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(54) **Polymeric PTC composition and circuit protection device made from the same**

(57) A polymeric PTC composition in which conductive particles having a melting point of at least 2000 °C are dispersed in an organic polymer, and a circuit protection device having a PTC element consisting of the PTC composition and at least two electrodes which are pressure welded to the PTC element and electrically connected thereto are presented. The composition and the device of the present invention exhibit a low resistance and good conductivity under normal operating conditions, and the conductive particles are not melted to locally form a conductive circuit even under large electric current and high voltage, but the resistance rises due to the PTC characteristics to protect the circuit against the over-current.

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## Description

### BACKGROUND OF THE INVENTION

#### Field of the Invention

The present invention relates to a PTC composition and a circuit protection device using the same, in particular it relates to a composition having a positive temperature coefficient (PTC) of resistivity, which undergoes a rapid and sharp increase in resistance over a relatively narrow temperature range as temperature increases, and to a circuit protection device employing an element comprising the PTC composition, which is particularly useful for a breaker and the like, having improved current-limiting performance and improved repeat stability.

#### Description of the Related Art

The PTC composition having the above-mentioned PTC characteristics has been generally used in a circuit protection element and the like for a circuit including a heater, a positive character thermistor, a heat sensor, a battery and the like, and it limits the current-flow in the circuit under short-circuit condition, and resets the circuit when the cause of the short-circuit is removed.

Further applications of the PTC composition include, for example, a PTC element comprising the composition and at least two electrodes that are electrically connected to the composition. This PTC element has been used as an element having temperature self controlling function, to protect a circuit against over-current and over-heat as described above.

Now, the protection mechanism obtained with a PTC element against over-current will be described. As the resistivity ( $\rho_L$ ) of a PTC composition at an ordinary room temperature is sufficiently low, normally current flows through the circuit. But, if large current flows through the circuit by short-circuit accident and the like, Joule heat is generated in the PTC element due to the large current, and the temperature of the element rises, thus the resistivity increases (exhibition of PTC behavior), so that the current does not flow through the element and the circuit can be protected (this is referred to as current limiting performance).

The PTC element, i.e., the PTC composition needs to have such current limiting performance that can be exhibited repeatedly even under high voltage. In order to improve the current limiting performance of the PTC element, a sufficiently lowered resistivity ( $\rho_L$ ) and an effective PTC characteristic (a large  $\rho_H/\rho_L$ ) are required.  $\rho_H$  refers to the peak resistivity which is given by a PTC curve at a high temperature.

Various materials have been developed as the PTC composition, and one of the conventionally known compositions comprises  $\text{BaTiO}_3$  and an oxide of a monovalent or trivalent metal added thereto. As a matter of fact, this material has a problem that it exhibits NTC charac-

teristics immediately after the PTC characteristics are exhibited, thus the current starts to flow again within 1 msec or less.

To cope with this problem, PTC compositions have been developed which comprise an organic polymer such as polyethylene (abbreviated as PE), polypropylene and ethylene-acrylic acid copolymer, and conductive particles such as carbon black (abbreviated as CB), carbon fiber, graphite or finely divided metal particles, dispersed therein. These PTC compositions are generally produced by adding, followed by kneading, conductive particles of a necessary amount to one or more kinds of resins which are used as the organic polymer.

If CB, carbon fiber or graphite is used as conductive particles,  $\rho_L$  of the resulting PTC element cannot be lowered to  $0.1 \Omega\text{cm}$  or less, even when the organic polymer is loaded with these conductive particles by closest packing, and when the  $\rho_L$  of the PTC element is decreased to the minimum value as low as  $0.1 \Omega\text{cm}$ ,  $\rho_H/\rho_L$  is decreased as well and only shows around 100. Accordingly, the current limiting performance cannot be improved sufficiently.

On the other hand, the resistivity of the metal particles is of the order of  $10^{-6} \Omega\text{cm}$ , and it is much lower than  $0.05 \Omega\text{cm}$  that is the resistivity of CB. Accordingly, the  $\rho_L$  of the resulting PTC device is expected to be lowered by the use of metal particles such as Cu and Ni, and yet those metal particles have not been used as often as CB as the conductive particles for PTC compositions in the past. One of the biggest reasons for that is that the PTC compositions containing the conventionally known metal particles, used under large current and high voltage, cause internal arc phenomenon (micro arc is generated between conductive particles) and the composition undergoes electric destruction. When the internal arc phenomenon is caused, the metal particles in the PTC composition are molten and the molten metal particles are bonded together to locally form a conductive circuit and the large current is concentrated on a part of the element and the element is destroyed. Discharge is also easily caused in a micro space between the composition and the electrode interface, the resin on the discharged part is degraded, and decomposed, thus the deterioration is accelerated, sometimes ending in an explosion. This inconveniency has been remarkable under an electric voltage of some 10 volts or higher. Accordingly, this type of composition has not been used for a self-reset type over-current protection element.

A PTC composition containing both CB and metal particles as conductive particles has been disclosed in the publication of Japanese Patent Laid-Open NO. 64-53503. There, the metal particles are contained in order to improve the heat-conductivity of the PTC composition.

