United States Patent

Meyer

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[54] **ELECTRICALLY HEATED DEVICE EMPLOYING CONDUCTIVE-CRYSTALLINE POLYMERS**

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[21] Appl. No.: **109,414**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 6,095, Jan. 27, 1970, abandoned.

[52] **U.S. Cl.** ....**219/222,** 132/33 R, 219/241, 219/505, 252/511, 338/22

[51] **Int. Cl.** **A45d 2/36,** H05b 1/02, H05b 3/12

[58] **Field of Search**......................219/222–226, 504, 219/505, 241, 210; 252/503, 502, 510, 511; 338/22, 23; 132/33 R

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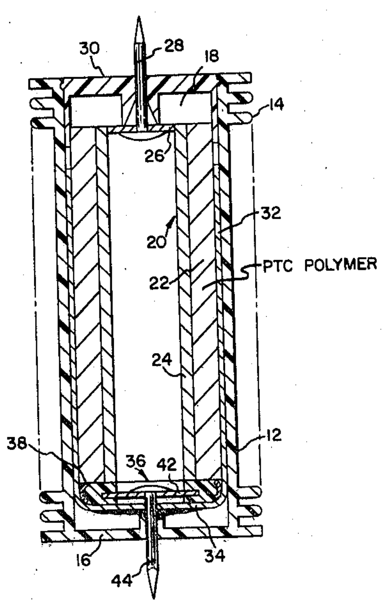
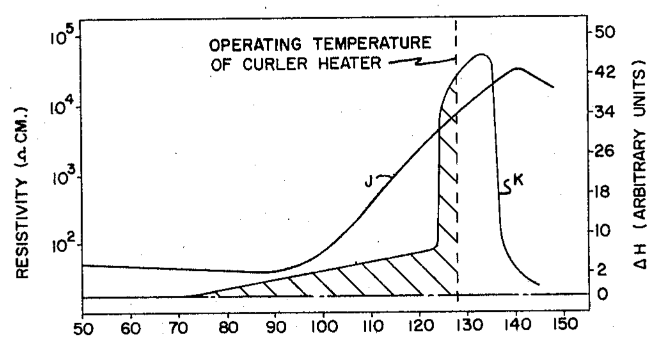
[57] **ABSTRACT**

A hair curler employing a heater element formed of a conductive crystalline polymer is disclosed. The polymer, loaded with conductive particles, such as carbon black, has a positive temperature coefficient (PTC) of resistivity characteristic and combines a fast warm-up time with a slow cool down time due to the phase change of amorphous polymer to crystalline polymer upon cooling. The heat of fusion curve of the crystalline polymer is related to the temperature versus resistivity curve such that a sharp rise in resistance above an anomaly temperature and in and around the operating temperature of the curler limits the heat generation and prevents some of the crystalline polymer from changing state and maintains the structural integrity of the polymer. Since the polymer retains its shape, no special sealing means is required to confine it as in fusible wax devices. Means are disclosed to make electrical contact to the heater element and for mounting it within an outer hair curler shell.

