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Description

This invention relates to conductive polymer compositions and devices containing them, especially circuit protection systems.

Conductive and semi-conductive compositions comprising carbon black dispersed in a polymer are known. They may have room temperature resistivities ranging from less than 1 ohm · cm to 10^8 ohm · cm or more, and may exhibit positive temperature coefficient (PTC) behaviour zero temperature coefficient (ZTC or constant wattage) behaviour or negative temperature coefficient (NTC) behaviour. Reference may be made, for example, to U.S. Patent Nos. 2,978,655, 3,243,753, 3,351,882, 3,823,217, 3,861,029, 3,950,604, 4,017,715, 4,177,376 and 4,246,468 (published 20.1.81), DE—A—2,413,475, 2,746,602, 2,755,076 and 2,821,570, to J. Applied Polymer Science *19* 813—815 (1975), Klason and Kubat, and to Polymer Engineering and Science *18*, 649—653 (1978), Narkis et al. Recent advances in this field are described in DE—A—2,948,350 (publ. 19.6.80), 2,948,281 (publ. 19.6.80), 2,949,173 (publ. 26.6.80) and 3,002,721 (publ. 7.8.80), in European Published Application Nos. 0,020,081 (publ. 10.12.80), 0,022,611 (publ. 21.1.81), 0,026,571 (publ. 8.4.81) and 0,028,142 (publ. 6.5.81), and in the European Patent Applications filed contemporaneously with this application and published as European Published Application Nos. 0,038,718, 0,038,714, 0,038,716 and 0,038,717.

US 3351882 discloses a device which comprises a PTC element composed of two electrodes and a conductive polymer composition, the composition comprising a polymer having carbon black dispersed therein.

In recent research into the use of circuit protection devices containing PTC conductive polymer elements, it was observed that previously proposed devices failed to give repeated and effective protection against fault conditions in which the device was subjected to a combination of high current and high voltage. We have found that the performance, under conditions of high electrical stress, of conductive polymer compositions containing carbon black or graphite as the sole conductive filler, can be markedly improved by adding to such compositions one or more of the additives which have previously been used to improve the tracking resistance of polymeric insulating compositions. Although it is not entirely clear precisely why such additives have this valuable effect, they are referred to herein as arc-controlling additives. It is thought that their efficacy is probably due, at least in part, to their ability to extinguish arcs after they have been formed, but the additives may also act to reduce the susceptibility of the composition to form arcs in the first place. In any event, it is to be noted that the prior use of these additives, described, for example in GB Patent No. 831490, which has been to extinguish arcs on the contaminated surface of an electrical insulator, involves a very different situation from the present one, where the additives are effective in controlling arcs within a mass of conductive polymer (as well as at the surface thereof).

The invention provides an electrical device which comprises:

(1) a PTC element composed of a conductive polymer composition which exhibits PTC behaviour and which comprises an organic polymer component and, dispersed in the polymer component a conductive filler component which comprises carbon, and

(2) at least two electrodes for passing current through the PTC element, characterised in that the PTC element is composed of a composition which has a resistivity at 23°C of less than 10^6 ohm· cm, and which comprises:

(a) 20 to 91% by volume of an organic polymer component;

(b) 4 to 65% by volume of a conductive filler component which consists essentially of carbon black and/or graphite; and

(c) an arc controlling additive which is a hydrated inorganic particulate material which is dispersed in the polymer component.

The PTC compositions defined above are particularly useful in circuit protection devices as described in the contemporaneously filed European Application Nos. 0,038,715, 0,038,716 and 0,038,717.

The compositions can be any of the PTC compositions which are disclosed in the prior art and the earlier applications referred to above, which have a resistivity at 23°C of less than 10^6 ohm · cm, which comprise 20 to 91% by volume of a conductive filler which consists essentially of carbon black and/or graphite, and which have been modified by the inclusion of at least one arc-controlling additive as defined in Claim 1. The invention is especially valuable in relation to circuit protection devices, which usually have a resistance below 50 ohms, at 23°C as described in European Published Application No. 0,038,715, and in which the PTC composition has low resistivity at 23°C, e.g. below 20 ohm · cm, preferably below 10 ohm · cm, especially below 2 ohm · cm.

