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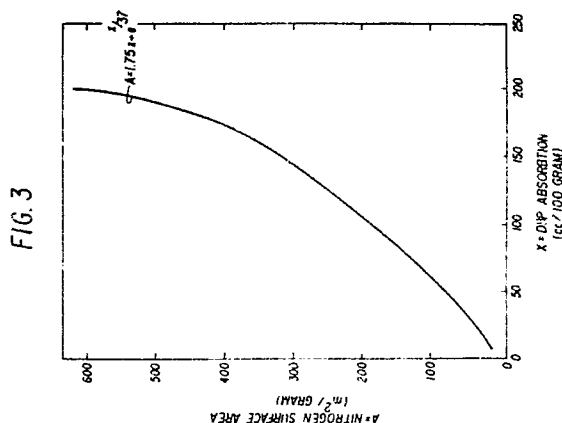
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(54) **PTC compositions containing carbon black.**

(57) A new semiconductive material includes a suitable polymer or blend of polymers and a carbon black material in an amount of 4% to 25% based on the total weight of the semiconductive material, having a relatively low reticulate structure; and being essentially non-chemically surface-treated (having essentially a non-oxidized surface) such that the pH of the carbon black is at least 4.0, and generally about 5.0 to 8.5. These non-surface treated carbon blacks generally have a dry volatile content of about 3.0 or less and usually 2.5 or less. The particular carbon blacks suitable for the semiconductive materials of the invention are essentially non-surface treated, have a midrange value for dry volume resistivity, and have a nitrogen surface area A in m^2/g greater than or equal to $1.75x + e^{x/37}$ where x is the DBP absorption of the carbon black in $\text{cm}^3/100$ grams. Such carbon blacks decrease the annealing times needed to less than about 3 minutes, and generally in the time period of less than 1 minute.



PTC compositions containing a non-surface treated carbon black having an intermediate resistivity for reduced annealing

The present invention relates to a new semiconductive material which includes a suitable polymer or blend of polymers and a carbon black material.

In about 1957 it was found that a ceramic material suitably loaded with conductive particles exhibited a sharp rise in electrical resistance at its Curie temperature and this phenomenon was named "The Positive Temperature Coefficient Phenomenon". Since 1957 extensive work has been done in Positive Temperature Coefficient (PTC) materials, particularly in the area of semicrystalline polymers loaded with finely divided conductive materials, particularly carbon black. This extensive work has been directed to improving the PTC phenomenon, especially for the purpose of providing a material having a built-in temperature control such that when the temperature of the material reaches a predetermined upper limit, the material becomes so resistive that it is essentially no longer conductive. This PTC phenomenon has been employed most effectively in the electric blanket industry to provide a grid of body heat-responsive PTC material surrounding a pair of conductive wires within a suitable blanket fabric material. The PTC materials have been developed with sufficient self regulating precision to provide electrode (conductor) surrounding material having the capacity to sense and deliver heat to all parts of the body in proportion to the body heat requirements at any given time or location under the blanket without the necessity of internal blanket thermostats.

In spite of the extensive work that has been done in the area of new PTC materials, as evidenced by the scores of patents and articles directed to new compositions and new theories, the PTC phenomenon is one which is to date very poorly understood. A number of theories have been proposed in an attempt to explain the conductivity phenomenon for PTC materials. One theory is that the sharp positive temperature coefficient of resistance at a predetermined temperature results from thermal expansion of the polymer/finely divided conductor matrix. This theory is based on the proposal that the conductive filler is initially spread through the polymer on a network of conductive chains and, as the material is heated, the conductive filler is spread out by thermal expansion until non-conductive behavior is experienced at the crystalline melting point. Others have theorized that the PTC phenomenon is due to a loss of conduction due to the more difficult electron tunneling through large intergrain gaps between conductive filler particles upon temperature rise. This theory is based upon the premise that the PTC phenomenon is due to a critical separation distance between carbon particles in the polymer matrix at the higher temperature. Still others have theorized that the PTC phenomenon is directly related to the polymer crystallinity for a given polymer so that increased crystallinity in a particular polymer causes increased PTC anomaly. For this last theory, however, there is no correlation between degrees of crystallization and the amount of PTC phenomenon that might be experienced in different polymers.

Much of the work directed to new PTC composite materials has been directed to particular conductive materials loaded into the polymer carrier and, in particular, to carbon blacks having particular reticulate structures, resistivities and/or particle sizes -see for example U.S. Patents Nos. 4,277,673 and 4,327,480 and 4,367,168 of Kelly and U.S. Patent No. 4,237,441 of Van Konynenburg et al. The patents and literature distributed by carbon black suppliers teach that the electrical conductivity of carbon blacks depends to a great extent upon the structure of the carbon blacks and the amount of surface treatment (oxidation). It is well known that higher reticulate structure grades impart higher conductivity than low reticulate structure grades and that surface treatment decreases conductivity. The reticulate structure of a carbon black is generally measured by its oil (dibutyl phthalate) absorption. Higher structure grades, which have a relatively large void area, absorb more oil than lower structure grades.

