PATENT SPECIFICATION (11) 1 597 007

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(21) Application No. 50917/77 (22) Filed 7 Dec. 1977
(31) Convention Application No. 751095
(32) Filed 16 Dec. 1976 in
(33) United States of America (US)
(44) Complete Specification published 3 Sept. 1981
(51) INT CL³ C08K 3/04
(52) Index at acceptance
C3K 100 400 HA
C3W 207 219
C3Y B340 B343 H490

(72) Inventors LESTER TUNGAN TOY
BERNARD JOHN LYONS
WENDELL WILLIAM MOYER and
DAVID AUGUST HORSMA

(54) CONDUCTIVE POLYMER COMPOSITIONS AND DEVICES

(71) We, RAYCHEM CORPORATION, a Corporation organized according to the laws of the State of California, United States of America, of 300 Constitution Drive, Menlo Park, California 94025, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to conductive polymer compositions, their preparation, and devices comprising them.

It is known that polymers, including crystalline polymers, can be made electrically conductive by dispersing therein suitable amounts of finely divided fillers. Some conductive polymers exhibit what is known as PTC (positive temperature coefficient) behaviour. The term "PTC" has been used in various different ways in the past, but in this specification, the terms "composition exhibiting PTC behavior" and "PTC composition" are used to denote a composition having at least one temperature range which is within the limits of −100°C and about 250°C; at the beginning of which the composition has a resistivity below about 10^5 ohm. cm., and in which the composition has an R_{14} value of at least 2.5 or an R_{100} value of at least 10 (and preferably both), and preferably has an R_{30} value of at least 6, where R_{14} is the ratio of the resistivities at the end and the beginning of a 14°C range, R_{100} is the ratio of the resistivities at the end and the beginning of a 100°C range, and R_{30} is the ratio of the resistivities at the end and the beginning of a 30°C range. The term "PTC element" is used hereinto denote an element composed of a PTC composition as defined above. A plot of the log of the resistance of a PTC element, measured between two electrodes in contact with the element, against temperature, will often show a sharp change in slope over a part of the critical temperature range, and in such cases, the term "switching temperature" (usually abbreviated to T_s) is used herein to denote the temperature at the intersection point of extensions of the substantially straight portions of such a plot which lie either side of the portion showing the sharp change in slope. The PTC composition in such a PTC element is described herein as having "a useful T_s". T_s is preferably between 0°C and 175°C, e.g. 50°C to 120°C.

PTC compositions and electrical devices, especially heaters, which contain PTC elements, have been described in a number of publications. Reference may be made for example to U.S. Patents Nos. 2,978,665; 3,243,753; 3,351,882; 3,412,358; 3,413,442; 3,591,526; 3,673,121; 3,793,716; 3,823,217; 3,858,144; 3,861,029; 3,914,363 and 4,017,715; British Patent No. 1,409,695; Brit. J. Appl. Phys. Series 2, *2* 569—576 (1969, Carley Read and Stow); Kautschuk und Gummi II WT, 138—148 (1958, de Meij); Polymer Engineering and Science, Nov. 1973, *13*, No. 6, 462—468 (J. Meyer); U.S. Patent Office Defensive Publication No. T905,001; German Offenlegungsschriften Nos. 2,543,314.1; 2,543,338.9; 2,543,346.9; 2,624,478.5; 2,634,931.5; 2,634,932.6; 2,634,999.5; 2,735,000.5; 2,655,543.1; 2,746,602.0; 2,755,077.2; 2,755,076.1; and 2,821,799.4; and German Gebrauchmuster 7,527,288.

The disclosure of each of these publications and applications is hereby incorporated by reference.

Particularly useful known PTC compositions comprise a thermoplastic crystalline polymer with carbon black dispersed therein, and such compositions have been widely used in self-regulating strip heaters. The polymers which have been used include polyolefins, e.g. polyethylene, and copolymers of olefins and polar comonomers, e.g. ethylene/ethyl acrylate copolymers, Such compositions show a rapid increase in resistance over a range which begins at the softening point of the polymer and have a useful T_s at or near the crystalline melting point of the polymer; the greater the crystallinity of the polymer, the smaller the temperature range over which the resistance increase takes place. Generally, the composition is cross-linked, preferably by irradiation at room temperature, to improve its stability at temperatures above T_s.