The preferred arc-controlling additive for use in the present invention is alumina trihydrate, $Al_2O_3 \cdot 3H_2O$. Another additive is magnesia hydrate.

The conductive filler and the arc-controlling additive preferably have a total surface area of at least 1,800, especially at least 3,000, particularly at least 4,000, $m^2/100\ cm^3$ of composition, with higher values, e.g., at least 8,000 $m^2/100\ cm^3$, at least 10,000 $m^2/100\ cm^3$ and at least 12,000 $m^2/100\ cm^3$ being particularly preferred.

The composition should contain an effective amount of the arc-controlling additive, typically 5 to 65%, preferably 10 to 35%, by volume of the composition.

The composition can also contain further additives which are known to enhance the effectiveness of

anti-tracking additives in insulating compositions. Examples of such additives include the phosphorus-containing compounds disclosed in British Patent No. 1,575,465 and the oxide of elements of the transition series, lanthanide series or non-transuranic actinide series disclosed in British Patents Nos. 1,337,951 and 1,337,952.

The conductive filler in the composition preferably consists essentially of at least one carbon black. The carbon black is selected with a view to the electrical characteristics desired in the composition, as taught by the various patents and applications referred to above. Thus for low resistivity PTC compositions, the carbon black preferably has a particle size, D, which is from 20 to 150 nm (millimicrons) and a surface area, S in m^2/g such that S/D is not more than 10.

When using such a carbon black, preferably the quantity

$$\frac{S}{D} \times \frac{\text{(volume of conductive filler+volume of arc-controlling additive)}}{\text{volume of polymer component}}$$

is less than 1.

The polymer component in the composition, which may comprise one or more polymers, preferably has a crystallinity of at least 1%, especially at least 5%, particularly at least 10%. Preferably the polymer component consists essentially of one or more crystalline polymers selected from polyolefins and copolymers of at least one olefin and at least one polar comonomer copolymerisable therewith, e.g. polyethylene or polypropylene. Other suitable polymers are referred to in the patents and applications referred to above.

The composition may be substantially free of cross-linking or may be cross-linked, e.g. to a gel fraction of at least 0.4 or 0.6. For some purposes, compositions free of cross-linking are preferred, because the presence of cross-linking tends to increase the likelihood of formation of carbonaceous conductive paths when arcing takes place.

The composition can be prepared by dispersing the carbon black or graphite, the arc-controlling additive and any other additives in the polymer component in any suitable way. The composition can be shaped by molding or extrusion or another melt-shaping technique into an element of the desired shape, any cross-linking thereof being carried out after such shaping.

Conductive polymer compositions comprising a crystalline polymer component, at least 4% by volume of carbon black and at least 4% by volume of a non-conductive particulate filler, the total surface area of the carbon black and filler being at least 1800 $m^2/100\ cm^3$ of composition, are described and claimed in the contemporaneously filed application corresponding to European Published Application No. 0,038,718.

The invention is illustrated by the following Examples. The words Fumex, Marlex, Sterling and Maglite are UK Registered Trade Marks.

Example 1

The ingredients and amounts thereof given in the Table 1 below were used in this Example.

TABLE 1

	Masterbatch			Final mix		
	g	wt%	vol%	g	wt%	vol%
Carbon black (Furnex N765)	1444	46.9	32.2	1143.9	33.8	26.9
Polyethylene (Marlex 6003)	1572	51.1	65.4	1246.3	36.8	54.7
Filler (Hydral 705)	—	—	—	948	28.0	16.5
Antioxidant	62	2.0	2.3	48.8	1.4	1.9

Notes:

Furnex N765 (available from City Services Co.) has a particle size (D) of 60 nm (millimicrons), a density of 1.8 g/cm^3, and a surface area (s) of 32 m^2/g.

Marlex 6003 is a high density polyethylene with a melt index of 0.3 which is available from Phillips Petroleum Co.

The antioxidant used was an oligomer of 4,4-thio bis (3-methyl-6-t-butyl phenol) with an average degree of polymerization of 3—4, as described in U.S. Patent No. 3,986,981.

Hydral 705 is alumina trihydrate.

The ingredients for the master batch were dry blended and then mixed for 8 minutes in a Banbury mixer turning at high gear. The mixture was dumped, cooled and granulated. The final mix was prepared by dry blending 948 g of the Hydral 705 with 2439 g of the master batch mixture, and then mixing the dry blend for 4—5 minutes in a Banbury mixer turning at high gear. The mixture was dumped, cooled, granulated and dried (at 70°C, 1 Torr for 16 hours; 1 Torr=233,3 Pa).