Carbon blacks consist of spherical particles of elemental carbon permanently fused together during the manufacturing process to form aggregates. These aggregates are defined by particle size and surface area; aggregate size or structure (reticulate structure); and surface chemistry. The particle size of carbon blacks is the size of the individual particles which are fused together during manufacture to make the aggregate and varies inversely with the total surface area of the aggregates. The surface area of carbon black aggregates is most commonly expressed in terms of nitrogen adsorption in m²/gram using the B.E.T. - (Brunauer, Emmet, Teller) procedure well known in the art. Carbon blacks having a relatively small particle size, and therefore a relatively high aggregate surface area, exhibit better conductivity or lower volume resistivity.

The size and complexity of the carbon black aggregates is referred to as "structure" or "reticulate structure". Low structure carbon blacks consist of a relatively small number of spherical carbon particles fused together compactly during manufacture to provide a relatively small amount of void space within the aggregate. High structure carbon blacks consist of more highly branched carbon particle chains which, when fused together during manufacture, provide a large amount of void space within the aggregate. The structure level of carbon blacks is measured by its oil (dibutyl phthalate) absorption. Higher structure grades of carbon blacks absorb more oil than lower structure grades because of the larger void volume within the aggregates.

During the manufacture of carbon blacks, some oxidation naturally occurs on the surface of the aggregates resulting in the presence of chemisorbed oxygen complexes such as carboxylic, quinonic, lactonic and phenolic groups on the aggregate surfaces. Some carbon blacks are further surface treated to provide more chemisorbed oxygen on the aggregate surfaces. These surface treated carbon blacks can be identified by their low pH, less than 4.0 and generally in the range of about 2.0 to 3.0, and/or by measuring the weight loss of dry carbon black when heated to 950° C. This weight loss is referred to as "volatile content" and for surface treated carbon blacks, generally is at least 3.0 weight percent and generally in the range of about 5.0 to 10.0 weight percent. The degree to which carbon blacks impart some electrical conductivity (or lessen volume resistivity) to normally non-conductive plastics depends upon four basic properties of the carbon black: surface area, structure, porosity and surface treatment. Higher structure carbon blacks impart higher conductivity (lower volume resistivity) than lower structure grades because the long, irregularly-shaped aggregates provide a better electron path through the compound. Surface treatment, on the other hand, always causes the volume resistivity to be high (low conductivity) because the surface oxygen electrically insulates the aggregates.

One of the knowns about PTC polymeric materials is that the polymer must, in its final state, be partly crystalline in order to exhibit PTC behavior. Experimentation with amorphous polymers filled with conductive particles, such as carbon black, do not show any increase in resistance on heating. Polymeric matrix material having a sharp increase in resistance at a predetermined temperature (PTC material) to date has not been electrically conductive without an annealing period ranging from minutes to days. U.S. Patent No. 3,861,029 points out that polymeric materials loaded with a sufficiently high percentage of carbon black to produce a conductive material when first prepared exhibit inferior flexibility, elongation, crack resistance and undesirably low resistivity when brought to peak temperatures. Accordingly, it has been necessary to limit the carbon black content of the polymeric matrix and to anneal (heat treat at or above the crystalline melting point) for a period of time to slowly develop crystallinity until the material reaches a constant room temperature resistance. In order to provide a degree of crystallinity in the polymeric matrix materials, after melting and extrusion, it has been necessary to anneal in order to allow the polymer matrix chains to be packed together in an ordered array so that the molecules have sufficient time during heat treatment - (annealing) for the required translational and conformational reorganizations necessary to fit the molecules into the necessary crystalline lattice structure of the polymeric material.

It is also known that the use of highly conductive carbon blacks results in a material requiring rigorous annealing to achieve a constant resistance, or results in compositions having resistances too high to be of practical use. The prior art compositions, however, have required the highly conductive carbon blacks to achieve a composition having sufficient electrical conductivity and exhibiting PTC behavior. As disclosed in the Kelly Patents, US Patents Nos. 4,277,633 and 4,327,480 and 4,367,168, the use of highly resistive (essentially non-conductive) carbon blacks such as the surface treated Mogul L and Raven 1255, when used in the range of 5 to 15%, substantially reduces the necessary annealing time down to a period of about two to three hours in some cases.

