

[54] **PROCESS FOR MAKING CONDUCTIVE POLYMERS AND RESULTING COMPOSITIONS**

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[58] Field of Search: **252/511, 512, 514; 260/41 B**

[56] **References Cited**

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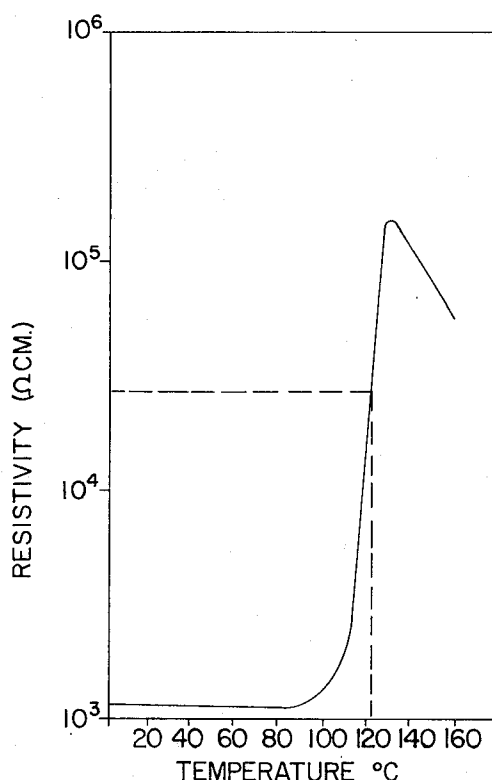
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[57] **ABSTRACT**

Conductive polymer having a steeply-sloped positive temperature coefficient (PTC) of resistance is composed of crystalline polymer having a narrow molecular weight distribution and filled with conductive particles such as carbon black, tin powder, gold powder, silver powder and other conductive particles which do not oxidize at the temperatures to which the composition is subjected during processing. Additional additives are incorporated to impart desired characteristics. Stabilizing agents which prevent deterioration of the resistance characteristics of the material include alkylated polyhydroxy phenol and phenylbetanaphthylamine. (Dialkylphenol-sulfide may be added to reduce degradation at a metal polymer interface thus reducing contact resistance). Flame retardants which do not deleteriously effect the resistance characteristics include phenylbetanaphthylamine high chlorinated perchloropentacyclodecane and antimony oxide. The several ingredients are for a preliminary mixed together, then subjected to a more thorough mixing step to effect an adequate dispersion of the filler material throughout the polymer, and then subjected to shearing forces for a limited period of time while maintaining the mix within a desired temperature range. The mix is then formed in the desired configuration as by inserting into a preheated mold while still at an elevated temperature. The formed element is removed from the mold and machined preferably to a rough finish to facilitate bonding of electrically conductive coatings to spaced locations thereof. The element is then coated with electrically conductive coating and annealed to minimize contact resistance.

