article 13 comprises a plurality of flattened, braided, electrodes 10, embedded in a layer 14 of a PTC polymer composition as hereinbefore described. The electrodes 10 are conterminous with the PTC layer. Adjacent pairs of electrodes 10 are connected in series to a source of electric potential 15.

In operation, current is conducted between the electrodes through the PTC composition. After generation of sufficient heat, recovery of the article 13 is effected. The PTC layer 14 can deform in either or both of two directions, i.e. in a direction to cause separation of the electrodes 10 and/or in a direction to cause elongation of the article 13 along the long axis of the electrodes 10, to impart heat recoverability. A conventional rigid electrode allows deformation only in a direction to cause separation of the electrodes 10. Since the separation of the electrodes 10 increases the path length and therefore the resistance of the article 13 this limits the power output of the article 13 in the expanded state.

Since the layer 14 of the article 13 comprises a PTC composition, the heating will be limited when the T_s temperature of the polymer in the composition is reached. The article is self-heating and capable of functioning advantageously as a heater after recovery whether or not the self-heating capability is employed to cause recovery of the article.

Referring to Figure 3, the heat recoverable article 30 comprises two layers of electrodes 10 embedded in a layer 4 of a PTC polymer composition. The electrodes 10 in the upper layer are connected parallel with one another and in series with those of the lower layer through the polymer layer. A layer of electrodes 10 is shown in Figure 4 before incorporation into the heat recoverable article. Each electrode layer has at both ends a bussing electrode 16. The bus or bussing electrodes 16 are fabric electrodes and can be caused to adhere to the electrodes 10 by heating their thermoplastic core above the softening point and pressing them together, or by conventional spot welding or soldering techniques. The bussing electrodes 16 are used to distribute power to the electrodes 10 of one layer. The heat-recoverable article 30 can be deformed along and/or perpendicular to the long axes of the electrodes 10.

It will be appreciated that the heat-recoverable articles shown in Figures 2 and 3 may comprise a constant wattage polymeric composition instead of a PTC composition.

Referring to Figure 5, the heat recoverable article 17 comprises a set of electrodes 10 embedded in a layer 18 of a constant wattage polymeric composition and a second set of electrodes 10 embedded in a layer 19 of a PTC polymeric composition. In Figure 6 a heat recoverable article employing three layers of polymeric composition is shown. Two sets of electrodes 10 are embedded in two layers 21 and 22 of a constant wattage polymeric material, which sandwich a layer 23 of a PTC polymeric material.

In a heat recoverable article using thin films of PTC compositions only in which the current flow is in the plane of the film, it has been found that even at moderate power outputs, the phenomenom of "hotlining" occurs, in which only a narrow band of the PTC layer functions as a heater. This problem has been discussed in the aforementioned British Patent Specification No. 1 529 354.

The temperature T_s at which the resistance of a PTC material increases sharply is at or below the crystalline m.p. for crystalline polymers. These polymers, if in a heat recoverable form, undergo recovery above their crystalline m.p. and sufficient mobility for efficient recovery requires temperatures at least 10°C above the crystalline m.p. In a layer system, for example one as shown in Figure 5 or 6, there may be a difference between resistance of the layer or layers of constant wattage material and that of the layer of PTC material, with the result that the layer of constant wattage material heats first, if its resistance is higher than the resistance of the PTC layer. The article can be heated above T_s, by rapidly heating the constant wattage material before thermal conduction raises the temperature of the PTC composition to T_s thereby cutting off the current.

A more efficient method for overcoming the disadvantage of "hotlining" is described in copending Application No. 3 227 5176 (Serial No. 1 562 085) and DE-OS 2 634 932. The article disclosed in the application has a structure in which a relatively low resistance, thermally insulating layer of constant wattage material is disposed between a heating layer of a constant wattage material and a layer of PTC composition, as shown in Figure 7. The heat recoverable article 24 comprises a layer 25 of a constant wattage material of relatively high resistance, a thermally insulating layer 26 of relatively low resistance and a layer 27 of a PTC composition of intermediate initial resistance. The layer 26 may be made from a foamed polymeric material so that it has good thermal insulating properties. When current is applied, the layer 25 heats up but the layer 27 is thermally shielded by the layer 26 and its temperature increase will lag behind that of layer 25. Thus the layer 25 can be caused to heat well above the crystalline melting point of the heat recoverable member before the power is cut off by the temperature of the PTC composition reaching T_s. Thermal conductivity effects will allow the entire article to eventually be heated above the recovery temperature, *i.e.*, the crystalline melting point by an amount adequate to insure efficient recovery. It will be appreciated that layer 25 may also be of a PTC material provided that it has a T_s higher than that of layer 27.

All of the layers of a multi-layer heat recoverable article need not be heat recoverable. Provided that at least one layer is heat recoverable and has sufficient strength (usually termed "hold-out") to retain the other layers in a deformed condition, or has sufficient recovery force to urge the other layers towards the heat stable configuration, the other layers need not be heat recoverable.

