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⑤④ **Conductive polymers and devices containing them.**

⑤⑦ The properties of conductive polymer compositions, especially PTC compositions, are improved by incorporating therein a thermally conductive filler, preferably a filler of high aspect ratio, eg. crystalline graphite. Self-limiting heaters having greatly increased power can be produced through use of these compositions.

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DESCRIPTIONCONDUCTIVE POLYMERS AND DEVICES CONTAINING THEM

This invention relates to conductive polymers and heaters comprising them.

Electrical devices comprising conductive polymer elements, in particular heaters, circuit control devices, and sensors, have been described in prior publications and in co-pending, commonly assigned, patent applications. Reference may be made for example to U. S. Patents Nos. 2,952,761, 2,978,665, 3,243,753, 3,351,882, 3,571,777, 3,757,086, 3,793,716, 3,823,217, 3,858,144, 3,861,029, 4,017,715, 4,072,848, 4,085,286, 4,117,312, 4,177,376, 4,177,446, 4,188,276, 4,237,441, 4,242,573, 4,246,468, 4,250,400, 4,255,698, 4,271,350, 4,272,471, 4,304,987, 4,309,596, 4,309,597, 4,314,230, 4,315,237, 4,317, 027, 4,318,881 and 4,330,704; J. Applied Polymer Science 19, 813-815 (1975), Klason and Kubat; Polymer Engineering and Science 18, 649-653 (1978), Narkis et al; German OLS 2,634,999; 2,755,077; 2,746,602; 2,755,076; and 2,821,799; and European Application Nos. 38713, 38714, 38715, 38716, 38717, 38718, and 63440; and U.K. Patent Application No. 2076106A.

We have now discovered that conductive polymer compositions, especially PTC compositions, can be surprisingly improved by incorporating into them a suitable amount of a thermally conductive filler, preferably one having a high aspect ratio. The amount of the filler is preferably such that a shaped element of the composition has a thermal conductivity in at least one direction which is at least 2.0 times the thermal conductivity of an element which is identical except that the thermally conductive filler is not

present therein. Such compositions are particularly useful as components of self-limiting heaters. The presence of the thermally conductive filler apparently results in a more uniform generation of heat in, and/or
5 dissipation of heat from, and/or absorption of heat into, the conductive polymer, this being particularly important when the conductive polymer exhibits PTC behavior, since it greatly increases the current density threshold at which a so-called "hot line" forms
10 when current is passed through the conductive polymer (as further discussed below) and furthermore results in broadening of the "hot line" when formed.

The thermally conductive fillers which are preferably used in this invention have an aspect ratio of
15 at least 10 and a thermal conductivity of at least 5 Btu. ft/hr sq.ft. °F; a preferred filler is highly crystalline graphite. Measurement of the aspect ratio of the filler can be carried out by known methods, employing for example a scanning electron microscope or
20 a suitable optical microscope to determine the maximum and minimum dimensions of a suitable number (at least 100) of randomly chosen particles, and where necessary employing suitable averaging techniques.

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

- (a) a polymeric component, and
- (b) dispersed in the polymeric component,
 - (i) a first filler which is electrically conductive, and

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- (ii) at least 2% by volume, based on the volume of the polymeric component, of a second filler which has an aspect ratio of at least 10 and a thermal conductivity of at least 5 Btu. ft/hr sq ft.°F.

In another aspect the invention provides a self-limiting heater comprising an element composed of a composition as defined above and at least two electrodes which can be connected to a source of electrical power and which, when so connected, cause current to flow through the conductive polymer element.