11 Claims, 7 Drawing Figures





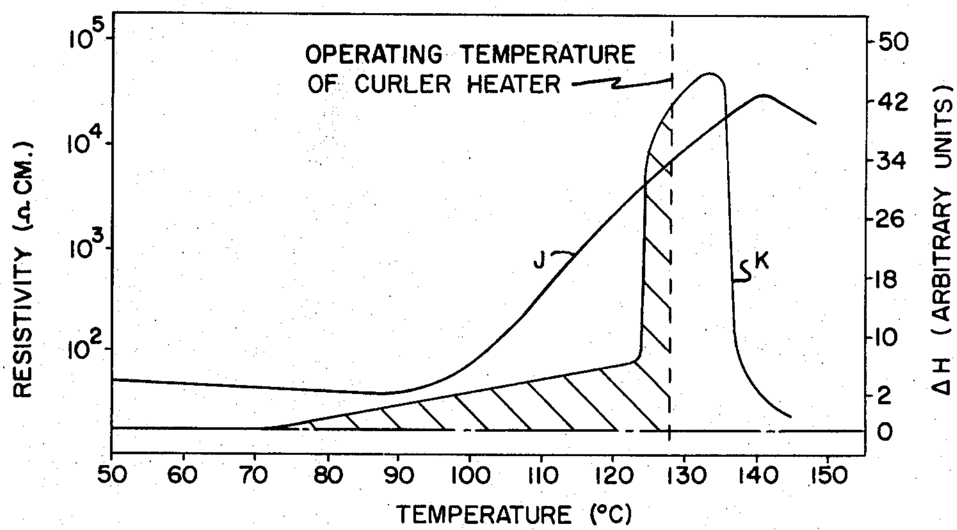


FIG. 3

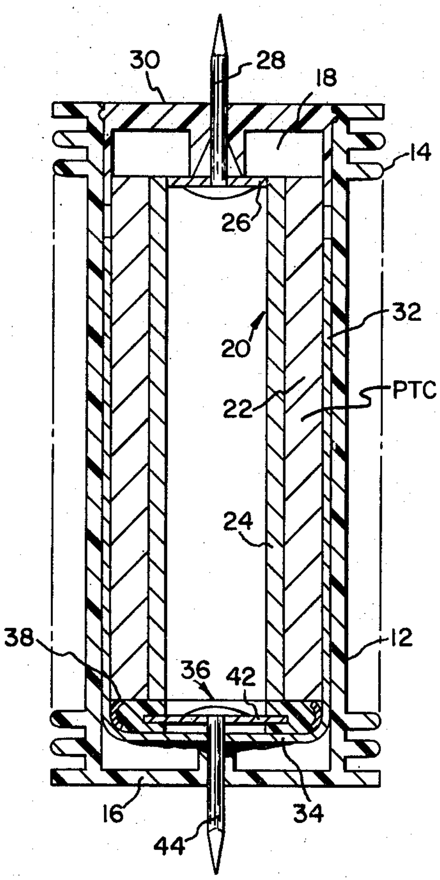


FIG. 1

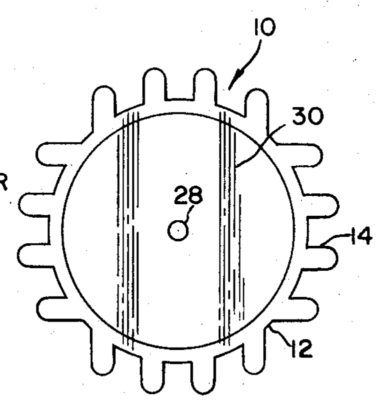


FIG. 2

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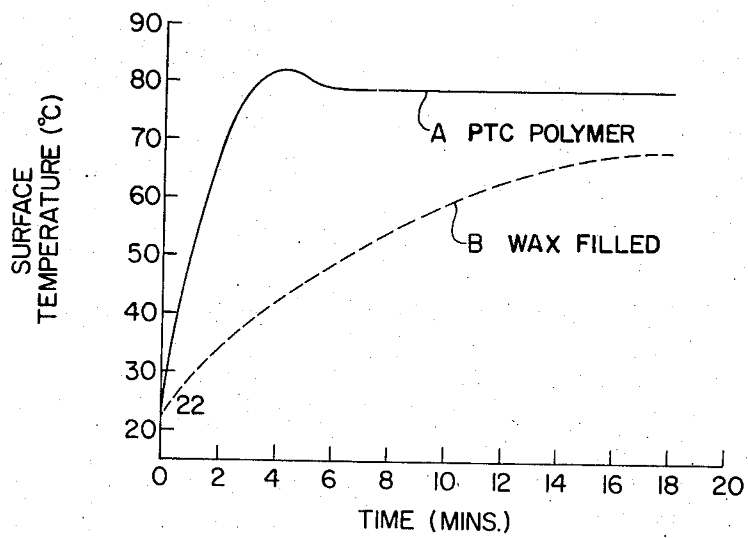

