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(54) Conductive polymer compositions containing fillers.

(57) The invention relates to conductive polymer compositions comprising carbon black or graphite dispersed in a polymer. The compositions of the invention further comprise an arc-controlling additive such as alumina trihydrate. Such compositions have improved performance when subjected to electrical stress and are, therefore, particularly useful in circuit protection devices.

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

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) behavior, zero temperature coefficient (ZTC or constant wattage) behavior or negative temperature coefficient (NTC) behavior. Reference may be made, for example, to U.S. Patent Nos. 2,978,665, 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, to German OLS Nos. 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 German OLS Nos. 2,948,350, 2,948,281, 2,949,173 and 3,002,721, in the applications corresponding to U.S. Serial Nos. 41,071 (MP0295), 67,207 (MP0299) and 88,344 (MP0701), and in the applications filed contemporaneously with this application corresponding to U.S. Serial Nos. 141,984 (MP0712), 141,987 (MP0713), 141,988 (MP0714), 141,991 (MP0720), 142,053 (MP0724) and 142,054 (MP0725).

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, 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).

5 In one aspect, the invention provides a conductive polymer composition which has a resistivity at 23°C of less than 10^6 ohm. cm and which comprises

(a) a polymer component which is present in amount 20 to 91% by volume of the composition;

10 (b) a conductive filler component which consists essentially of carbon black or graphite or a mixture of carbon black and graphite, which is dispersed in said polymer component and which is present in amount 4 to 65% by volume of the composition; and

15 (c) an arc-controlling additive which is distributed in said polymer component and which is effective in reducing the susceptibility of the composition to damage when subjected to electrical stress sufficient to cause arcing in the absence
20 of said additive.

In another aspect the invention provides an electrical device, especially a circuit protection device, which comprises:

(a) an element composed of a conductive polymer composition as defined above, and

(b) at least two electrodes which can be connected to a source of electrical power and which, when so connected, cause current to flow through said element.

The compositions are particularly useful in electrical devices as described in the contemporaneously filed applications corresponding to U.S. Serial Nos. 141,987, 142,053 and 142,054 (MP0713, MP0724 and MP0725).

The compositions may exhibit PTC, ZTC, or NTC behavior; for example any of the compositions disclosed in the prior art and the earlier applications referred to above may be modified by the inclusion of at least one arc-controlling additive. The invention is especially valuable in relation to PTC compositions, particularly those having low resistivities at 23°C, eg. below 20 ohm. cm, preferably below 10 ohm. cm, especially below 2 ohm. cm, which are useful in circuit protection devices.

The preferred arc-controlling additives for use in the present invention are particulate materials, particularly inorganic materials, especially hydrated inorganic materials.

Particularly good results have been obtained using alumina trihydrate, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. Other inorganic materials include magnesia hydrate, magnesia and alumina.

5 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/cc of composition, with higher values, eg. at least 8,000 m^2/cc , at least 10,000 m^2/cc and at least 12,000 m^2/cc being particularly preferred.

10 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.

15 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 oxides of elements of the transition series, lanthanide series or non-transuranic actinide series disclosed in
20 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

5 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 50 millimicrons and a surface area, S in m^2/g such that S/D is not more than 10.

10 When using such a carbon black, preferably the quantity

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

is less than 1.

The polymer component in the composition, which
15 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
20 at least one polar comonomer copolymerisable therewith, eg. 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, eg. to a gel fraction of at least 0.4 or 0.6. For some purposes, compositions free of cross-linking are preferred, because
5 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
10 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.

15 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 $1800 \text{ m}^2/\text{cc}$
20 of composition, are described and claimed in the contemporaneously filed application corresponding to U.S. Serial Nos. 141,984 and 141,988 (MP0712 and MP0714).

The invention is illustrated by the following Examples.

Example 1

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

TABLE 1

		<u>MASTERBATCH</u>			<u>FINAL MIX</u>		
		g	wt%	vol%	g	wt%	vol%
10	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
15	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 millimicrons, a density of 1.8 g/cc, and a surface area (s) of 32 m²/g.

20 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.

25 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
5 948 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).

10 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
15 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 U.S. Serial No. 142,053 (MP0724).

20

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 millimicrons	Density g/cc	Surface Area m ² /g
5	Sterling NS Carbon black (N774)	75	1.8	25
	Sterling SO Carbon Black (N550)	41	1.8	42
	Hydral 705 Al ₂ O ₃ 3H ₂ O	0.5-2,000	2.42	12-15
	Maglite D MgO	< 44	3.32	-
		130	5.52-6.52	8.5

10 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;
 15 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
 20 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					
Polymer	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%
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 N5	14.8	48.5	32.8	32.2	26.3	-	-	-	-	-	-	-	-
Sterling S0	-	-	-	-	-	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

CLAIMS

1. A conductive polymer composition which has a resistivity at 23°C of less than 10^6 ohm. cm and which comprises a polymer having carbon black and/or graphite dispersed therein, characterised by comprising

- (1) 20 to 91% by volume of a polymer component;
- (2) 4 to 65% by volume of a conductive filler component which consists essentially of carbon black and/or graphite; and
- (3) an arc-controlling additive which is distributed in the polymer component.

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

3. A composition according to Claim 2 characterised in that the particulate material is a hydrated inorganic material, preferably alumina trihydrate.

4. A composition according to Claim 2 or 3 characterised in that the conductive filler and the arc-controlling additive have a total surface area of at least $1,800 \text{ m}^2$ per cc. of composition.

5. A composition according to any one of 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 50 millimicrons and a surface area, S, in m²/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 composition according to Claim 5 characterised in that the quantity

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

is less than 1.

7. An electrical device which comprises an element composed of a conductive polymer composition and at least two electrodes for passing current through the element, characterised in that the conductive polymer composition is as claimed in any one of claims 1 to 6.

8. A circuit protection device comprising an element composed of a conductive polymer composition which exhibits PTC behavior and a pair of electrodes for passing current through the element, 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 $1,800 \text{ m}^2/\text{cc}$ of
composition.