Carbon blacks vary widely in their ability to impart conductivity to polymers with which they are mixed, and mixtures of polymers and carbon blacks generally have poor physical properties when the proportion of carbon black becomes too high, e.g. above 30% to 50%, depending on the polymer (percentages are by weight throughout this specification). Not surprisingly, therefore, only a very limited number of carbon blacks have been used or recommended for use in conductive polymer compositions, i.e. compositions whose utility depends upon their electrical characteristics, especially when the conductive polymer forms part of a circuit through which current must flow. The carbon blacks in question are, in general, those which have been recognised to have the ability to impart high conductivity, for example acetylene blacks and various furnace blacks, such as Vulcan (Registered Trade Mark) XC-72 and Vulcan SC (both sold by Cabot corporation), which are characterised by high surface area (as measured by nitrogen absorption) and high structure (as measured by dibutyl phthalate absorption). The latter two parameters and the particle size are often used to characterise carbon blacks, and for details of how they are measured, reference should be made to "Analysis of Carbon Black" by Schubert, Ford and Lyon, Vol. 8, encyclopedia of Industrial Chemical Analysis (1969), 179, published by John Wiley & Son, New York. For details of the nomenclature used in the carbon black industry, reference should be made to ASTM standard D 1765—67. Another characterising property of a carbon black is its d-spacing (the average distance in pico-meters between adjacent graphitic planes in the carbon black); thus acetylene black has a substantially smaller d-spacing (less than 360, typically about 355) than other carbon blacks. The d-spacings given herein are measured by electron microscopy. For further details reference may be made to "Carbon Black" by Donnet and Voet, published by Marcel Dekker Inc., New York (1976).

The conductivity of conductive polymers containing carbon black can be increased by annealing, as described in U.S. Patents Nos. 3,861,029 and 3,914,363. By making use of this annealing procedure, it is possible to prepare PTC compositions which contain less than 15% of carbon black but which have satisfactory initial conductivity, for example for use in strip heaters.

A serious problem that arises with conductive polymers, perticularly those exhibiting PTC behavior, is lack of voltage stability, i.e. tendency for the resistivity to rise irreversibly when the composition is subjected to voltages greater than about 110 volts, e.g. 220 or 480 volts AC, generally at a rate which is dependent on the voltage. This problem is particularly serious with heating devices, because the rise in resistance results in a corresponding loss in power output. Although voltage instability is a serious problem, it appears not to have been recognized as such in the prior art. German Offenlegungsschrift No. 2,634,931.5 is concerned with improving the voltage stability of PTC compositions comprising carbon black dispersed in a polymer containing fluorine, e.g. polyvinylidene fluoride, by cross-linking the composition with an unsaturated monomer. However, this expedient does not yield improved voltage stability with other polymers.

We have now discovered that improved voltage stability is possessed by a conductive polymer composition which comprises

(a) at least one crystalline copolymer which consists essentially of units derived from at least one olefin and at least 10 weight %, based on the copolymer, of units derived from at least one olefinically unsaturated comonomer containing a polar group, and

(b) dispersed in said copolymer, a conductive carbon black having a particle size greater than 18 millimicrons, a d-spacing greater than 360, and a surface area (A) which is less than

$$1.2S+e^{S/50}$$

where S is the DBP absorption of the carbon black.

In one aspect, the present invention provides a conductive polymer composition which comprises

(a) at least one crystalline copolymer as defined above, and

(b) a conductive carbon black as defined above;

subject to the provisos that

(1) if the crystalline copolymer is substantially the only polymeric component in the composition, then the composition is in the form of an element which is in electrical contact with at least two electrodes which are adapted to be connected to a source of electrical power and which when so connected cause current to pass through the element; and

(2) if the composition comprises 65 to 85% by weight of polyethylene and the content (L) of carbon black is less than 15% by weight of the composition, then the resistivity (R) of the composition at 25°C in ohm.cm is such that $2L+5\log_{10}R$ is greater than 45.

The Melt Indexes referred to herein are expressed in g/10 min.