FIG. 4

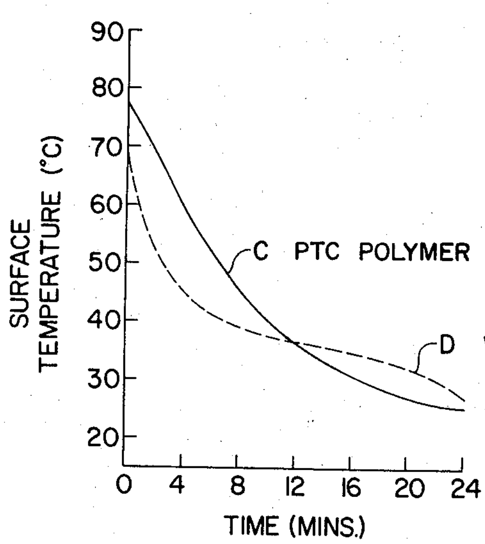

FIG. 5

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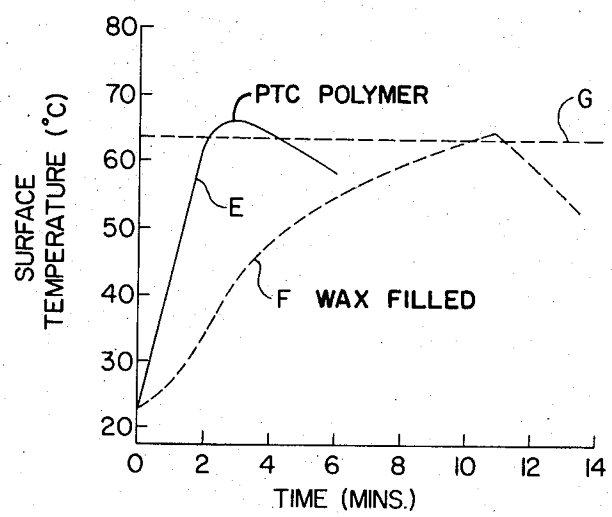

FIG. 6

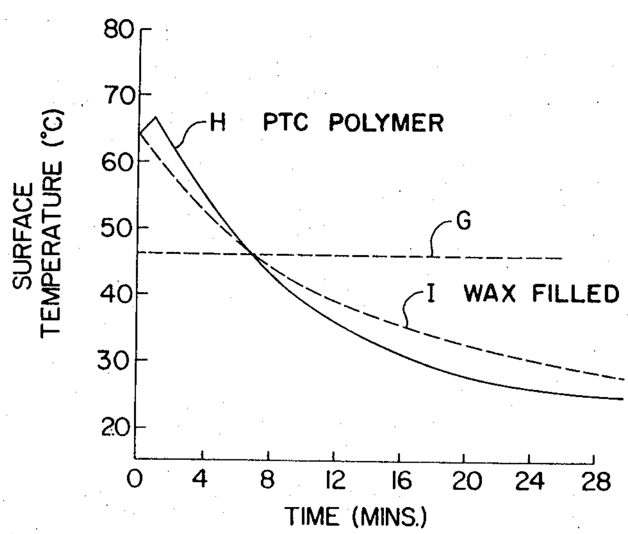

FIG. 7

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ELECTRICALLY HEATED DEVICE EMPLOYING CONDUCTIVE-CRYSTALLINE POLYMERS

This is a continuation-in-part of application, Ser. No. 6,095, filed Jan. 27, 1970, **now abandoned**.

BACKGROUND OF THE INVENTION

The invention relates to hair curlers and more particularly to electrically heated hair curlers.