In accordance with the present invention, it has been found that the selection of a carbon black having essentially no chemical surface treatment (oxidation), as indicated by a pH of at least 4.0 and generally in the range of 5.0 to 8.5, and having relatively low reticulate structure as defined by the relation between nitrogen surface area and DBP absorption according to the following equation: $A = 1.75x + e^{x/37}$ where A = nitrogen surface area in m²/gram and x = DBP absorption in cc/100 grams, substantially reduces the annealing time necessary for the PTC material to a period of time less than about 3 minutes, and generally less than about 30 seconds, e.g., 15-20 seconds.

In brief, the present invention is directed to a revolutionary new semiconductive material having a sharp rise in electrical resistance at a predetermined maximum temperature. This revolutionary new material exhibits a sharp positive temperature coefficient (PTC) of resistance at a predetermined temperature with substantially reduced annealing times necessary after extrusion to achieve an essentially constant resistance at room temperature. The PTC composition includes a suitable semicrystalline polymer; a suitable

polymeric material including a sufficient number of polar molecules for electrical conductivity; and a finely divided, non surface-treated (essentially non-oxidized surface as indicated by a pH of at least 4.0 and generally 5.0 to 8.5) carbon black having an intermediate dry volume resistivity with a critical relationship between N_2 surface area and DBP absorption.

5 In accordance with an important feature of the present invention, the carbon blacks incorporated into the compositions of the present invention are extremely mobile to permit rapid movement of the carbon particles during crystallization. The mobility of the carbon blacks provides new and unexpectedly rapid crystallization after an extrusion or other material shaping process resulting in unexpectedly short thermal structuring (annealing) times. The carbon blacks defined herein have been found to be capable of easily
10 moving into the amorphous regions of the polymer portion of the composition of the present invention for the purpose of being disposed, quickly, sufficiently close to one or more polar moieties of the amorphous, polar material for interaction with the polar moieties to achieve excellent electrical conduction while exhibiting PTC behavior.

Without being limited to any particular theory as to the carbon-polar moiety interaction, it is believed
15 that the carbon particles conduct electrons onto the polar moieties, e.g., carboxyl groups, of the amorphous polymer which then conduct electrons onto the crystal structure of the crystalline portion of the semicrystalline polymer resulting in electrical conductivity. Further, the mobility of the carbon blacks defined herein is extremely important in the crystallization process so that the carbon particles are capable of rapid movement away from the forming crystallites to permit the relatively unhindered, rapid formation of a
20 regular crystal lattice structure through orderly chain packing, thereby substantially lessening the required annealing time.

In accordance with another important feature of the present invention, the finely divided carbon black dispersed throughout a mixture of a semicrystalline polymer and a polymer having polar molecules has a nitrogen surface area A related to the DBP absorption in accordance with the following equation: $A = 1.75x$
25 $+ e^{x/37}$ where A is the nitrogen surface area in $m^2/gram$ and x is the DBP absorption in cc/100 grams. These polymeric matrix materials are essentially non-conductive upon initial mixing and before a short anneal period since they contain about 25% or less carbon black. After holding the material at or above the melt temperature (annealing) for a period of only about 3 minutes or less and generally less than 1 minute, the materials exhibit excellent PTC characteristics.

30 Accordingly, an object of the present invention is to provide a new and improved semiconductive composite polymer/conductive particle material wherein the conductive particles exhibit new and unexpected mobility to permit rapid crystallization of a semicrystalline polymer to achieve a material having a constant resistance at room temperature with an unexpectedly short annealing period.

Another object of the present invention is to provide a new and improved semiconductive composite
35 polymer material containing a crystalline or semicrystalline polymer; a polymeric material containing polar molecules; and dispersed, finely divided conductive carbon black particles requiring substantially shorter annealing after extrusion.

Still another object of the present invention is to provide a new and improved semiconducting composite polymeric material exhibiting a sharp positive temperature coefficient of resistance at a predetermined
40 temperature.

Another object of the present invention is to provide a new and improved PTC material including a partially crystalline polymer containing dispersed conductive, essentially non-surface treated carbon black particles having a pH of at least 4.0 and generally in the range of 5.0 to 8.5, wherein the nitrogen surface area and DBP absorption are related in accordance with the equation $A = 1.75x + e^{x/37}$ wherein A =
45 nitrogen surface area in $m^2/gram$ and $x =$ DBP absorption in cc/100 grams, to establish a sharp rise in electrical resistance at a predetermined temperature.

Still another object of the present invention is to provide a new and improved polymeric composite material containing electrically conductive particles in an amount of 25% by weight or less while achieving a material having a stable conductivity and exhibiting sharp PTC behavior with very little annealing of the
50 material needed after shaping.

A further object of the present invention is to provide a new and improved PTC material having non-surface treated low reticulate structure carbon blacks capable of substantial electrical conductivity with very little annealing needed.