The compositions of the invention may contain other polymers, preferably crystalline polymers, in addition to the crystalline copolymer as defined above. Preferably the carbon-black-containing copolymer is dispersed in a second polymer which serves as a matrix therefor, i.e. which forms a continuous phase in the composition. The other polymer is preferably substantially free of carbon black but may contain a relatively small proportion of carbon black, e.g. by migration from the copolymer, such that the resistance/temperature characteristics of the composition are dominated by the carbon-black-containing copolymer.

The compositions of the invention preferably exhibit useful PTC behavior, and will then generally have a useful T_s, which is preferably from 0° to 120°C. The compositions are preferably cross-linked, and it is often preferred that the gel fraction of the compositions is at least 0.6; the term "gel fraction" as used throughout this specification referring to the polymer in the composition, i.e. excluding the carbon black. Generally it is desirable that the composition should have a resistivity of 25°C of at least 80 ohm.cm.

The invention is illustrated in the accompanying drawings, in which the Figure shows the relationship between the surface area and the DBP absorption of the class of carbon blacks defined above, the continuous line corresponding to the relationship $A=1.2S+e^{S/50}$, and, more especially, of the specific carbon blacks used in the Examples, lying to the left of the continuous line, and Comparative Examples, lying to the right, given below, with the exception of Shawinigan Black, used in comparative Example 12, which has a d-spacing of about 355 and is executed from the scope of the invention by this feature rather than the relationship between A and S, and Ketjen Black EC, used in Example 23, for which the values of A and S are too high to be shown.

The copolymer (a) should be a crystalline copolymer which consists essentially of units derived from at least one olefin, preferably ethylene and at least 10% by weight, based on the weight of the copolymer, of units derived from at least one olefinically unsaturated comonomer containing a polar group, preferably an acrylate ester, e.g. methyl acrylate or ethyl acrylate, or vinyl acetate, or acrylic or methacrylic acid. The term "crystalline" is used herein to mean that the polymer has a crystallinity of at least 1%, preferably at least 3%, especially at least 10%. Increasing polar comonomer content leads to reduced crystallinity, and the polar comonomer content is preferably not more than 30%. The Melt Index of the copolymer is preferably less than 20, especially less than 10. The higher the Melt Index, the more desirable it is that the composition should be cross-linked to a relatively high level, especially when the composition is prepared by a process in which annealing is used to decrease the resistivity of the composition. Thus the composition should preferably have a gel fraction of at least 0.6 when the copolymer has a melt index of more than 20 and the composition has been annealed so that

$$2L+5\log_{10}R\leq 45$$

where L is the content of carbon black in percent by weight, based on the weight of the composition, and R is the resistivity of the composition at 25°C in ohm.cm.

When the composition comprises a polymer which serves as a matrix for the carbon-black-containing copolymer, i.e. for the dispersion of the carbon black in the copolymer, then the matrix polymer preferably has a higher softening point than the copolymer. Preferably the matrix polymer has limited compatibility for the copolymer, so that migration of the carbon black into the matrix polymer is minimised. Particularly suitable matrix polymers are crystalline polymers which consist essentially of units derived from one or more olefins, e.g. high, medium or low density polyethylene. Other polymers which can be used are crystalline polymers which comprise 50 to 100%, preferably 80 to 100%, by weight of $-CH_2CF_2-$ or $-CH_2CHCl-$ units, and in compositions which are not annealed, polymers which contain at least 50 %, preferably at least 80%, by weight of units derived from one or more olefins, together with suitable comonomers.

Suitable blacks for use in the invention include blacks selected from furnace blacks, thermal blacks and channel blacks. The content of carbon black is preferably 5 to 25% by weight of the composition. The content may be relatively low, e.g. not more than 12 or 15%, in which case it is preferred that the composition should be annealed, prior to any cross-linking, at a temperature above the melting point of the copolymer, and preferably above the melting point of the highest-melting polymer in the composition, so as to decrease its resistivity. Typically the composition will be annealed so that

$$2L+5\log_{10}R\leq 45,$$

where L and R are as defined above. Alternatively, the content of carbon black may be relatively high, e.g. above 15%, especially from 20 to 50%, in which case annealing prior to cross-linking may be unnecessary, or may be for a limited time such that, at the end of the annealing,

$$2L+5\log_{10}R>45.$$

In such compositions the particle size of the carbon black is preferably greater than 30 millimicrons. It is often advantageous, whether or not the composition has been annealed before cross-linking, to heat the cross-linked composition for a short period at a temperature above its melting point.