Electrically heated hair curlers have found wide market acceptance in recent years. In general, these curlers comprise an outer cylindrical shell of a suitable polymer provided with a plurality of fingers extending outwardly from the outer peripheral surface of the shell for grasping hair wound about the shell. The curlers are heated to a desired temperature, then taken by the user who trains hair about the periphery. The hair is generally kept in contact with the curler for a short period of time to effect curling of the hair. Various ways have been used to heat the curlers but all have certain disadvantages. One type of curler employs, mounted within the shell, a housing which contains a fusible wax. The curler is placed in heat transfer relation with a heating element until the wax melts and is then removed from the heat source and is ready for use. However, since the wax is changed to a liquid, special precautions must be taken to insure a good seal. Further, the time which is required for the curler to be heated is longer than desirable due to the inefficiency of heat transfer to the wax. The wax-filled device does, however, offer the advantage of being an excellent heat storage means due to the latent heat released during phase change of the wax from liquid to solid upon cooling although the melting point of the waxes used is somewhat lower than optimum. Attempts have been made to avoid the above disadvantages by using a resistance element in the curler both as the heater and as the heat storage means. This avoids the liquid sealing problem but the warm-up time for the device is still excessive since a relatively massive resistance element must be employed in order to store the heat for the required time after de-energization. Still another disadvantage is that both of the above types require current controlling devices, such as thermostats. Further, heat distribution along the surface of the curler for both types is relatively non-uniform giving rise to hot and cold spots along the curler surface with a concomitant non-uniform degree of curling for different sections of the hair.

Thus it is an object of the invention to obviate the disadvantages of the prior art curlers mentioned above.

Another object of the invention is the provision of a hair curler heater which combines the functions of various components used in prior art devices.

Yet another object is the provision of a simple, reliable, rugged hair curler device, one which provides uniform heating with no hot or cold spots. Another object is the provision of a hair curler heater which has an extremely fast warm-up time along with the characteristic of maintaining its heat for a prolonged period after de-energization. Yet another advantage is the provision of a hair curler device which needs no thermostats yet provides close temperature control.

Other objects and features will be in part apparent and in part pointed out hereinafter.

Briefly, a hair curler made in accordance with the invention employs an element which serves as a heater, heat exchanger and as a heat storage means. The element is composed of a conductive-filled crystalline polymer in which the conductive paths through the polymer are, at temperatures below the melting point of the crystalline polymer, made up primarily of alternate conducting links of carbon particle and crystalline polymer. The element has a positive temperature coefficient (PTC) of resistance and combines the heat storage means of wax-filled curlers due to a phase change in the polymer from amorphous to crystalline upon cooling and the concomitant latent heat released, with the fast warm up time of curlers using a resistance element as the heater and heat storage means The PTC effect prevents thermal run away of the element and self destruction without use of separate thermostat and also obviates the need for special sealing means required in wax-filled curlers since the anomalous increase in resistance and concomitant decrease in heat generation prevents the polymer from becoming molten.

In the accompanying drawings, in which one of the various possible embodiments of the invention is illustrated:

FIG. 1 is a cross section of a hair curler device made in accordance with the invention;

FIG. 2 is a top plan view of the FIG. 1 device;

FIG. 3 shows a curve for resistivity and one for heat of fusion plotted against temperature for a heater element made in accordance with the invention;

FIG. 4 shows a curve of surface temperature versus time during warm-up of a curler made in accordance with the invention and of a prior art curler, the curlers allowed to reach maximum temperature;

FIG. 5 shows a curve of surface temperature versus time during cooling after reaching maximum temperature of a curler made in accordance with the invention of a prior art curler;

FIG. 6 shows a curve similar to FIG. 4 but with the curlers deenergized when an indicating spot has been actuated; and

FIG. 7 shows a curve similar to FIG. 5 but of curlers cooled from the indicated temperature of FIG. 6.

Dimensions of certain of the parts as shown in the drawings may have been modified and/or exaggerated for the purposes of clarity of illustration.