The above and other objects and advantages of the present invention will be come apparent from the
55 following detailed description of the preferred embodiment taken in conjunction with the drawings.

FIG. 1 is a enlarged, elevated, partially broken-away view of the heating cable of the present invention;

FIG. 2 is a broken-away top view of an electrical blanket containing the heating cable used in conjunction with the present invention; and

FIG. 3 is a graph of N₂ surface area vs. DBP absorption defining the carbon blacks incorporated into the polymeric matrix compositions of the present invention.

5 The polymer component used in the semiconductive materials of the present invention may be a single polymer or a mixture of two or more different polymers. The polymers should have at least 10% crystallinity, and since greater crystallinity favors more intense PTC behavior, its crystallinity is preferable about 15% to 25% based on the polymer volume. Suitable polymers include polyolefins, especially polymers of one or more α -olefins, e.g., polyethylene, polypropylene and ethylene, propylene copolymers.
10 Excellent results have been obtained with polyethylene, preferably low density polyethylene.

In addition to the semicrystalline polymers, a material, e.g., polymer, copolymer or terpolymer, providing a sufficient number of polar groups, e.g., carboxyl groups, is produced in an amount of about 5% by weight to about 20% by weight of the composition to provide sufficient conductivity to the composition. The conductivity of the semiconductive materials of the present invention no longer increases at polar
15 polymer loadings above about 20% by weight although more than 20% by weight of the polar polymer can be included so long as consistent with the structural (strength) requirements of the material. Materials having more than one polar group, e.g., di-carboxyls, provide the necessary conductivity to the materials at lower loadings, e.g., 2 to 3% by weight of the composition, while polymers having a single polar group such as ethylene ethyl acrylate, generally are required in an amount of at least about 5% by weight and
20 preferably 10% to 20%. Suitable examples of polar polymers include copolymers of one or more α -olefins, e.g., ethylene with one or more polar copolymers, e.g., vinyl acetate acrylic acid, ethyl acrylate and methyl acrylate such as ethylene vinyl acetate, ethylene ethyl acrylate, and its metal (e.g., Na, Zn) salts, ethylene acrylic acid, terpolymers of ethylene acrylic acid and/or its metal salts and methacrylic acid, polyethylene oxide and its metal salts and polyvinyl alcohol; polyarylenes, e.g., polyarylene ether ketones and sulfones
25 and polyphenylene sulfide; polyesters, including polylactones, e.g., polybutylene terephthalate, polyethylene terephthalate and polycaprolactone; polyamides; polycarbonates; and fluorocarbon polymers, i.e., polymers which contain at least 10%, preferably at least 20%, by weight of fluorine, e.g., polyvinylidene fluoride, polytetrafluoroethylene, fluorinated ethylene/propylene copolymers, and copolymers of ethylene and a fluorine-containing comonomer, e.g., tetrafluoroethylene, and optionally a third comonomer. In processing, it
30 is preferred to mix the carbon blacks into the polar polymer prior to adding the semicrystalline polymer to the composition.

As indicated in the prior art, and particularly Kelly U.S. Patents Nos. 4,277,673, 4,327,480 and 4,367,168, all of the prior art teachings, with the exception of the Kelly patents, relating to the compounding of a PTC material have dealt specifically with low volume resistivity (high conductivity) relatively high
35 reticulate structure carbon blacks for the purpose of achieving sufficient carbon particle to particle conductivity. As disclosed in the Kelly patents, it was found that the inclusion of about 5 to 15% by weight of a low conductivity (high dry volume resistivity) carbon black material having a 5% volatile content (Mogul L) results in better conductivity and shorter annealing times.

The low structure, medium conductivity, low volatile content carbon blacks incorporated in the polymer
40 matrix compositions of the present invention heretofore have not been used with the prior art polymers to obtain suitable PTC materials. As shown in the drawing, these carbon blacks are defined by nitrogen surface area and DBP absorption as falling on or above the curved line represented by the equation $A = 1.75x + e^{x/37}$ where A is the carbon black nitrogen surface area in m²/gram and x is the DBP absorption in cc/100 grams.

45 It should be understood that other carbon blacks can be dispersed in the polymeric matrix materials of the present invention, so long as one or more of the above-defined carbon blacks are present in an amount of 4 to 25% by weight and preferably 10 to 20% by weight of the polymeric matrix composition of the present invention. Examples of suitable carbon blacks include Black Pearls 800, 880, 900 and 1100 and Regal 660 from Cabot Corp. and Raven 1250 and 1500 from Columbian Chemicals Company. The above
50 Cabot Corp. carbon blacks have apparent densities of 29, 23, 28, 24 and 31 pounds/ft³, respectively. Apparent density is informative of the physical condition of the carbon black -that is, whether the carbon black is in a fluffy or pelletized condition. Either fluffy or pelletized (beaded) forms of carbon black are useful in the present invention to achieve the new and unexpected properties and advantages found in the compositions disclosed herein.