Cross-linking of the compositions is carried out after they have shaped, e.g. by melt extrusion, and can be effected by any of the methods well known in the art, preferably with the aid of ionising radiation or an organic peroxide. Preferably the composition is cross-linked at least to an extent equal to that induced by exposure to ionising radiation to a dosage of at least 0.75 M megarads, where M is the Melt Index of the copolymer, e.g. to a gel fraction of at least 0.6.

The compositions of the invention may contain other ingredients which are conventional in the art, e.g. antioxidants, flame retardants, inorganic fillers, thermal stabilisers, processing aids and cross-linking agents or the residues of such ingredients after processing. The addition of a prorad (an unsaturated compound which assists radiation cross-linking) is often useful in improving stability, especially in unannealed products; suitable amounts of prorad are less than 10%, preferably 3 to 6%.

The compositions of the invention in which the only polymeric component is the copolymer (a) can be made by blending the ingredients in conventional mixing equipment at a temperature above the melting point of the copolymer, followed by annealing and cross-linking as desired. Alternatively, a master batch containing the carbon black and part of the copolymer can first be prepared, and the master batch then blended with the remainder of the copolymer. Simiarly, when the composition contains a matrix polymer in which the carbon-black-containing copolymer is distributed, such compositons are made by blending the matrix polymer and a master batch of the carbon black in the copolymer, followed by annealing and cross-linking as desired. The master batch preferably contains 20 to 50%, e.g. 30 to 50% of the carbon black.

The invention includes electrical devices comprising an element composed of a composition of the invention and at least two electrodes adapted to be connected to a source of electrical power so as to cause current to flow through the element. One class of such devices comprise a pair of laminar electrodes having a said element in the form of a lamina therebetween. Another class of such devices comprise an elongate element of a composition of the invention; at least two

longitudinally extending electrodes embedded in said element parallel to each other and an outer layer of a protective and insulating composition.

The invention is illustrated by the following Examples.

EXAMPLES

In the examples which follow, the test samples were prepared in accordance with the procedure described below unless otherwise stated. The ingredients for the master batches were milled together on a 2 roll mill, 10 to 30°C above the melting point of the polymer. When used, additives were added before the carbon black. The preferred range of carbon black concentration in the master batch is 30 to 50% and most of the mixes prepared were in this range, although for some compositions loadings as low as 20 or as high as 70% were used. The carbon black master batch was milled for five minutes, then removed from the mill and either cooled to room temperature for subsequent use, or immediately mixed with the matrix polymer to form the final blend. For the preparation of the final blend, the desired amount of master batch was fluxed of a 2 roll mill at a temperature 10—30°C higher than the melting temperature of the highest melting polymer in the final blend. The remaining constituents, including the other polymer(s), were immediately added to the master batch and the mixture blended for five minutes. The amount of master batch was chosen to yield a resistance of about 10 kilo ohm. in the test samples. The final blends were hydraulically pressed into 15×15×0.06 cm. sheets at 2,800 kg/cm² and a temperature of at least 175°C. Samples 2.5×3.75 cm. were cut from the slabs and 0.6 cm. strips of conductive silver paint were coated on each end of the longest dimension to define a test area 2.5×2.5 cm.

Where indicated, prior to crosslinking, the above samples were annealed at 150 to 160° (200° for polypropylene) cyclically for up to two hours periods followed by cooling to room temperature until a minimum resistance level was reached. (Usually, two or three annealing cycles sufficed). Usually the samples were crosslinked by radiation; the doses used ranged from 6 to 50 Mrads, with most samples receiving 12 Mrads.

Voltage stability was assessed by measuring the room temperature resistance of the sample before (Ri) and after (Rf) the sample had been subjected to a period of operation at high voltage stress. In most instances this involved operating the heater for 72 hours at 480 volts in ambient air, then disconnecting from the source of electrical power and cooling to room temperature before remeasurement. The voltage stability is expressed as the ratio of initial resistance to final resistance (R_i/R_f).