In the embodiments shown the electrodes 10 are embedded in a layer comprising a polymeric composition. This is advantageously achieved by disposing the electrodes between two polymer sublayers that are subsequently laminated together, for example, sublayers that have been heated above their softening points and bonded together using laminating rollers.

Although the articles shown have been relatively planar articles it will be appreciated that articles of regular or irregular configurations can be constructed. For example, a tubular article having a plurality of fabric electrodes disposed in one or more layers either parallel to the long axis of the tube or perpendicular to that axis can be employed. A particularly preferred article is described in British Patent Specification No. 1 529 353 and in DE-OS 2 543 338. Alternatively the tubular structure can be disposed about a cylindrical conduit and used after installation to heat the contents of the conduit to prevent freezing or salting out of solids.

WHAT WE CLAIM IS:

1. An article which comprises electrically resistive material at least a part of which material is in the form of a member which is heat-recoverable, or is capable of being dimensionally altered to become heat-recoverable or which has been heat-recovered and which article also comprises at least one fabric electrode sufficiently compliant and dimensionally deformable that it does not substantially impede dimensional alteration of the member to a heat-recoverable configuration and does not substantially impede recovery of the member from that configuration to a heat-recovered configuration and a second electrode, the electrodes being capable on connection with a source of electrical power of causing current to flow through the electrically resistive material.

2. An article as claimed in claim 1 which comprises a pair of such fabric electrodes incorporated in the electrically resistive material.

3. An article as claimed in claim 1 or claim 2 wherein the or each fabric electrode comprises a woven, knitted or braided electrode.

4. An article as claimed in claim 3 wherein the or each fabric electrode comprises a braided electrode.

5. An article as claimed in claim 4 wherein the braided electrode comprises a tubular braid.

6. An article as claimed in claim 5 wherein the tubular braid is braided about a core of a thermoplastic material.

7. An article as claimed in claim 6 wherein the core is in the form of a tube.

8. An article as claimed in claim 7 wherein the tubular braid has a braid angle relative to the axis of the tube of at least 50°.

9. An article as claimed in claim 8 wherein the braid angle is 75°.

10. An article as claimed in any one of claims 1 to 9 wherein the or each fabric electrode is capable of undergoing a change in a dimension, relative to its dimension when the recoverable member is in its heat stable state, of greater than 100%.

11. An article as claimed in claim 10 wherein the or each fabric electrode is capable of undergoing a change in a dimension, relative to its dimension when the recoverable member is in its heat stable, state of at least 300%.

12. An article as claimed in any one of claims 1 to 11 wherein at least one of the electrodes comprises copper wire strand.

13. An article as claimed in claim 12 wherein the copper wire strand has a gauge within the range of from 28 to 40.

14. An article as claimed in any one of claims 1 to 13 wherein the heat recoverable member comprises a layer of a polymeric composition incorporating a particulate conductive filler.

15. An article as claimed in claim 14 wherein the heat recoverable member comprises a layer of a material exhibiting constant wattage behaviour (as hereinbefore defined).

16. An article as claimed in claim 14 or claim 15 wherein the heat recoverable member comprises a layer of material having a positive temperature coefficient of resistance.

17. An article as claimed in claim 14 or claim 15 wherein the heat recoverable member comprises a first layer of material exhibiting constant wattage behaviour and a second layer of material having a positive temperature coefficient of resistance, each layer having incorporated therein at least one fabric electrode capable on connection with a source of electrical power of causing current to flow from one layer to the other layer.

18. An article as claimed in claim 14 or claim 15 wherein the heat recoverable member comprises a first layer having a positive coefficient of resistance which layer is positioned between two second layers exhibiting constant wattage (as hereinbefore defined) behaviour each second layer incorporating at least one fabric electrode capable, on connection with a source of electrical power, of causing current to flow from one second layer to the other second layer through the first layer.

19. An article as claimed in claim 17 wherein a layer of an electrically conductive constant wattage material having a resistance lower than that of the first or second layers is sandwiched between the first and second layers.

20. An article as claimed in claim 1 substantially as described herein with reference to and as illustrated by one or more of the accompanying drawings.

21. An article which comprises electrically resistive material at least a part of which material is in the form of a member which is heat-recoverable, or is capable of being dimensionally altered to become heat-recoverable or which has been heat-recovered and which article also comprises at least one fabric electrode sufficiently compliant and dimensionally deformable that it does not substantially impede dimensional alteration of the member to a heat-recoverable configuration and does not substantially impede recovery of the member from that configuration to a heat-recovered configuration, the electrode being capable, on connection with a second electrode and a source of electrical power, of causing current to flow through the electrically resistive material.

22. An article as claimed in claim 21, wherein the fabric electrode is incorporated in the electrically resistive material.

23. An article as claimed in claim 21 or claim 22 wherein the fabric electrode comprises a woven, knitted or braided electrode.