55 The semiconductive polymer matrix compositions containing dispersed carbon black particles forming the PTC materials of the present invention preferably contain an antioxidant in an amount of, for example, 0.5 to 4% based on the volume of the polymeric material, as well known in the art, for example, a 1,3-di-*t*-butyl-2-hydroxy phenyl antioxidant. The antioxidant prevents degradation of the polymer during processing

and during ageing. The matrix also can include conventional components such as non-conductive fillers, processing aids, pigments and fire retardants. The matrix is preferably shaped by melt-extrusion, molding or other melt-shaping operation. Excessive working of the polymer matrix composition should be avoided to prevent excessive resistivity in the material. It appears that restricting the work done on the polymeric matrix material allows the formation of a material conducive to the tunneling conduction mode. Underworking of the material will not bring this tunneling conduction mode to complete development and overworking will destroy the tunneling mode and cause the resistivity of the polymeric matrix material to increase beyond recovery. If the material is slightly underworked, additional working at the extruder will enhance the conduction properties. It appears from the data collected on the polymeric compositions of the present invention that specific work of 0.1 to 0.15 horsepower-hour per pound of material is a suitable operating range for the compounding equipment. In accordance with a preferred embodiment, external heat should be supplied such that the polymer matrix mix will discharge, after the appropriate mixing time, at about 335°F.

In the mixing step, the carbon black and any other components are incorporated into polymeric materials using a high-shear intensive mixer such as a Banbury Mixer. The material from the Banbury Mixer can be pelletized by feeding it into a chopper and collecting the chopped material and feeding it to a pelletized extruder.

The pelletized mix can be used for subsequent casting of the mix or for extrusion onto appropriate electrodes to produce heating wire, sensing devices, and the like, and thereafter the product is provided, if desired, with the extrusion of a suitable shape retaining and/or insulating jacket followed by relatively short thermal structuring (annealing).

After the polymeric matrix composition has been shaped, it is then cross-linked to immobilize the conductive carbon black particles dispersed throughout the polymeric material. The cross-linking traps the conductive particles to prevent them from migrating, although there is some mobility in migration of the carbon particles during crystallization when it is believed that the conductive particles are swept into the amorphous regions of the semicrystalline polymeric material. Cross linking not only immobilizes the carbon particles, but also cross-links the amorphous polymer molecules thereby immobilizing the crystalline portion of the polymer and the carbon black in proper position for electron tunneling. The polymeric matrix preferably is cross-linked by irradiation. The cross-linking forms strong carbon-carbon bonds to effectively immobilize the free carbon particles in their positions at the time of cross-linking to prevent the formation of conductive carbon chains above the melt transition temperature.

To achieve the full advantage of the present invention, the polymeric matrix material should be irradiated to a total dose that exceeds 20 Mrads, preferably at least 30 Mrad. The carbon black, while necessary in order to produce a polymeric matrix having a sharp increase in resistance at a predetermined temperature requiring a relatively short anneal time appears to be a relatively minor although necessary conduction material in the PTC materials of the present invention.

It is preferred to use an amount of conductive particles less than about 25% by weight of the polymeric matrix. The composition of the present invention, containing possibly less carbon black loading than the materials of the prior art, have excellent properties of elongation, flexibility and crack resistance. Further, because the tunneling mode of electrical conductivity is the major mode of electrical conduction in the materials of the present invention, although the carbon black loading is relatively small, the material has good initial conductivity shortly after exiting the extruder while also achieving very high resistance at the higher temperatures as necessary in accordance with the PTC phenomenon.

The polymeric matrix materials of the present invention are particularly useful for the manufacture of self limiting heating wire, for electric blankets and the like. Turning to the drawings, and initially to FIGS. 1 and 2, there is shown a suitable electric blanket, generally designated by numeral 10, containing heating wire, generally designated 12, manufactured with the polymeric matrix compositions of the present invention. As shown in FIG. 1, the heating wire 12 contains a pair of spaced conductors 14 and 16 which may be suitably wrapped around core materials 18 and 20, respectively, as well known in the art. As shown in FIG. 2, this heating cable 12 is disposed within a suitable fabric material, e.g. polyester and/or acrylic fabric 28 provided with an electrically connected on-off switch 30 and an ambient responsive control 32.