The granulated final mix was melt extruded in the form of a strip about 1.27 cm wide and about 0.27 cm thick, using a cross-head die, around a pair of pre-heated 20 AWG (diameter 0.095 cm) 19—32 stranded nickel-plated copper wires whose centers were 0.6 cm apart. The extruded product was cut into 2.5 cm lengths, and the polymeric composition removed from half of each length to produce a circuit control device as shown in Figure 4 of the contemporaneously filed application corresponding to European Published Application No. 0,038,716.

Examples 2—4

The ingredients used in these Examples and the amounts thereof are shown in Table 2 below. The antioxidant is as specified in Table 1. Sterling NS and Sterling SO are available from Cabot, Hydral 705 from Alcan, Maglite D from Merck, and Kadox 15 from Gulf and Western, and they have the following properties

	Material	Particle size nm (millimicrons)	Density g/cm^3	Surface area m^2/g
Sterling NS	Carbon black (N774)	75	1.8	25
Sterling SO	Carbon black (N550)	41	1.8	42
Hydral 705	Al_2O_3 $3H_2O$	0.5—2,000	2.42	12—15
Maglite D	MgO	<44	3.32	—
Kadox 15		130	5.52—6.52	8.5

In Example 2, the Master Batch ingredients were blended in a pre-heated Banbury mixer, and the mixture dumped, cooled and granulated. 67 g of the granulated mixture was banded on a 7.6 cm electric roll mill, and the Hydral was added in portions to give a uniform mixture; mixing was continued for several more minutes and the mixture was then removed from the mill, cooled, granulated and compression-molded into slabs.

In Example 3, the Master Batch ingredients were blended in a pre-heated Banbury mixer, and the mixture dumped, cooled and granulated. 67 g of the granulated mixture was banded on a 3 inch electric roll mill, and the Hydral was added in portions to give a uniform mixture; mixing was continued for several more minutes and the mixture was then removed from the mill, cooled, granulated and compression-molded into slabs.

In Example 4 the procedure described for Example 2 was followed, using the different ingredients shown in Table 2, except that 50 g of the granulated Master Batch was used and 50 g of the filler (Maglite D) added to it.

TABLE 2

	Example 2					Example 3			Example 4				
	Master batch			Final mix		Final mix			Master batch			Final mix	
	Wt(g)	Wt%	Vol%	Wt%	Vol%	Wt(g)	Wt%	Vol%	Wt(g)	Wt%	Vol%	Wt%	Vol%
Polymer													
Polyethylene (Marlex 6003)	14.0	45.5	58.4	30.5	46.8	148.6	38.2	61.8	61	61	71.3	30.5	53.3
EPDM Rubber (Epsyn 5508)	14	4.5	6.5	3.0	5.1	14.8	3.8	6.9	—	—	—	—	—
EPDM rubber (Nordel 1440)	—	—	—	—	—	—	—	—	5	5	6.6	2.5	4.9
Carbon black													
Sterling NS	14.8	48.5	32.8	32.2	26.3	—	—	—	—	—	—	—	—
Sterling SO	—	—	—	—	—	90.6	23.3	20.1	—	—	—	—	—
Furnex N765	—	—	—	—	—	—	—	—	32	32	20	16	14.9
Filler													
Alumina trihydrate (Hydral 705)	—	—	—	33	20	—	—	—	—	—	—	—	—
Magnesium oxide (Maglite D)	—	—	—	—	—	—	—	—	—	—	—	50	35.2
Zinc oxide (Kadox 15)	—	—	—	—	—	129.5	33.3	9.2	—	—	—	—	—
Antioxidant	6	2	2.3	1.3	1.8	5.4	1.4	2.0	2	2	2.1	1.0	1.7

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Claims

1. An electrical device which comprises: (1) a PTC element composed of a conductive polymer composition which exhibits PTC behaviour and which comprises an organic polymer component and, dispersed in the polymer component a conductive filler component which comprises carbon, and (2) at least two electrodes for passing current through the PTC element, charactersed in that the PTC element is composed of a composition which has a resistivity at 23°C of less than 10^6 ohm · cm, and which comprises:

(a) 20 to 91% by volume of an organic polymer component;

(b) 4 to 65% by volume of a conductive filler component which consists essentially of carbon black and/or graphite; and

(c) an arc-controlling additive which is a hydrated inorganic particulate material which is dispersed in the polymer component.