9 Claims, 6 Drawing Figures



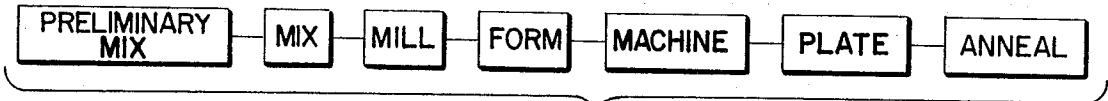


FIG. 2

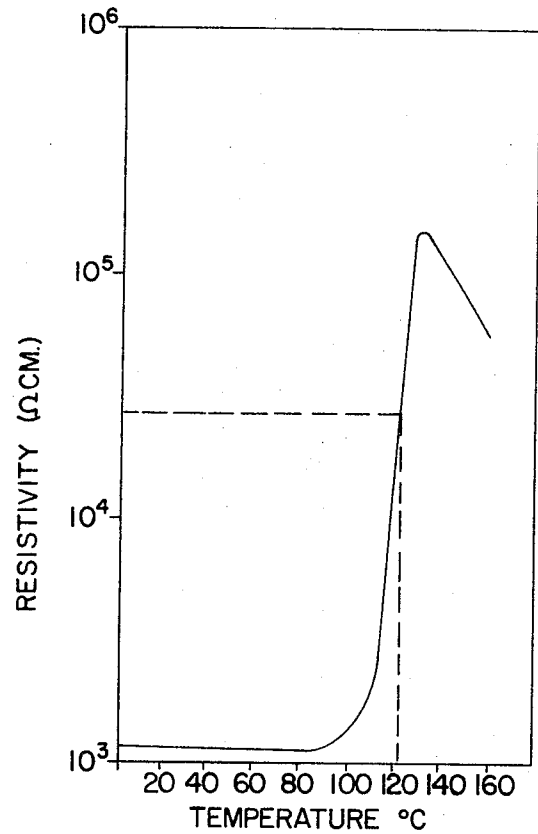


FIG. 1

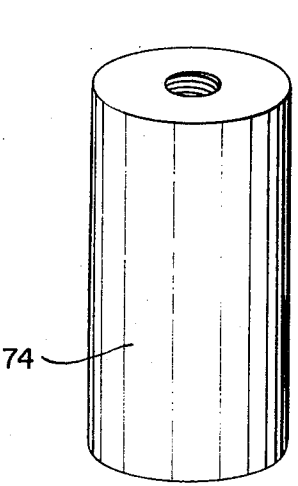
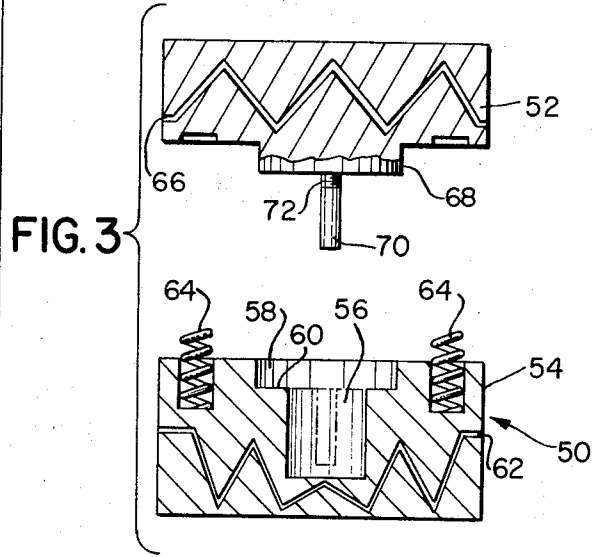


FIG. 4

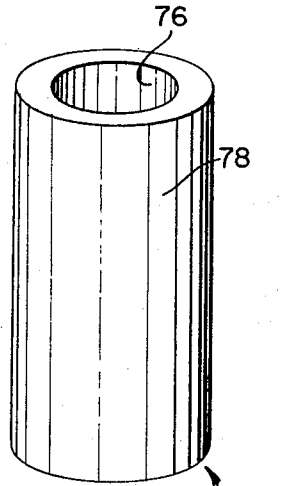


FIG. 5

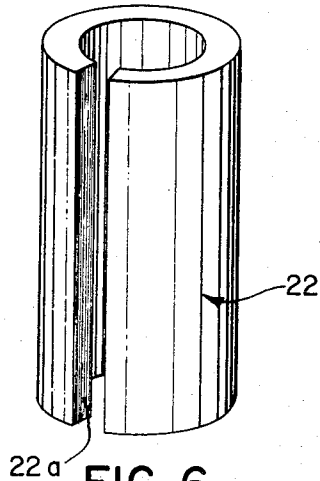


FIG. 6

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PROCESS FOR MAKING CONDUCTIVE POLYMERS AND RESULTING COMPOSITIONS

This invention relates to electrically conductive polymer, and more particularly, to polymeric material having a controlled steeply sloped positive temperature coefficient (PTC) of resistance.

An object of the invention is the provision of conductive polymeric material having an improved PTC characteristic. Another object is the provision of a method for making such material. Yet another object is the provision of PTC polymeric materials and process for making same which obviates the disadvantages of the prior art.