The invention accordingly comprises the elements and combinations of elements, features of construction, and arrangements of parts which will be exemplified in the structures hereinafter described, and the scope of the application of which will be indicated in the following claims.

The heater of the present invention is made out of conductive filled polymer having a positive temperature coefficient of resistance above an anomaly or threshold temperature. The heater is connected to line voltage so that current flows therethrough, causing I^2R heating. When the temperature rises above the anomaly point, there is a sudden and marked increase in resistance to effectively cut off the current through the heater. Thus, this self-limiting of current eliminates the need for a thermostat or similar control employed by prior art devices. Among the other advantages the present invention offers is that extremely fast warm-up time is obtained while storing the heat for an extended period of time since the polymer acts as a heater, heat exchanger and heat sink or heat storage means.

In the prior art PTC characteristic has been produced in conductive polymers by utilizing the difference in thermal expansion between the polymer and the conductive fillers. That is, if the polymer has a greater thermal coefficient of expansion than the conductive filler particles the prior art teaches that this gives rise to a PTC effect. As the temperature is raised, the polymer expands more than the conductive particles, thus spreading the conductive particles apart. See, for instance, U.S. Pat. Nos. 2,978,665 and 3,243,753. However, while the PTC effect caused by this mechanism functions to limit the current level and thus use of such material obviates the need of a thermostat assuming the PTC effect is sufficiently large, the instant invention results in a further advantage.

In accordance with the present invention, a PTC effect is produced in the polymer which is related to the phase change in polymers having crystalline structure. When a crystalline type polymer, such as polyethylene, is loaded with carbon particles, such as carbon black, the carbon black is distributed unevenly in the polymer even with extensive mixing. So called crystalline polymers include amorphous regions, normally to an extent of up to 30 percent by volume and into which the carbon particles move preferentially when the molten polymer is cooled after mixing. With the proper carbon loading and thorough dispersion, the carbon particles form large aggregates separated by crystalline regions with the separation being in the order of several hundred angstroms. Thus the polymer contains a few chains of carbon particles forming a continuous chain through the material but the bulk of such chains will be broken up by crystalline regions of polyethylene. Electron tunneling can occur fairly readily through tin films of crystalline polymer so that carbon chains broken up by crystalline regions can have conductivities approaching those of uninterrupted carbon chains. As temperature rises, the carbon black masses separate due to the greater thermal expansion coefficient of the polymer in comparison to the carbon particles increasing the difficulty of electron tunneling between carbon masses which offsets the increased electron tunneling effect due to temperature rise while the crystalline regions remain intact. This may seen in FIG. 3 which shows a typical temperature versus resistivity curve J for a carbon loaded polyethylene polymer. At temperatures below roughly 100° C., the resistance level is relatively flat or even decreases slightly with increasing temperature. As the temperature rises further the carbon black masses move further apart and, more importantly, the macrostructure of the crystalline regions and at higher temperatures the microstructure, is destroyed with a concomitant reduction in their ability to allow electron tunneling. These effects, especially during the early stages of the crystalline phase change, give a resultant increase in resistivity as seen in the roughly 100°–140° C. range of curve J, FIG. 3. Further increase of temperature causes the crystalline regions to melt completely and the polymer to become semi-molten which permits the strained carbon masses to expand in the polymer and form a partial network of carbon through the material resulting in an increase in conductivity, as seen in curve J, FIG. 3 at temperatures above roughly 140° C.

In order to optimize the PTC effect care must be taken not to employ an excessive amount of the carbon filler. That is, rather than having essentially all chains made of alternate conducting links of carbon particles and crystalline polymer in the material at temperatures below the melting point of the crystals, excessive carbon will cause the formation of conductive paths formed predominantly of carbon chains (in much the same way as taught by U.S. Pat. Nos. 2,978,665 and 3,243,753 mentioned supra). The existence of a substantial number of such parallel conductive paths will result in material having a low base resistivity and a low PTC anomaly which would render the material unsafe for use as a hair curler element because of the danger of thermal run away unless supplemental protective means were employed and would also decrease the amount of latent heat available upon cooling.