2. A device according to Claim 1, characterised in that the arc-controlling additive is present in amount 5 to 65%, preferably 10 to 35%, by volume of the composition.

3. A device according to Claim 1 or 2, characterised in that the arc-controlling additive is alumina trihydrate.

4. A device according to Claim 1, 2 or 3, characterised in that the conductive filler and the arc-controlling additive have a total surface area of at least 1,800 m^2 per 100 cm^3 of composition.

5. A device according to any one of the preceding Claims 2 to 4, characterised in that the polymer component has at least 5% crystallinity and the conductive filler component (a) comprises carbon black having a particle size, D, which is from 20 to 150 nm (millimicrons) and a surface area, S, in m^2/g such that S/D is not more than 10, and (b) is present in amount such that the composition has a resistivity at 23°C of less than 20 ohm · cm.

6. A device according to Claim 5 characterised in that the quantity

$$\frac{S}{D} \times \frac{\text{(volume of conductive filler+volume of arc-controlling additive)}}{\text{volume of polymer component}}$$

is less than 1.

7. A device according to any of the preceding claims characterised in that it is a circuit protection device having a resistance at 23°C of less than 50 ohms, preferably 0.1 to 25 ohms.

8. A device according to Claim 7, characterised in that said conductive polymer composition has a resistivity of less than 10 ohm · cm and comprises

(a) 20 to 91% by volume of a polymer component having at least 10% crystallinity;

(b) 4 to 65% by volume of carbon black; and

(c) 5 to 65% by volume of alumina trihydrate the carbon black and the alumina trihydrate having a total surface area of at least 1,800 $m^2/100$ cm^3 of composition.

Patentansprüche

1. Elektrische Vorrichtung, welche aufweist: (1) ein PTC-Element, bestehend aus einer Zusammensetzung von leitfähigem Polymeren, die PTC-Verhalten zeigt und eine organische Polymerkomponente und in der Polymerkomponente verteilt eine leitfähige kohlenstoffhaltige Füllstoffkomponente enthält, und (2) mindestens zwei Elektroden zum Hindurchleiten von Strom durch das PTC-Element, dadurch gekennzeichnet, dass das PTC-Element aus einer Zusammensetzung besteht, welche einen spezifischen Widerstand bei 23°C von weniger als 10^6 Ohm · cm hat und aufweist:

(a) 20 bis 91 Vol.% einer organischen Polymerkomponente;

(b) 4 bis 65 Vol.% leitfähige Füllstoffkomponente, die im wesentlichen aus Russ und/oder Graphit besteht; und

(c) einen Lichtbogensteuerungszusatz, der ein hydratisiertes anorganisches Teilchenförmiges Material ist, das in der Polymerkomponente dispergiert ist.

2. Vorrichtung nach Anspruch 1, dadurch gekennzeichnet, dass der Lichtbogensteuerungszusatz in einer Menge von 5 bis 65 Vol.%, vorzugsweise 10 bis 35 Vol.%, der Zusammensetzung enthalten ist.

3. Vorrichtung nach Anspruch 1 oder 2, dadurch gekennzeichnet, dass der Lichtbogensteuerungszusatz Aluminiumtrihydrat ist.

4. Vorrichtung nach Anspruch 1, 2 oder 3, dadurch gekennzeichnet, dass der leitfähige Füllstoff und der Lichtbogensteuerungzusatz eine Gesamtoberfläche von mindestens 1800 m^2 je 100 cm^3 der Zusammensetzung haben.

5. Vorrichtung nach einem der vorhergehenden Ansprüche 2 bis 4, dadurch gekennzeichnet, dass die polymere Komponente eine Kristallinität von mindestens 5% hat und die Komponente des leitfähigen Füllstoffes (a) Russ von einer Teilchengrösse, D, aufweist, welche 20 bis 150 nm beträgt und eine solche Oberfläche, S, in m^2/g hat, dass S/D nicht mehr als 10 beträgt, und (b) in einer solchen Menge anwesend ist, dass die Zusammensetzung einen spezifischen Widerstand von weniger als 20 Ohm · cm bei 23°C hat.