Such heating wires exhibiting PTC characteristics are well known and have extruded thereon (in accordance with standard extrusion techniques) the composition of this invention generally designated by reference numeral 22 in what is referred to as a "dumbbell" cross-section so as to cover the conductors 14, 16 and cores 18 and 20 and provide a continuous inter-connecting web 24 of polymeric matrix material forming heating paths, as shown in FIG. 1. A suitable form-retaining and insulating jacket or covering 26 is

also extruded by conventional techniques over the full length of the heating cable 12. Cross-linking is effected preferably by irradiation immediately after extrusion. The desired annealing for the requisite time is thereafter provided at the desired temperature, the cable being conventionally spooled for ease of handling and placed in a suitable oven.

5 As shown in FIG. 2, this heating cable 12 is disposed within a suitable fabric material, e.g., polyester and/or acrylic fabric 28 provided with an electrically connected on-off switch 30 and an ambient responsive control 32.

Further, it has been found that at a point where the polymeric matrix material exits an extruder, for example, if the ratio of surface area to volume of the material exceeds 35 square centimeters per cubic centimeter, it is preferred to anneal at 13 watts per cubic centimeter or less. This figure can be substantially different where the material is formed into substantially different configurations than the wire configuration investigated for the purposes of the present invention.

After final cross-linking, the polymeric matrix material forming the ground wire or other configuration becomes relatively insensitive to temperatures in the melting range of most jacketing materials. Accordingly, if the jacket is extruded around the polymeric matrix material at 2 to 3 hundred feet per minute, there will be no problems with heat degradation. However, if the extrusion process is stopped for any reason, the polymeric matrix material in the extruder cross head may undergo degradation.

20 EXAMPLE

Composite polymeric matrix materials were prepared using only 14.4% Regal 660 carbon black from Cabot Corporation having a nitrogen surface area of 112 m²/gram, a particle size of 24 millimicrons, a DBP of 60cc/100grams, a volatile content of 1.0%, a pH of 7.5, and an apparent density of 31 pounds/ft³. The polymer used was a combination of Union Carbide DFD 6005 polyethylene and an ethylene ethyl acrylate copolymer. The formulation was as follows:

<u>Component</u>	<u>% By Weight</u>
30 Regal 660 carbon black	14.4
Union Carbide DFD 6005 polyethylene	53.2
35 Ethylene Ethylacrylate copolymer	14.4
Alumina trihydrate	18.0
	100.0
40	

The materials of the above formulation were granulated, mixed in a Banbury mixer, and plaques were pressed from the ground materials around a pair of electrodes at a temperature of 350°F at 1500 p.s.i.g. for three minutes and the volume resistivity measured and found to be 6,154 ohm-cm. The material of the above formulation was then extruded around a pair of electrodes, as shown in the drawing, and it was found that constant room temperature conductivity was achieved within 70 seconds of annealing at 350°F. The resulting PTC wire had a room temperature conductivity of 2.4 watts per foot and excellent steeply sloped PTC behavior.

50 Obviously, many modifications and variations of the present invention are possible in light of the above teachings. Thus, it is to be understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described above.

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Claims

1. An electrically conductive material having an electrical resistance that increases with increasing temperature, wherein said material comprises a polymer having at least 10% crystallinity as determined by X-ray diffraction, and carbon black dispersed in the polymer in an amount of 4% to 25% based on the total weight of material, said carbon black having a pH of at least 4.0 and having a N_2 surface area A in $m^2/gram$ of at least $1.75x + e^{x/37}$ where x is the dibutyl phthalate absorption of the carbon black in cc/100 grams, said material requiring only a short period of annealing to achieve a constant room temperature resistance.
2. An electrically conductive material exhibiting PTC behaviour comprising a first, semicrystalline polymer having at least 10% crystallinity; a second polymer having one or more polar groups in an amount of at least 2% by weight of the material and carbon black dispersed in the polymer in an amount of 4% to 25% by weight of the material, said carbon black having a pH of at least 4.0 and having a N_2 surface area A in $m^2/gram$ of at least $1.75x + e^{x/37}$ where x is as defined in claim 1.
3. A material as claimed in either of claims 1 and 2 wherein the carbon black has a pH in the range of 5.0 to 8.5.
4. A material as claimed in any one of claims 1 to 3, wherein the carbon black has a pH in the range 5.5 to 8.0.
5. A material as claimed in either of claims 1 and 3, wherein the carbon black has a dry volatile content of about 3.0% by weight or less.
6. A material as claimed in any one of claims 1, 3 and 4 wherein the carbon black has a pH of at least 5.0 and has a dry volatile content of 2.5% by weight or less.
7. A material as claimed in any one of claims 1 and 3 to 6, wherein the carbon black has a dry volatile content, when heated at 950°C, of 1.0 to 1.5%.
8. A material as claimed in claim 2 wherein the second polymer is included in an amount of 5% to 20% by weight of the composition.
9. A material as claimed in either of claims 2 and 8, wherein the second polymer is included in an amount of 10 to 20% by weight of the material.
10. A material as claimed in any one of claims 1 to 8, wherein the carbon black is included in the composition in an amount of 10% to 20% by weight of the material.
11. A material as claimed in any one of claims 1 to 9 wherein the carbon black is included in the composition in an amount of 10% to 15% by weight of the material.
12. A material as claimed in claim 2 wherein the semicrystalline polymer comprises 40% to 80% by weight of the material.
13. A material as claimed in any of the preceding claims in the form of an article of manufacture comprising a pair of electrodes interconnected by said material.
14. A material as claimed in any of claims 2 to 12 in the form of an article of manufacture comprising a pair of electrodes interconnected by said material.