EXAMPLE 1

It should be noted that the proportion of master batch (and hence of carbon) required to achieve the desired resistance level of 10 kilo ohms is somewhat dependent on the processing conditions and on the type of carbon black. To illustrate this, blends containing Sterling SO, Vulcan XC-72 and Black Pearls 880 were prepared as described above and also using a 0.45 kg Banbury mixer in place of the two roll mill, the temperatures and times being the same in each experiment. The master batch polymer was an ethylene—(18%) ethyl acrylate copolymer (DPD6169) and the matrix polymer was a low density polyethylene (Alathon 34). The concentration of carbon in the master batch in each case was 36%. Table I shows the percentage of master batch in the final blend (% MB) and the percentage of carbon black in the final blend (% CB).

TABLE I

	Two Roll Mill		Banbury Mixer	
Carbon Black	%MB	%CB	%MB	%CB
Sterling (Registered Trade Mark) SO	50	18	60	22
Vulcan XC-72	40	14.4	50	18
Black Pearls (Registered Trade Mark) 880	40	14.4	40	14.4

EXAMPLE 2

A variety of carbon blacks were blended with dpd 6169 to provide master batches which were then mixed with Alathon (Registered Trade Mark) 34 as the matrix polymer in the amount needed to achieve a resistance level in the final product of 10 kilo ohms. All the samples were irradiated to a dosage of 12 Mrads, and most were annealed prior to irradiation.

The carbon blacks employed are identified in Table II below, giving the trade name, the ASTM code, the particle size in millimicrons (D), the surface area as

measured by nitrogen absorption in M^2/g (A) and the dibutylphthalate D.B.P. absorption in ml/100 g(s). Table II also shows the percentage of carbon black in the different samples,and the results of stability tests on these samples. In Table II, the samples marked C are comparative Examples.

TABLE II

	Carbon Black					Annealed samples		unannealed samples	
	Trade Name	ASTM code	D	A	S	% Carbon black	Ri/Rf	% Carbon black	Ri/Rf
	1. Sterling NS	N774	75	27	70	15.1	0.76		
	2. Philblack (Registered Trade Mark) N765	N765	60	30	102	11.1	0.56		
	3. Furness (Registered Trade Mark) N765	N765	60	30	107	9.7	0.4		
	4. Sterling N765	N765	60	30	116	9.4	0.58	16.2	0.76
	5. Sterling V	N660	50	35	91	10.8	0.7		
	6. Sterling VH	N650	60	36	122	9.4	0.49		
	7. Statex (Registered Trade Mark) N550	N550	42	40	122	7.9	0.83		
	8. Sterling So-1	N539	42	42	109	10.8	0.55		
	9. Sterling SO	N550	42	42	120	9.7	0.6	18	0.63
	10. Philblack N550	N550	42	44	118	9.4	0.65		
	11. Regal (Registered Trade Mark) 99	N440	36	46	60	19.1	0.35		
C	12. Shawinigan (Registered Trade Mark) Black	—	42	64	—	15.1	0.004		
	13. Vulcan K	N351	28	70	124	10.8	0.47		
	14. Vulcan 3	N330	27	80	103	10.1	0.48		
	15. Vulcan 3H	N347	26	90	124	7.9	0.38		
C	16. Regal 330	N327	25	94	70	16.2	0.19		
	17. Vulcan 6H	N242	21	124	128	10.1	0.38		
C	18. Vulcan C	N293	23	145	100	11.9	0.29	16.2	*
C	19. Vulcan SC	N294	22	203	106	10.1	0.24		
C	20. Black Pearls 880	—	16	220	110			14.4	*
C	21. Vulcan XC-72	N472	35	254	178	10.8	0.23		
C	22. Black pearls 74	—	17	320	109	10.8	*		
	23. Ketjen (Registered Trade Mark) black EC	—	30	1000	340	5.3	0.52		

*Sample has such poor voltage stability that it burns.

The relationship between A and S is depicted graphically on the drawing and the thick continuous line corresponds to the relationship

$$A=1.2S+e^{S/50}.$$

EXAMPLE 3

Tests similar to those described in Example 2 were carried out using different polymers in place of the DPD 6169 and/or the Alathon 34. The tests are summarized in Table III below.