The conductive polymer compositions of the present invention may exhibit PTC, ZTC or NTC behavior. However, the most dramatic improvements in performance are obtained when PTC conductive polymer compositions are used. The presence of the thermally conductive filler in a PTC conductive polymer not only greatly increases the current density threshold at which a hot line forms, but also broadens the hot line if a hot line does form. In a PTC conductive polymer heater, the most important benefit provided by the thermally conductive filler is that the heater can now be operated at a higher current density (and therefore higher power output in a given geometry and thermal environment) without hot line formation. This benefit can be exploited in a number of different ways. For example, increased power output can be obtained by increasing the length of the current path through the PTC element, or by decreasing the crosssectional area of the PTC element at right angles to the current flow, or by increasing the voltage of the power source. When higher voltage sources are used, compositions of lower

resistivity can be used; this is very valuable when the resistivity would otherwise be on a steep part of the loading curve (i.e. the graph of conductive filler content vs. resistivity, usually resistivity at room temperature). The presence of the thermally conductive filler also provides the benefit that if, through some mischance, a hot line does form, it is a relatively broad hot line which is less likely to damage the heater.

10 The first filler which is used in this invention
is electrically conductive and is selected primarily
to provide the conductive polymer with desired resist-
ivity at different temperatures. The second filler is
selected primarily to provide the conductive polymer with
15 desired thermal properties. The second filler can be
electrically conductive. If an electrically conductive
second filler is used in the conductive polymer, its
presence may (but does not necessarily) have a signifi-
cant effect on the electrical properties of the
20 conductive polymer. The first filler generally has an
aspect ratio less than 10, preferably less than 5. The
preferred first filler is carbon black, but other
conductive fillers can also be used. Especially for
self-limiting strip heaters, it is preferred to make
25 use of a carbon black which (in combination with the
second filler) will produce a composition having a
resistivity which initially increases relatively slowly
(or remains substantially constant or decreases slightly)
with a rise in temperature above ambient and which then
30 increases gradually to a moderately high level.

The second filler preferably has an aspect ratio of at least 10, particularly at least 20, especially at least 50. The particles may be plate-like, which is preferred, or rod-like. The higher the aspect ratio the better, and, therefore, the processing techniques employed preferably do not break the particles so that their initial aspect ratio is reduced. The second filler is composed of a substance having a thermal conductivity of at least 5, preferably at least 20, especially at least 50, Btu. ft/hr sq.ft.°F. The higher the thermal conductivity the better. The average maximum dimension of the particles is usually from 10 to 600 microns, preferably 25 to 100 microns. The amount of the second filler is at least 2%, preferably at least 6% by volume, based on the volume of the polymeric component. Processing of the composition becomes increasingly more difficult as the percentage of total filler increases. The amount and type of the second filler are preferably such that the thermal conductivity of the composition (in at least one direction if it is anisotropic) is at least twice, preferably at least 2.5 times, eg. about 3 times, that of the same composition without the second filler. The preferred second filler is graphite in a form which has an aspect ratio of at least 5, especially premium (or highly crystalline) graphite. Other possible fillers include metal (eg. aluminum) flakes and fibers, metal-coated flakes and fibers, and metal flakes and fibers having an insulating coating, e.g. of a polymer, thereon.

It is desirable that the second filler, when it is part of a PTC heater element, should have at least a substantial degree of orientation in the direction of current flow through the composition. When the heater is so constructed that the direction of current flow changes with temperature, the particles should preferably have at least a substantial degree of orientation in the direction of current flow when the device is in a high temperature high resistance state.

10 In the conductive compositions containing the second, thermally conductive filler, the ratio by volume of the second filler to the first filler may be for example 2:1 to 3:1, and the total filler content may be for example 10 to 30% by volume.

15 In the self-limiting heaters of the invention, the resistivity at room temperature of the conductive polymer composition may for example be 0.1 to 200 ohm.cm for heaters to be used at low voltages, e.g. 12 to 60 volts DC; 50 to 10,000 ohm.cm for heaters to be used at normal supply voltages, e.g. 100-360 volts AC; and 10,000 to 100,000 ohm.cm for heaters to be used at higher voltages. The invention is particularly useful for the simplest form of self-regulating strip heater, in which two or more parallel elongate electrodes are embedded in an elongate strip of PTC conductive polymer which has been melt-extruded around the electrodes. The electrodes, which are usually solid or stranded wires, can be in physical contact with the PTC composition or separated therefrom by a conductive layer, eg. a priming layer or a layer of a ZTC conductive polymer.