As mentioned above, in order to optimize the PTC effect, it is necessary to produce a structure consisting essentially of carbon particles separated by crystalline polymer regions. During the anomaly, but before the complete melting of most of these crystalline regions, and anomalous change of the conductivity of these crystalline regions occurs which makes the material essentially non-conductive. This phenomena is shown in FIG. 3 for material having such structure consisting essentially of carbon particles separated by crystalline polymer regions. It will be seen that the resistance, curve J, experiences an anomalous increase before most of the crystalline region melts, curve K. Empirically it has been found that a 14–20 percent loading by weight of polymer such as polyethylene with a carbon black ASTM classification N–330, such as Vulcan 3 of Cabot Corporation, an oil furnace black with particles of 30 millimicrons produced such optimum results. Carbon loadings higher than this results in the existence of undesired chains formed only of carbon as mentioned above. To achieve this optimum condition the specific loading will vary somewhat with different types of carbon black for instance between N227 and N332 (ASTM) and with different polymers. Further, the degree and method of mixing affects dispersion and, hence, local resistivity and the quality of the PTC anomaly. That is, the method of mixing apparently influences the nature of the microcrystallinity and therefore, as previously shown, the conductivity of the PTC polymer. In the example mentioned above with an N–330 carbon black loading of 14–20 percent, specifically 19 percent, mixing with a Banbury mixer for 5 minutes while maintaining the temperature below 350° F. followed by mixing on a two roll mill with the rolls maintained at 305° and 308 F. respectively produce material having basal resistivity of 100 ohm-cm and a PTC anomaly covering approximately 3 orders of magnitude of resistance change. The same composition if mixed for only a few minutes results in material having a higher basal resistivity (in the order of several hundred ohm-cm) and a smaller PTC anomaly (in the order of two orders of magnitude).

Thus use of PTC polymeric material in accordance with the invention not only permits combining of several functions mentioned above but also utilizes a significant portion of the extra heat storage capabilities associated with the phase change. That is, changing of the crystalline polymer composition to the amorphous phase upon heating stores latent heat associated with the phase change which is released upon cooling to make a very efficient heat storage device.

Referring now particularly FIGS. **1** and **2**, numeral **10** indicates generally a hair curler made in accordance with the invention and comprises an outer generally cylindrical shell **12** of any suitable synthetic resin having a plurality of fingers **14** extending therefrom to facilitate holding of hair thereon. Shell **12** is formed with a closed end **16** and an open end **18** to permit passage therethrough of a heater assembly **20**. Assembly **20** includes an elongated annular heating element **22** formed of a conductive filled polymer having a positive temperature coefficient of resistance above an anomaly or threshold temperature. In order to provide optimum and reliable electrical contact with this polymeric composition, the inner and outer peripheral surfaces of element **22** are coated with a conductive material, such as electroless copper or electroless nickel and electroplated tin, which cooperate with sleeve members in close physical connection therewith. Sleeve **24**, formed of a good electrically conductive material, such as copper, and being of a size and sufficiently thick so that when pressed into the bore of element **22**, is firmly biased against the inside surface thereof. This serves both to make electrical contact with the conductive coating and also to support the coating and prevent it from peeling upon continued cycling of energization. A cap **26** is attached to sleeve **24** at one end thereof by conventional means, such as by soldering, and a pin **28**, attached as by soldering, extends therefrom. It will be understood that cap **26** could be formed integrally with sleeve **24** if so desired. Pin **28** extends through an aperture provided in cap **30** which is received in and closes the open end of shell **12**. Sleeve **32**, also of good electrically conductive material, is placed about the outer periphery of element **22** in tight physical contact therewith and is formed over at **34** as by crimping to enclose header **36**. Header **36** comprises and outer rim **38** of any conventional material, such as aluminum, surrounding an annulus **40** of dielectric material, such as a polymer, which in turn supports shelf **42**. Pin **44** extends from shelf **42** and is attached thereto by any convenient means, such as welding. To enhance the electrical connection between pin **44** and sleeve **32**, solder may be placed on surface **34** around the pin location or alternatively, shelf **42** could be electrically connected to rim **38** (not shown).