In the accompanying drawings, in which several of the various possible embodiments of the invention are illustrated:

FIG. 1 is a resistivity versus temperature curve of an electrically conductive polymeric element made in accordance with this invention;

FIG. 2 illustrates the main process steps employed in making such an electrically conductive polymeric element;

FIG. 3 is a cross section of a mold useful in forming an element from the polymeric mixture of this invention;

FIG. 4 is a pictorial view of polymeric form as it is removed from the FIG. 3 mold;

FIG. 5 is a pictorial view of the FIG. 4 form after it has been machined into an elongated annular element; and

FIG. 6 is a variation of the FIG. 5 polymeric element.

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

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

Conductive polymers having a PTC effect are known in the art. See for instance U.S. Pat. Nos. 2,918,665 and 3,243,753. Such polymers are useful for instance in electrical circuits as a sensor sensing ambient temperature or as a heater with an inherent function of current limiting thereby obviating the need for thermostats or other current limiting devices. Further, polymeric materials offer the advantage of permitting relatively low cost fabrication techniques such as molding and extruding while being readily machinable. Used as a heater an element constructed out of such polymer is connected to line voltage so that current flows therethrough, causing I^2R heating. When this temperature rises above the anomaly point, there is a sudden and marked increase in resistance to effectively cut off current through the heater with heat dissipation matching heat generation. Making such polymers has been a problem however since if the teaching of the prior art, such as the patents referred to supra, was followed inconsistent results are obtained. That is, although conductive polymers having a PTC effect are known, the prior art does not teach how to make conductive polymers having the desired characteristics of a controlled steeply sloped PTC characteristic with an anomaly at a chosen temperature and with a basal (room temperature) resistivity at a desired level. Further, due to the lack of understanding of the mechanism giving rise to the PTC characteristic the prior art processing techniques have not been satisfactory. The prior art has generally taught that a PTC characteristic in conductive polymers has been caused by a difference in thermal expansion between the polymer material and the conductive filler, that is, it was believed that if the polymer had a greater thermal coefficient of expansion than the conductive filler particles, this would give rise to a PTC effect. As the temperature is raised, the polymer expands more than the conductive particles, thus spreading the conductive particles apart. However, this is not a satisfactory explanation since many materials, such as polyvinylchloride and polystyrene do not exhibit a marked PTC effect even though the thermal coefficient of expansion of the polymer is greater than the conductive particle.

Rather than being primarily dependent upon rates of thermal expansion, the PTC effect appears related to the phase change in polymers having crystalline structure and a narrow molecular weight distribution. 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. Such material also includes amorphous regions and it happens that most of the carbon particle is found in these amorphous regions. The carbon particles form large aggregates separated by crystalline regions with the separation being in the order of several hundred angstroms. The polymer will contain 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 thin films of crystalline polymer so that carbon chains broken up by crystalline regions can have conductivities approaching those of carbon chains. As temperature rises, the carbon black masses separate due to the greater thermal expansion coefficient of the polymer, 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 be seen in FIG. 1 which is a typical temperature versus resistivity curve for a carbon loaded polyethylene polymer made in accordance with the invention. At temperatures below roughly 90° C., the resistance level is relatively flat. When the temperature rises to the crystalline melting point, the carbon masses become separated by amorphous regions in which electron tunneling is very limited, thus causing high resistance of the material, as seen in the roughly 90° - 130° C range of FIG. 3. Further increase of temperature causes 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 FIG. 1 at temperatures above roughly 130° C.

As stated above the amount of crystallinity of the polymer effects PTC characteristics. More particularly, it is found that the crystallinity effects the amount that the resistance rises with increased temperature in the anomaly range. It is also found that the narrower the molecular weight distribution the sharper the knee of the PTC curve will be at this anomaly temperature.

A high density polyethylene having a low melt index and filled with conductive particles, for instance Alathon 7030 of E.I. du Pont de Nemours & Co., Inc., which has a melt index of 2.8 in a scale from 1 to 20 has a particularly sharp knee at the anomaly temperature.