For reasons explained above (and further explained below in connection with Figure 1), this invention makes it possible to design heaters in novel configurations, for example, strip heaters which have the relatively wide and flat configurations which are desirable for example for heating flat substrates, but which have hitherto been so susceptible to hot lining that they have not been made. Thus a preferred embodiment of the invention is a strip heater comprising two or more elongate parallel electrodes embedded in a PTC conductive polymer element as defined, the distance between the closest points of the electrodes being at least 7 times, preferably at least 10 times, the thickness of the strip between the electrodes (or, if the thickness varies, the average thickness). A heater of this kind is illustrated in cross-section in Figure 2, and comprises wire electrodes 1 and 2 embedded in PTC conductive polymer element 3 which is surrounded by insulating jacket 4.

Referring now to the accompanying drawing, Figure 1 shows the relationship between the passive power and active power of a comparative PTC strip heater, not in accordance with the invention, and various PTC strip heaters of the invention when suspended in air and when in continuous contact with a good heat sink, e.g. when pressed into intimate contact with a metal block. The passive power is the power initially generated by the heater when first connected to the power supply, while the active power is the power generated by the heater when equilibrium is reached. Curves of the kind shown

in Figure 1 can be generated by systematically changing the voltage of the power source. The curves shown in Figure 1 are not intended to be completely accurate for any particular heater, but they are generally representative of the curves that would be obtained for heaters which employ a PTC conductive polymer composition based on polyethylene and which have dimensions as shown in the Examples.

It will be seen that on each curve, the active power reaches a maximum and then declines. The decline is the result of the formation of a hot line. It will also be seen that the maximum active power (and maximum permissible "passive" power) is much greater when the heater is attached to a heat sink. Unfortunately, however, it is seldom, if ever, possible to make use of this fact, because in practice some part of the heater nearly always becomes separated from the heat sink and then behaves substantially as though it were in air, thus initiating a progressive deterioration of the heater if it is operated at a power level which would be satisfactory if it were bonded to the heat sink. Curves 1 and 2 in Figure 1 are curves for a strip heater in which neither the conductive polymer nor the jacket contains a thermally conductive filler, in air (Curve A) and attached to a heat sink (Curve B); these curves show that the heater cannot be used in conjunction with a power source which results in a passive power greater than about 20 watts/ft (and a corresponding active power of about 15 watts/ft for any part of the heater which is not heat sunk and about 22 watts/ft for any part of the heater which is heat sunk). Curve 3 is for a strip heater of the invention, without a jacket,

suspended in air. Curve 4 is for a strip heater of the invention, with a conventional polymeric insulating jacket, attached to a heat sink. These curves show that these heaters can be safely connected to a power source which results in a passive power of up to about 75 watts/ft (and corresponding active power of about 25 watts/ft for Curve 3 and about 90 watts/ft. for Curve 4). Curves 5 and 6 are curves for a strip heater which contains the thermally conductive filler in both the conductive polymer and the jacket; the improvement is even more dramatic.

EXAMPLES

The invention is illustrated by the following Examples, which are summarized in the Table below.

15 In Examples 1, 3 and 4, the ingredients and amounts thereof (in volume percentages) shown in the Table under MB 1 (masterbatch 1) were mixed in a preheated Banbury mixer; dumped; placed on a mill heated to 149°C; extruded into water through an 8.9 cm extruder fitted with a strand die; and pelletized. The same procedure was followed for masterbatch 2 (MB2). The same procedure was used to convert into pellets a mixture of the indicated weights of the two masterbatches and additional amounts of polyethylene, EPDM rubber and antioxidant to give a final mix containing the indicated volume percentages of the different ingredients. In Example 2, the indicated ingredients and amounts thereof were dry-blended in a Henschel mixer; mixed in Werner-Pfleiderer twin screw extruder at 180-215°C; extruded into water through a strand die; and pelletized.