6. Vorrichtung nach Anspruch 5, dadurch gekennzeichnet, dass die Menge

$$\frac{S}{D} \times \frac{\text{(Volumen leitfähiger Füllstoff+Volumen Lichtbogensteuerungszusatz)}}{\text{Volumen Polymerkomponente}}$$

weniger als 1 ist.

7. Vorrichtung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, dass sie eine Schaltungsschutzvorrichtung von einem spezifischen Widerstand bei 23°C von weniger als 50 Ohm, vorzugsweise 0,1 bis 25 Ohm, ist.

8. Vorrichtung nach Anspruch 7, dadurch gekennzeichnet, dass die leitfähige Polymerzusammensetzung einen spezifischen Widerstand von weniger als 10 Ohm · cm hat und

(a) 20 bis 91 Vol.% einer Polymerkomponente von einer Kristallinität von mindestens 10%;

(b) 4 bis 65 Vol.% Russ; und

(c) 5 bis 65 Vol.% Aluminiumtrihydrat

enthält, wobei der Russ und das Aluminiumtrihydrat eine Gesamtoberfläche von mindestens 1800 $m^2/100$ cm^3 Zusammensetzung hat.

Revendications

1. Dispositif électrique qui comprend:

(1) un élément CPT composé d'une composition polymère conductrice qui présente un comportement CPT et qui comprend un constituant polymère organique et, en dispersion dans le constituant polymére, un constituant de charge conductrice qui comprend du carbone, et (2) au moins deux électrodes destinées à faire passer un courant à travers l'élément CPT, caractérisé en ce que l'élément CPT est composé d'une composition qui présente une résistivité, à 23°C, de moins de 10^6 ohms · cm, et qui comprend:

(a) 20 à 91% en volume d'un constituant polymère organique;

(b) 4 à 65% en volume d'un constituant de charge conductrice qui est constitué essentiellement de noir de carbone et/ou de graphite; et

(c) un additif de limitation d'arc qui est une matière en particules inorganique hydratée, en dispersion dans le constituant polymère.

2. Dispositif selon la revendication 1, caractérisé en ce que l'additif de limitation d'arc est présent en quantité de 5 à 65%, avantageusement 10 à 35%, en volume de la composition.

3. Dispositif selon la revendication 1 ou 2, caractérisé en ce que l'additif de limitation d'arc est du trihydrate d'alumine.

4. Dispositif selon la revendication 1, 2 ou 3, caractérisé en ce que la charge conductrice et l'additif de limitation d'arc ont une surface spécifique totale d'au moins 1800 m^2 par 100 cm^3 de composition.

5. Dispositif selon l'une quelconque des revendications précédentes 2 à 4, caractérisé en ce que le constituant polymère présente une cristallinité d'au moins 5% et le constituant de charge conductrice (a) comprend du noir de carbone ayant une dimension, D, de particules qui va de 20 à 150 µm (micromètres) et une surface spécifique, S, en m^2g telle que S/D n'est pas supérieur à 10, et (b) est présent en quantité telle que la composition présente une résistivité à 23°C de moins de 20 ohms · cm.

6. Dispositif selon la revendication 5, caractérisé en ce que la quantité

$$\frac{S}{D} \times \frac{\text{(volume de charge conductrice+volume de l'additif de limitation d'arc)}}{\text{volume du constituant polymère}}$$

est inférieure à 1.

7. Dispositif selon l'une quelconque des revendications précédentes, caractérisé en ce qu'il s'agit d'un dispositif de protection de circuit ayant une résistance à 23°C de moins de 50 ohms, avantageusement de 0,1 à 25 ohms.

8. Dispositif selon la revendication 7, caractérisé en ce que ladite composition polymère conductrice présente une résistivité de moins de 10 ohms · cm et comprend

(a) 20 à 91% en volume d'un constituant polymère ayant une cristallinité d'au moins 10%;

(b) 4 à 65% en volume de noir de carbone; et

(c) 5 à 65% en volume de trihydrate d'alumine, le noir de carbone et le trihydrate d'alumine ayant une surface spécifique totale d'au moins 1800 $m^2/100$ cm^3 de composition.