Various conductive particles can be used in the practice of the invention, such as any type of carbon particle and electrically conductive powder of materials which are not subject to oxidation at temperatures to which the material is subjected during processing. Examples of such powder include tin, silver and gold. The desired anomaly temperature can be obtained by choosing from a variety of polymers.

By controlling the above noted variables, a polymer having a much improved PTC effect compared to prior art teaching is achieved as well as enabling better control of the PTC effect as to steepness of the PTC curve above the anomaly temperature, sharpness of the knee of the PTC curve and desired anomaly temperature.

In practicing the invention, a crystalline polymer, such as a polyolefin, the conductive filler, such as a carbon black, and other additives are mixed together for several minutes in a conventional manner as in a standard V-type blender, then the resulting mixture is placed in a different mixer to effect a more complete dispersion of the fillers throughout the polymer. A standard Banbury type mixer, has been found suitable for this purpose. Essentially, it consists of two interdigitating screw-like vanes contained in a close fitting housing which also mounts a ram used to exert pressure on the mix during mixing if so desired. Heat transfer fluid can be circulated through passages in the vanes to provide heating or cooling if desired.

In order to avoid deleteriously effecting the resistance characteristics of the material, it is necessary to prevent the temperature of the mix from exceeding 350° F., preferably in the 300°-350° F. range. That is, at temperatures above 350° F., the basal resistivity of the material begins to rise. It is also necessary to limit the mixing time in the Banbury to 5 minutes once the temperature reaches 200° F. or again the basal resistivity increases. This can be offset to some extent by increasing the carbon black content of the mix; however, as carbon black loading is increased, the strength of the material decreases as well as ultimate life. That is, the material does not have sufficient structural integrity to maintain its configuration at such loading levels.

The temperature of the material rises due to internal friction during the mixing process. Very little mixing is effected until the temperature reaches 200° F. Although the reason is not understood, it was found that initially mixing for 1 minute at a reduced speed of approximately 77 rpm was important in obtaining good results.

As soon as the mixing step is completed, the material is transferred to a shearing apparatus, such as a two roll mill. Essentially, this comprises two rolls whose axes are mounted in parallel relation and with a variable distance between the rolls, with one roll rotating faster than the other. The rolls are heated to a temperature between 300° and 325° F. The temperature of the rolls is kept lower than in the Banbury mixer since there is a greater tendency of the polymer to oxidize due to the increased exposed surface areas associated with the shearing action of the mill. Best results are obtained if one roll is kept cooler than the other, with up to 5° F. differential being acceptable. The mixing is maintained for approximately 5 minutes, with two material fold-overs per minute. This is accomplished by placing a doctor against the roll, peeling the material from it and folding it over into the nip of the rolls, after which the material is ready for forming. It then can be ground, transfer molded or extruded into a desired configuration, such as rod or pipe, depending on the desired end use. One possible application is for a heater element for an electrically heated hair curler as set forth in copending and coassigned application Serial No. 6,095 filed Jan. 27, 1970, abandoned in favor of continuation-in-part application Ser. No. 109,414 filed Jan. 25, 1971 now U.S. Pat. No. 3,619,953. For such use an elongated cylindrical annulus 22, as shown in FIG. 5, is useful. One way to make element 22 is by using mold 50 shown in FIG. 3. The mixture is taken hot from the two roll mill, roughly shaped into a cylindrical form and inserted into a mold cavity 56, as seen in FIG. 3. This is done before the mixture has had a chance to cool in order to avoid the formation of air bubbles in the mold. The mold is closed and pressure applied. Mold 50 is formed of platen 52 and bed member 54. Bed member 54 is formed with a cylindrically shaped mold cavity 56. An enlarged portion 58 communicates with cavity 56 and forms shelf 60. Passageway 62 which extends through bed member 54 permits passage of a heat exchange medium therethrough. Mold release members 64 are mounted in bed member 54 to facilitate movement of platen 52 away from the bed member for removal of the molded element. Another passageway 66, similar to and for the same purpose as passageway 62, is provided in platen 52. Cylindrical hub 68 formed on platen 52 closely fits into cavity 58 and rests in surface 60 when fully lowered. Core member 70 extends from hub 68 and is provided primarily as a heat conducting member to conduct heat into the inner portions of the annular polymeric material. When in the lowered position in mold cavity 56, as seen in dashed lines, it will be noted that a slight clearance is provided. The upper portion 72 of core 70 is threaded to facilitate handling of the polymeric element once molded. The molded element is depicted in FIG. 4 as element 74. Element 74, after removing from the mold, is then machined into the elongated annulus 22 shown in FIG. 5 by boring it out. Preferably, a rough machined finish is provided on element 22 both on the inner and outer peripheral surfaces 76, 78 respectively, to facilitate adherence of an electrically conductive coating placed thereon. In instances where a par-