In each of the Examples, the pellets of the Final Mix were fed to a 3.8 cm Davis Standard Extruder and extruded through a rectangular die around two 18 AWG nickel-coated copper wires separated by 2.54 cm, to give a heater strip
5 0.2 x 2.92 cm. The extrudate was passed through a water bath at 71°C, dried and spooled.

In each of the Examples, the ingredients and amounts thereof (in volume percentages) shown under "Jacket" in the Table were mixed and converted into pellets by the
10 same procedure as for the masterbatches. After drying, the pellets were extruded through a 3.8 cm Davis Standard extruder into a sheet 15.25 cm wide and 0.05 cm thick, which was then slit into strips 3.2 cm wide and 30 cm long. Pairs of these strips were belt-laminated
15 around 30 cm lengths of the heater strips to give insulated strip heaters substantially as shown in Figure 2.

The heater strips (without jackets) and one of the jacketed heaters were tested to determine their maximum
20 active power outputs, with the results shown in the Table. The procedure used was to suspend the heater strip in air at 70° F. and then to determine the power output of the heater (at equilibrium) when connected to a succession of different voltage sources.

The various ingredients shown in the Table are further identified as follows:

Polyethylene is a high density polyethylene available from Phillips under the trade name Marlex 6003.

- 5 Rubber is an ethylene-propylene-diene rubber available from Exxon under the trade name Vistalon 3708 (Examples 1, 3 and 4 and Jacket) or an ethylene-propylene rubber available from Exxon under the trade name Vistalon 719 (Example 2).
- 10 Polypropylene is polypropylene available from Reichold Chemicals under the trade name Polybond 1016.

The graphites are highly crystalline flake graphites available from Superior.

CLAIMS

1. A conductive polymer composition, particularly a PTC composition, which comprises
 - (a) a polymeric component, and
 - (b) dispersed in the polymeric component, a first
5 filler which is electrically conductive,
characterized in that that the composition also contains
at least 2% by volume, based on the volume of the polymeric
component, of a second filler which has an aspect ratio
of at least 10 and a thermal conductivity of at least
10 5 Btu. ft/hr. sq ft. °F.
2. A composition according to claim 1, characterized
in that the second filler has an aspect ratio of at
least 20, preferably at least 50.
3. A composition according to claim 1 or 2, char-
15 acterized in that the second filler has a thermal
conductivity of at least 20 Btu. ft/hr. sq ft. °F.,
preferably at least 50 Btu. ft/hr. sq. ft. °F.
4. A composition according to any one of claims 1 to
3, characterized in that it contains at least 6% by
20 volume of the second filler.
5. A composition according to any one of claims 1 to
4, characterized in that the second filler is highly
crystalline graphite.

6. A composition according to any one of claims 2 to 5, characterized in that the first filler is carbon black and the second filler is graphite.

5 7. A composition according to any one of claims 1 to 6, characterized in that it has a thermal conductivity in at least one direction which is at least 2.5 times the thermal conductivity of a composition which is identical except that the second filler is not present therein.

10 8. A self-limiting heater which comprises

(1) a PTC element composed of a conductive polymer which exhibits PTC behavior and

(2) at least two electrodes which can be connected to a source of electrical power and which, when
15 so connected, cause current to flow through the conductive polymer element;

characterized in that the conductive polymer composition is a composition as claimed in any one of claims 1 to 7.

20 9. A heater according to claim 8 characterized in that the PTC element is in the form of an elongate strip having the electrodes embedded therein, the distance between the electrodes being at least 7 times, preferably at least 10 times, the thickness of the strip.

10. A self-limiting strip heater which comprises

(1) a PTC element which is in the form of an elongate strip and which is composed of a conductive polymer, the conductive polymer exhibiting PTC behavior and comprising

5

(a) a first polymeric component and

(b) dispersed in the first polymeric component,

(i) a first filler which is electrically conductive and

10

(ii) a second filler which is thermally conductive; and

(2) two elongate parallel electrodes which are surrounded by said PTC element, the distance between the electrodes being at least 7 times the thickness of the PTC element.