Element **22** is formed from a polymer material filled with conductive particles and having a PTC effect. The polymer is of a type having crystalline structure, such as a polyolefin, which gives rise to the PTC characteristic as well as providing the heat storage capabilities associated with the phase change from the crystalline phase to the amorphous phase. As mentioned above, in order to optimize the PTC characteristic and use of the phase change latent heat loading of the polymer with the conductive filler such as carbon, is kept within the range of 14–20 percent by weight. A unique advantage that this material offers is that the current, and hence heat generation, is limited by the marked increase in resistance before the material becomes semi-fluid. That is, the elongated annulus **22** still maintains its configuration so that there is no need for providing elaborate sealing means as in the case of devices using fusible waxes. Yet the advantages derived from the phase change are utilized. The material is chosen so that using line voltage, resistance will approach the level shown in FIG. 3 by the dashed lines. At this point, heat generation matches heat dissipation with very little change in temperature. The polymer material may be made as follows. A crystalline polymer, such as a high density polyethylene with a high crystallinity is mixed with carbon black such as Vulcan 3 of Cabot Corporation, an oil furnace black with particles of 30 millimicrons, along with desired additives such as an antioxidant and a flame retardant. One such antioxidant found to be useful is a phenylbetanapthylamine, such as Antioxygene MC of Ugine-Kuhlmann, Organic Products Division of F.M.C. s.a., of France. A suitable flame retardant is a combination of Antimony Oxide and a highly chlorinated perchloropentacyclodecane, such as Dechlorane of Hooker Chemical Company. The optimum ratio has been found to be between 1:3 and 1:5 respectively. Mixing is continued until the carbon black is well dispersed throughout the polymer after which the material is formed by standard plastic processing procedures. Further details on mixing and forming similar material but with different carbon loadings may be had by reference to coassigned and copending application, Ser. No. 6,086, filed Jan. 27, 1970.

Combining the heating and heat storing functions by means of the PTC polymeric element results in a very fast warm-up time along with the slow cooling characteristics of the wax-filled devices. In FIG. **4** a comparison is shown between a wax-filled curler (curve B) and a curler made in accordance with the instant invention (curve A). Both curlers have been allowed to warm up to their maximum temperature. It will be noted that approximately 18 minutes is required for the wax-filled curler to reach its maximum temperature compared to approximately 4 minutes for the curler of the instant invention. On the other hand, as seen in FIG. **5**, when these same curlers are permitted to cool, the wax-filled device (curve D) and the PTC curler (curve C) are quite similar with the PTC curler retaining more heat for approximately the first **12** minutes, which period covers the time curlers are normally left in contact with hair.

Another way to compare operation of the PTC curler with a wax-filled device is shown in FIGS. **6** and **7**. It is common to place on the surface of the curler a spot or dot of temperature-responsive paint which changes color when a predetermined temperature is reached. When the paint turns color, for instance, from red to black, the user is notified that the curler is ready for use. A dot of this material was placed on both the PTC curler and the standard wax-filled curler. The heating curves of FIG. **6** and cooling curves of FIG. **7** were plotted for devices which were de-energized when the indicating paint changed color. The dashed line G in FIG. **6** represents the temperature at which the indicating paint changed from red to black, indicating that the curlers were ready for use and in FIG. **7** the temperature at which the indicating point turns back from black to red. The PTC curler (curve E) was ready in approximately two minutes while the standard wax-filled version required approximately 11 minutes. Upon cooling from these indicated "ready" temperatures, as seen in FIG. **7**, the heat storage for both devices is quite similar, the PTC curler (curve H), retaining more heat for the first portion of the cool down curve and the wax-filled retaining more heat for the last portion of the curve. As stated above, it is desirable to provide more heat during the first few minutes since the curler is normally left in contact with the hair for only a short time, usually 10 minutes or less.