ticularly high number of heating cycles are required, it is useful to provide an axial slit 22a as seen in FIG. 6, which mitigates the effect of thermal stress due to repeated expansion and contraction of the element.

For most uses, several additives to the mixture are found to be beneficial. For instance, it is found that eventually some degradation of the PTC characteristic occurs in the material. This is referred to as aging. This effect appears to be related to a change in form of the crystallinity of the polymer material, which crystallinity is necessary for the marked PTC characteristic and to some extent the base resistivity. Certain stabilizing agents materially delay the occurrence of aging in the material. While there are many stabilizers used in polymers, most are not suitable for conductive polymers. An alkylated polyhydroxy phenol, such as Santovar A, a product of Monsanto Chemical Co., is very effective, especially when polyethylene is used as the polymer. Phenylbetanaphthylamine, such as Antioxygen MC of Ugine-Kuhlman, Organic Products, Division of F.M.C. s.a., of France is also effective in stabilizing the resistance characteristics. These additions stabilize the basal resistivity but does not materially effect the PTC characteristic. However, since the decomposition products are rather volatile, care must be exercised in processing to reduce losses of the additive. Dialkyl phenol-sulfide, such as Santowhite, also a product of Monsanto Chemical Co., is found to be acceptable for reducing degradation at a metal polymer interface thus reducing contact resistance and is particularly useful if the elements formed from the mixture are to be plated with copper.

Another characteristic that many polymers have that is undesirable for many applications is that they are not self-extinguishing if heated to the combustion temperature through overheating. It is found that antimony oxide is effective in making the material self-extinguishing, that is, once the heat source is removed (whether it be external or internal through I²R heating), the material will not continue to burn. A highly chlorinated perchloropentacyclodecane, such as Dechlorane plus 25 of Hooker Chemical Company is found to be effective. The Dechlorane 125 to be effective, however, must be used with antimony oxide. Specifically, it should be noted that although antimony oxide and Dechlorane 125 are effective when used in high density polyethylene, the amounts of these fillers to be used are determined by the amount of conductive filler employed. The total filler used in the mixture should not exceed 50 percent or the strength will be notably effected. It has been found that, in general, higher percentages of filler are desirable to give the desired characteristics with 40 percent an optimum percentage of filler material. The amount of conductive filler is determined by the warm-up time desired. For instance, for oil furnace black, such as Vulcan 3 of Cabot Corporation, with particle diameters of 30 millimicrons, percentages are given in Table I for various warm-up times for a curler having an elongated annulus heater 22.

The range of carbon black useful in making such heaters include 20 to 35 percent by weight of the carbon black plus the polymer with a preferred range of 20 to 35 percent.

TABLE I

Carbon Black (% by weight) to total of carbon black and polymer	Warm-up Time (Minutes ± 0.5)	Applied Voltage
25	1	120
24.5	1.75	120
24	2.5	120
22	5	120
25	.5	240
24.5	1	240
24	1.75	240
22	3	240

Thus, the percentage of carbon black filler is selected and then the amounts of other additives are calculated from a chosen level of fillers.

Specific examples illustrative of the invention are given below.