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Fig. 1.

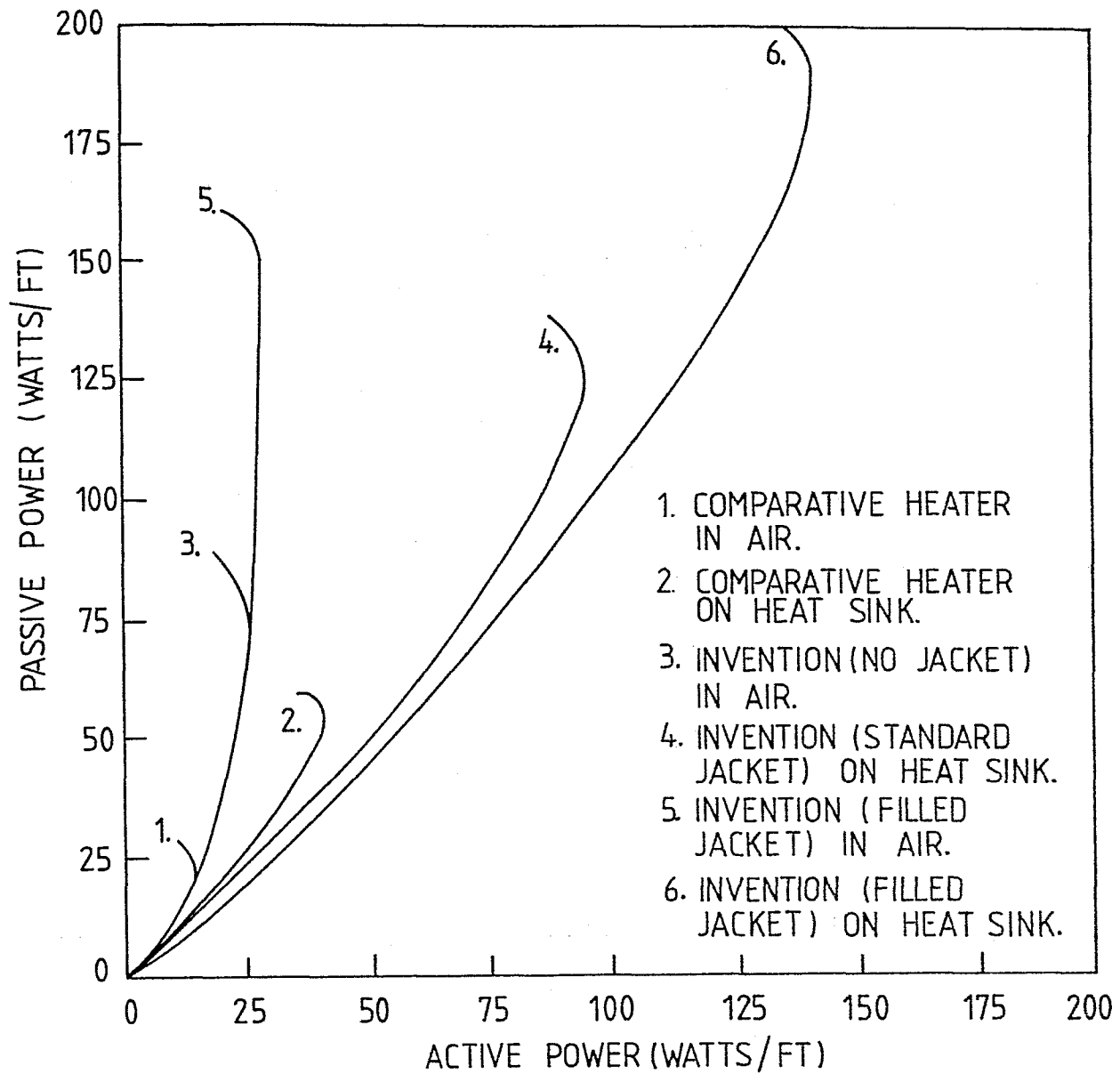


Fig. 2.