Thus the use of a polymer PTC heater for a hair curler results in a very fast warm-up time, yet also has a very favorable cool down time. It further obviates the need for additional thermostats to limit the current since the PTC characteristic, as seen in FIG. 3, effectively limits the current flow when the operating temperature has been reached. Additionally, the polymer is rugged and not subject to damage upon dropping, is extremely uniform in heating along its surface, and is readily shaped using conventional polymer forming techniques.

In view of the above, it will be seen that the several objects of the invention are achieved and other advantageous results attained.

It is to be understood that the invention is not limited in its application to the details of construction and arrangement of parts illustrated in the accompanying drawings, since the invention is capable of other embodiments and of being practiced or carried out in various ways. Also, it is to be understood that the phraseology or terminology employed herein is for the purpose of description and not of limitation.

As many changes could be made in the above constructions without departing from the scope of the invention, it is intended that all matter contained in the above description or shown in the accompanying drawings, shall be interpreted as illustrative and not in a limiting sense, and it is also intended that the appended claims shall cover all such equivalent variations as come within the true spirit and scope of the invention.

What is claimed is:

1. An electrically heated hair curler comprising a generally cylindrical outer shell, a plurality of fingers extending outwardly therefrom, an element which serves both as a heater and as a heat storage means mounted within the shell in close heat transfer relation therewith, the element composed of a crystalline polymer filled with conductive particles and having a positive temperature coefficient of resistance in which the conductive paths through the polymer are made up primarily of alternate conducting links of conductive particles and crystalline polymer at temperatures below the melting point of the crystalline polymer, the element having a first relatively low resistance mode at ambient room temperature and a second high resistance mode at an operating temperature, the element having a heat of fusion curve such that heat is stored in the element as crystalline regions change to the amorphous state, the second high resistance mode limiting the temperature rise of the element before all of the crystalline polymer changes state whereby the structural integrity of the element is maintained yet permitting latent heat of fusion to be used to keep the curler warm for an extended period of time after deenergization; and means for making electrical connection with the element.

2. A hair curler according to claim **1** in which the conductive filler is carbon black.

3. A hair curler according to claim **1** in which upon sufficient heating of the hair curler the electrical resistance of the element increases several orders of magnitude, most of the increase occurring prior to the phase change of most of the crystalline polymer regions to amorphous polymer.

4. A hair curler according to claim **1** in which the polymer is a crystalline polyolefin.

5. A hair curler according to claim **2** in which the polymer is a copolymer of polyethylene.

6. A hair curler according to claim **1** in which the polymer is a high density polyethylene.

7 A hair curler according to claim **2** in which the carbon black comprises 14–20 percent by weight of the element.

8. A hair curler according to claim **1** in which the polymer is a polypropylene.

9. A hair curler according to claim **1** in which the warm up time is less than 5 minutes.

10. An electrically heated device comprising an element which serves both as a heater and as a heat storage means, the element composed of crystalline polymer filled with 14–20 percent by weight of carbon particles and having a positive temperature coefficient of resistance, the element having a first relatively low resistance mode at ambient room temperature and a second high resistance mode at an operating temperature, the element having a heat of fusion curve such that heat is stored in the element as crystalline regions change to the amorphous state, the second high resistance mode limiting the temperature rise of the element before all the crystalline polymer changes state whereby the structural integrity of the element is maintained yet permitting latent heat of fusion to be used to keep the device warm for an extended period of time after deenergization, and means for making electrical connection with the element.

11. An electrically heated device according to claim **10** in which the element is in the form of an elongated annulus and further including a generally cylindrical outer shell, a plurality of fingers extending outwardly from the shell, and the element located within the shell in good heat transfer relation therewith

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