TABLE III

Copolymer in master batch	Commercial name and Melt Index (M.I.)	Polymer in final blend	Commercial name Melt Index (M.I.)	Remarks
Ethylene (18%) ethyl acrylate	DPDA 61 81 M.I. 2.2	Polyethylene 0.93 density	Alathon 34 M.I.-3	Very similar results to those of Table II
Ethylene-(18%) ethyl acrylate	DPDA 9169 M.I. 20	as above	as above	Similar results to those of Table II
Ethylene-(6.6%) ethyl acrylate	DPD 7365 M.I. 8	as above	as above	Voltage stability very poor with most carbon blacks
ethylene-(5.5%) ethyl acrylate	DPD 7070 M.I. 8	as above	as above	Voltage stability very poor with most carbon blacks
Ethylene-(18%) vinyl acetate	Alathon 3175 M.I. 8	as above	as above	Very similar results to those of Table II
Ethylene-(28%) vinyl acetate	Alathon 3172 M.I. 6	as above	as above	Very similar results to those of Table II
Ethylene-(30%) propylene	Vistalon (Registered Trade Mark) 702 Mooney Visc.~30	as above	as above	Voltage stability very poor with most carbon blacks
Polyethylene 0.93 density	DYNH M.I. 2	Polyethylene 0.96 density	Alathon 7030 M.I.3	
Ethylene-(18%)ethyl acrylate	DPD6169 M.I. 6	Ethylene-(6.6%) ethyl acrylate	DPD 7365 M.I. 8	Results similar to Table II slightly different preferred range
Polyethylene 0.93 density	DYNH M.I. 2	Polypropylene (High Impact)	Profax 8263	Voltage stability very poor with most carbon blacks
Ethylene-(18%) ethyl acrylate	DPD 6169 M.I. 6	Vinylidene Fluoride copolymer	Kynar (Registered Trade Mark) 7201 M.I. 33	Results similar to Table II
as above	as above	none	—	Results very similar to Table II

WHAT WE CLAIM IS:—

1. A conductive polymer composition which comprises

(a) at least one crystalline copolymer which consists essentially of units derived from at least one olefin and at least 10 weight %, based on the copolymer, of units derived from at least one olefinically unsaturated comonomer containing a polar group, and

(b) dispersed in said copolymer, a conductive carbon black having a particle size greater than 18 millimicrons, a d-spacing greater than 360, and a surface area (A) which is less than

$$1.2S+e^{S/50}$$

where S is the DBP adsorption of the carbon black;

subject to the provisos that

(1) if the crystalline copolymer is substantially the only polymeric component in the composition, then the composition is in the form of an element which is in electrical contact with at least two electrodes which are adapted to be connected to a source of electrical power and which when so connected cause current to pass through the element; and

(2) if the composition comprises 65 to 85% by weight of polyethylene and the content (L) of carbon black is less than 15% by weight of the composition, then the resistivity (R) of the composition at 25°C in ohm.cm is such that $2L+5\log_{10}R$ is greater than 45.

2. A composition according to Claim 1 which also comprises at least one crystalline polymer (c) which has a softening point higher than copolymer (a) and which consists essentially of units derived from one or more olefins or which contains at least 50% by weight of $—CH_2CF_2—$ units or $—CH_2CHCl—$ units.

3. A composition according to Claim 2 wherein the polymer (c) forms a continuous phase in the composition.

4. A composition according to Claim 3 wherein the polymer (c) is a polyolefin.

5. A composition according to any one of the preceding claims wherein the copolymer (a) has a Melt Index less than 20.

6. A composition according to Claim 5 wherein the copolymer (a) has a Melt Index less than 10.

7. A composition according to any one of the preceding claims wherein the copolymer (a) is a copolymer of ethylene and one or more of methylacrylate, ethyl acrylate and vinyl acetate.

8. A composition according to any one of the preceding claims which has a gel fraction (as hereinbefore defined) of at least 0.6.

9. A composition according to any one of the preceding claims, wherein the carbon black has a particle size of not more than 75 millimicrons.

10. A composition according to any one of the preceding claims which contains less than 15% by weight of carbon black.

11. A composition according to Claim 10 wherein

$$2L+5\log_{10}R\leq 45.$$

12. A composition according to Claim 8 wherein the copolymer (a) has a Melt Index of less than 10.

13. A composition according to any one of claims 1 to 9 which contains at least 15% by weight of carbon black.

14. A composition according to Claim 13 wherein the carbon black has a particle size of at least 30 millimicrons.

15. A composition according to any one of the preceding claims which has a resistivity at 25°C of 80 to 10^5 ohm.cm.

16. A composition according to any one of the preceding claims wherein the carbon black is a furnace black, channel black or thermal black.