EXAMPLE 1

To produce an electric curler heater having a 2½ minute warm-up time, that is the time necessary for the surface temperature of the central portion of the curler to reach 62° C. using 120 volt supply, one was prepared from a batch consisting of 1,356 grams: 264 grams of oil furnace carbon black (Vulcan 3 of Cabot Corporation) having an average particle size of 30 millimicrons, 108 grams antioxidant (Santovar A), 96 grams of Dechlorane 125 flame retardant, 48 grams of antimony oxide flame retardant and 840 grams of high density polyethylene (Alathon 7030 of E.I. duPont DeNemours & Co., Inc. were added in the order recited in a V-blender for several minutes. The resultant blend was added to a Banbury mixer at a load speed of 77 rpm for 1 minute in four equal batches, the ram lowered at 40 psi and speed raised to 116 rpm for 5 minutes after the blend had reached its minimum volume (when the ram bottoms). Cooling water was circulated through the mixing blades to keep temperature below 350° F. except for the last 2 minutes when the cooling water was turned off. The temperature remained below 350° F. The material was then placed in a two roll mill with the rolls heated to a temperature of 308 and 305° F. respectively. The rolls were initially set at 0.200 inches until the material was molten, then the space between the rolls was reduced to 0.110 inches. The material was milled for 5 minutes with two material foldovers per minute. The material was taken in approximately 140 gram quantities still hot from the two roll mill, roughly shaped by hand and placed in the mold cavity (as seen in FIG. 4) which was preheated to 300° F. The mold was closed and pressure increased gradually to 50 tons in 1½ minutes. The pressure was maintained for 5 minutes. Cooling water was then circulated through the mold while pressure was maintained, until temperature decreased below 100° F. The mold was opened and the piece removed. The molded piece was then machined to produce an annulus or tubular cylinder.

EXAMPLE II

Same as Example I except that a hair curler heater having a warm-up time of 1 minute with a 120 volt supply was prepared in a batch of 1,356 grams; 276 grams of oil furnace carbon black, 828 grams of high density polyethylene with the remainder of the ingredients being the same.

EXAMPLE III

Same as Example II except that a hair curler heater having a warm-up time of 0.5 minutes with a 240 volt supply was prepared.

The heaters were then coated on the inner and outer peripheral surfaces with an electrically conductive coating, such as electroless nickel and electroplated tin, as described more fully in copending coassigned application Ser. No. 6,093 filed Jan. 27, 1970.

After coating with conductive coatings including a layer of electroless nickel, optimum low contact resistance between the electroless nickel coating and the polymer material is obtained by annealing the heaters for at least 2 days and at a temperature up to 110° C. Actually higher temperatures would be useful, however, the heaters begin to physically deform at temperatures above 110° C.

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.

I claim:

1. The method of making an electrically conductive polymeric element having a positive temperature coefficient of resistance comprising the steps of providing a high density polyethylene, said polyethylene being crystalline and having a relatively narrow molecular weight distribution, dispersing into the polyethylene filler material including conductive carbon particles, mixing the polyethylene and filler material at a temperature between 250° and 350° F., subjecting the mix to shearing forces for no longer than 5 minutes and forming the mix into a desired configuration.

2. The method according to claim 1 in which the mixing is effected at a first slow rate for approximately 1 minute and a second fast rate for the remainder of the mixing period.

3. The method according to claim 1 in which the shearing forces are effected by two surfaces which are maintained at different temperatures.

4. The method according to claim 3 in which the differential of temperature is 5° F. or less.

5. The method according to claim 1 in which the mixing causes an increase in temperature to a range of 300°-350° F. and the forming includes insertion of still hot mix into a mold preheated to approximately 300° F.

6. The method according to claim 1 in which the mix includes a stabilizing agent selected from the group consisting of alkylated polydroxy phenol and dialkylphenol-sulfide.

7. The method according to claim 1 in which the mix includes a flame retarding agent selected from the group consisting of a chlorinated perchloropentacyclodecane and antimony oxide, Dechlorane plus 25 and antimony oxide and antimony oxide.

8. The method according to claim 1 in which the total filler in the mix is limited to 50 percent of the mixture.

9. An electrically conductive polymeric element made in accordance with claim 1.

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