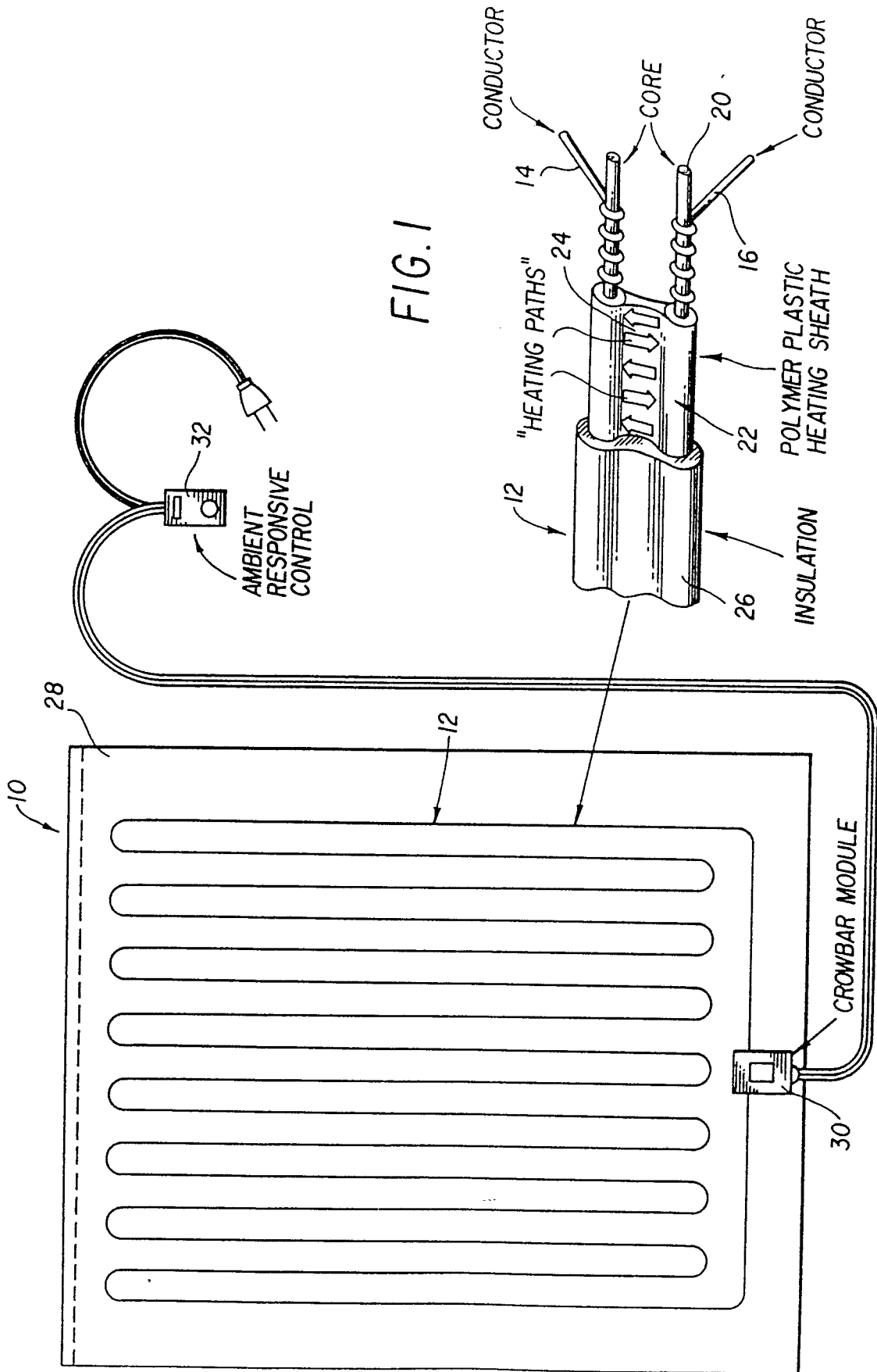
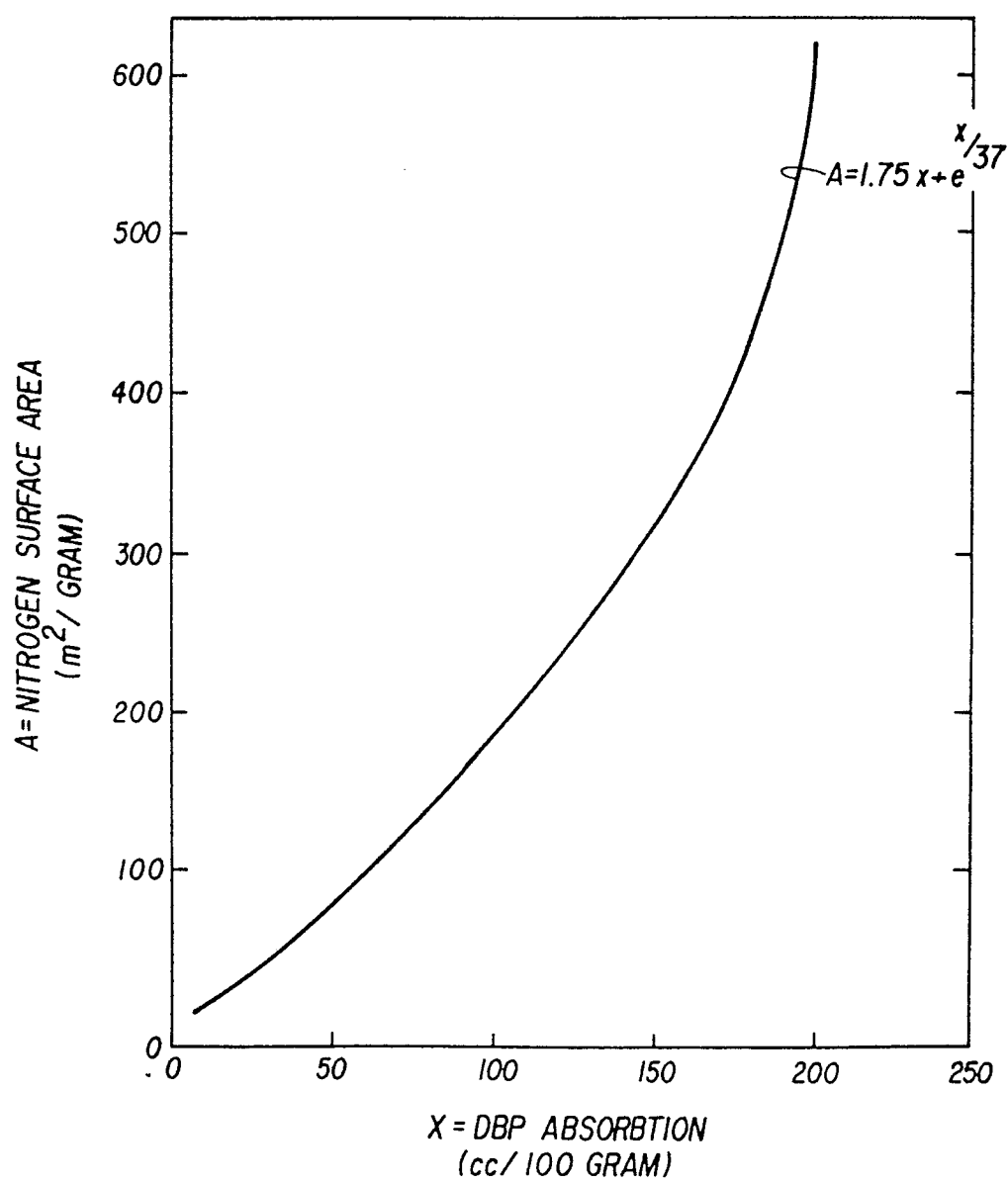


FIG. 3





DOCUMENTS CONSIDERED TO BE RELEVANT			EP 86309505.5
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X;Y	JP - A2 - 60-93 702 (MATSUSHITA) * Claims; examples * & CHEMICAL ABSTRACTS, vol. 103, no. 14, October 7, 1985, Columbus, Ohio, USA page 647 * Abstract-no. 114 488r * ---	1,3-7, 10,11, 13; 2,8,9, 12,14	H 01 B 1/24 //H 05 B 3/14 C 08 K 3/04
Y	US - A - 4 388 607 (TOY et al.) * Abstract; examples * ----	2,8,9, 12,14	TECHNICAL FIELDS SEARCHED (Int. Cl. 4) H 01 B H 05 B 3/00 H 01 C 7/00 C 08 K
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 05-03-1987	Examiner KUTZELNIGG
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			