17. A composition according to Claim 13 or 14 which contains 20 to 50% by weight of carbon black.

18. A composition according to any one of the preceding claims which exhibits PTC behavior (as hereinbefore defined).

19. A composition according to Claim 18 which has a useful T_s (as hereinbefore defined) of 0° to 175°C.

20. A composition according to claim 1 substantially as hereinbefore described.

21. A composition according to Claim 1 substantially described in any one of the foregoing Examples.

22. A process for the preparation of a conductive polymer composition as claimed in any one of the preceding claims which contains a polymer (c) as defined in Claim 2, which process comprises mixing the polymer (c) with a dispersion of carbon black in the copolymer (a).

23. A process according to Claim 22 wherein the dispersion obtained in step (1) contains 30 to 50% by weight of the carbon black.

24. A process according to Claim 21 or 22 wherein the mixture obtained in step (2) contains less than 15% by weight of carbon black and is annealed at a temperature above the melting point of the highest melting polymer in the composition for a time such that

$$2L+5\log_{10}R\leq 45$$

where L is the content of carbon black in percent by weight of the composition, and R is the resistivity of the annealed composition at 25°C in ohm.cm.

25. A process according to any one of claims 22 to 24 wherein the composition, after annealing, is cross-linked by exposure to ionising radiation.

26. A process according to Claim 25 wherein the composition is exposed to ionising radiation to a dosage of at least 0.75M megarads, where M is the Melt Index of the copolymer (a).

27. A process according to Claim 25 or 26 wherein the cross-linked conductive polymer composition is heated at a temperature above the melting point of polymer (a).

28. A process according to Claim 22 substantially as hereinbefore described.

29. A process according to claim 22 substantially as described in any one of the foregoing Examples.

30. A composition according to any one of Claims 1 to 21 when prepared by a process as claimed in any one of Claims 22 to 29.

31. An electrical device comprising an element composed of a conductive polymer composition as claimed in any one of Claims 1 to 21 and 30 and at least two electrodes adapted to be connected to a source of electrical power so as to cause current to pass through the element.

32. A device according to Claim 31 which comprises a pair of laminar electrodes having a said element in the form of a lamina therebetween.

33. A device according to Claim 31 which comprises

(1) an elongate element of a said composition;

(2) at least two longitudinally extending electrodes embedded in said element parallel to each other; and

(3) an outer layer of a protective and insulating composition.

34. A device according to any one of claims 31 to 33 wherein said element is a PTC element having a useful T_s (as hereinbefore defined) of 0° to 120°C.

35. A self-regulating strip heater which comprises

(1) an elongate element of a conductive polymer composition which exhibits PTC behavior;

(2) at least two longitudinally extending electrodes which are embedded in said element parallel to each other and which are adapted to be connected to a source of electrical power and which when so connected cause current to pass through the element; and

(3) an outer layer of a protective and insulating composition, said conductive polymer composition comprising

(a) a copolymer of ethylene and at least 10%, based on the weight of the copolymer, of one or more of methyl acrylate, ethyl acrylate and vinyl acetate; and

(b) dispersed in said copolymer, at least 15%, by weight of the composition, of a conductive carbon black having a particle size of 18 to 75 millimicrons, a d-spacing greater than 360, and a surface area (A) which is less than

$$1.2S+e^{S/50}$$

wherein S is the DBP absorption of the carbon black.

36. A heater according to claim 35 wherein the composition is cross-linked.

37. A heater according to claim 36 wherein the polymer in the composition has a gel fraction (as hereinbefore defined) of at least 0.6.

38. A heater according to any one of claims 35 to 37 wherein the composition also comprises polyethylene.

39. A heater according to claim 38 wherein the polymeric components of the composition consist essentially of polyethylene and a copolymer of ethylene and ethyl acrylate.

40. A heater according to claim 38 wherein the polymeric components of the composition consist essentially of polyethylene and a copolymer of ethylene and vinyl acetate.

ABEL & IMRAY,
Chartered Patent Agents,
Northumberland House,
303—306 High Holborn,
London, WC1V 7LH.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1981
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

1597007 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*