24. An article as claimed in claim 23 wherein the fabric electrode comprises a braided electrode.

25. An article as claimed in claim 24 wherein the braided electrode comprises a tubular braid.

26. An article as claimed in claim 25 wherein the tubular braid is braided about a core of a thermoplastic material.

27. An article as claimed in claim 26 wherein the core is in the form of a tube.

28. An article as claimed in claim 27 wherein the tubular braid has a braid angle relative to the axis of the tube of at least 50°.

29. An article as claimed in claim 28 wherein the braid angle is 75°.

30. An article as claimed in any one of claims 21 to 29 wherein the fabric electrode is capable of undergoing a change in a dimension, relative to its dimension when the recoverable member is in its heat stable state, of greater than 100%.

31. An article as claimed in claim 30 wherein the fabric electrode is capable of undergoing a change, relative to its dimension when the recoverable member is in the heat stable state, of at least 300%.

32. An article as claimed in any one of claims 21 to 31 wherein the electrode comprises copper wire strand.

33. An article as claimed in claim 32 wherein the copper wire strand has a gauge within the range of from 28 to 40.

34. An article as claimed in any one of claims 21 to 33 wherein the heat recoverable member comprises a layer of a polymeric composition incorporating a particular conductive filler.

35. An article as claimed in claim 34 wherein the heat recoverable member comprises a layer of a material exhibiting constant wattage behaviour (as hereinbefore defined).

36. An article as claimed in claim 34 or claim 35 wherein the heat recoverable member comprises a layer of material having a positive temperature coefficient of resistance.

37. An article as claimed in claim 34 or claim 35 wherein the heat recoverable member comprises a first layer of material exhibiting constant wattage behaviour and a second layer of material having incorporated therein at least one fabric electrode capable, on connection with a source of electrical power, of causing current to flow from one layer to the other layer.

38. An article as claimed in claim 34 or claim 35 wherein the heat recoverable member comprises a first layer having a positive coefficient of resistance which layer is positioned between two second layers exhibiting constant wattage (as hereinbefore defined) behaviour each second layer incorporating at least one fabric electrode capable, on connection with a source of electrical power, of causing current to flow from one second layer to the other second layer through the first layer.

39. An article as claimed in claim 37 wherein a layer of an electrically conductive constant wattage material having a resistance lower than that of the first or second layers is sandwiched between the first and second layers.

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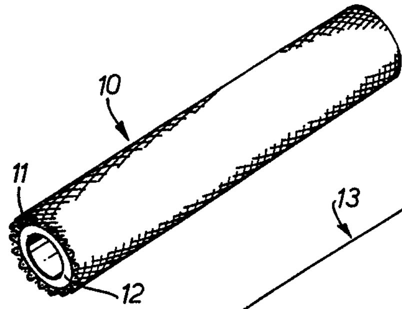

FIG. 1.

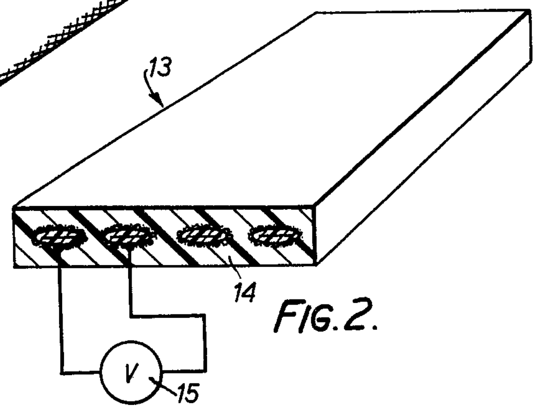

FIG. 2.

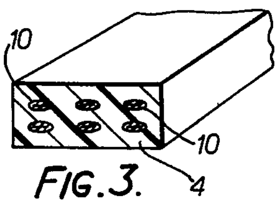

FIG. 3.

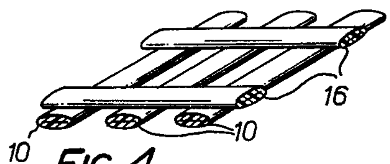

FIG. 4.

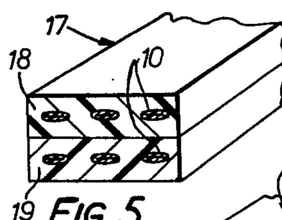

FIG. 5.

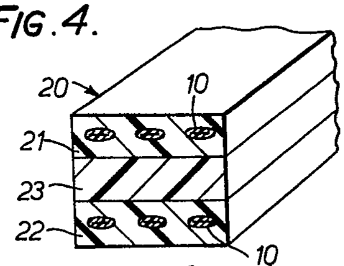

FIG. 6.

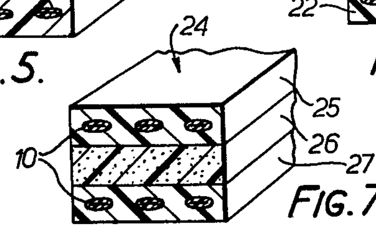

FIG. 7.