In a circuit protection device, the PTC element and the electrode are generally fusion-bonded by heat (such as is referred to as fusion bond electrode system) so as to

materialize best electric contact to minimize the contact resistance. An illustrative example comprises a PTC element and copper foils thermally fusion bonded thereto. A merit of this system is that the contact resistance between the PTC element and the electrode is decreased and the resistance is reduced as a whole. Its demerit, however, is that the peak current (current limiting peak value:  $I_P$ ) at the cut-off of the over-current cannot be reduced sufficiently, resulting in insufficient current limiting performance. Also when the short-cut current flows repeatedly, the cut-off cannot be carried out under the same conditions as those in the initial state, therefore the device has unsatisfactory repeat stability.

On the other hand it is disclosed in Japanese Patent Laid-Open NO.4-266001 that a PTC element electrically connected to electrodes by simply pressing the element from both sides so that the electrodes are contacted with the PTC element (such is referred to as pressure welding electrode system). The circuit protection device of the pressure welding electrode system has such advantages that it can decrease the current limiting peak value ( $I_P$ ), has excellent current limiting performance and works with high repeat stability. But, in comparison with the product of the fusion bond electrode system, the contact resistance between the PTC element and the electrode is bigger, therefore the resistance under normal operating conditions is increased, and the conductivity becomes a little inferior. In order to obtain good current limiting performance without sacrificing the conductivity under normal operating conditions, a PTC element having sufficiently small resistivity at a normal temperature ( $\rho_L$ ) is required.

As described above, the metal particles used as conductive particles in the PTC composition have very low resistivity compared to that of CB, allows the resistivity ( $\rho_L$ ) of the PTC element at an ordinary room temperature to decrease, and accordingly expected to show good conductivity normally, but the PTC composition containing the conventionally known metal particles causes internal arc phenomenon when used under large current and high voltage, thus metal particles are melted and a conductive circuit is locally formed, resulting in the destruction of the composition thereby the PTC element, and therefore, the resulting circuit protection device lacks in safety and reliability and cannot protect a circuit repeatedly against the over-current.

The circuit protection device in which the electrodes are provided on the above-mentioned PTC element by pressure welding electrode system, shows good current limiting performance and works with high repeat stability, but the normal resistance is increased to show a little inferior conductivity. And in order to improve the conductivity, a PTC element having a sufficiently small resistivity at an ordinary room temperature is required.

The present invention has been achieved in order to solve the above-mentioned problems, and an object of the present invention is to provide a PTC composition

having a low resistance and good conductivity under normal operating conditions, which does not form any local conductive circuit under large current and high voltage, and which protects a circuit against over-current. That means, an object of the present invention is to provide a PTC composition having excellent current limiting performance, high safety, and high reliability and which can be used favorably, for example, for a self-reset type over-current protection element.

Another object of the present invention is to provide a circuit protection device which has a low resistance, and good conductivity under normal operating conditions, which shows excellent current limiting performance and which works with high repeat stability.

## SUMMARY OF THE INVENTION

As a result of intensive studies, the present inventors have solved the above-mentioned conventional problems.

Accordingly, the present invention provides a polymeric PTC composition which comprises an organic polymer and conductive particles having a melting point of at least 2000 °C which are dispersed therein.

Further, the present invention provides the above-mentioned polymeric PTC composition wherein the average particle size of the conductive particle is 0.01 - 50 microns.

Furthermore, the present invention provides the above-mentioned polymeric PTC composition wherein the conductive particles are contained in an amount of 50 - 99 % by weight based on the composition.

Still further, the present invention provides the above-mentioned polymeric PTC composition wherein the conductive particles are particles containing at least one kind of substance selected from the group consisting of a metal, metal carbide, metal boride, metal silicide and metal nitride.

Yet further, the present invention provides the above-mentioned polymeric PTC composition wherein the conductive particles are particles of at least one kind of substance selected from the group consisting of tungsten, carbide thereof, boride thereof, silicide thereof, and nitride thereof.

Further, the present invention provides the above-mentioned polymeric PTC composition wherein the conductive particle is tungsten.

Furthermore, the present invention provides a circuit protection device comprising a PTC element consisting of the above-mentioned polymeric PTC composition and at least two electrodes which are welded to the PTC element with pressure and electrically connected thereto.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a characteristic diagram showing the relationship between the resistivity of the PTC element

at an ordinary room temperature and the particle size of the conductive particle (tungsten) according to the present invention;

FIG. 2 is a characteristic diagram showing the relationship between the resistivity of the PTC element at an ordinary room temperature and the loading ratio of the conductive particle (tungsten) according to the present invention;

FIG. 3 is a characteristic diagram showing the relationship between the torque during the kneading and the loading ratio of the conductive particle (tungsten) according to the present invention;

FIG. 4 is a characteristic diagram showing the PTC curve representing the relationship between the temperature and the resistivity of the PTC element according to Example 1 of the present invention;

FIG. 5 is a characteristic diagram showing the relationship between the peak current ( $I_P$ ) at the cut-off of the over-current and the resistivity of the PTC element according to Example 1 and those of the PTC elements according to Comparative Examples;

FIG. 6 is a schematic illustration of an optical microscope photograph taken before and after current limiting test, showing the dispersion condition of tungsten particles, which are the conductive particles of the PTC element according to Example 1 of the present invention; and

FIG. 7 is a schematic illustration of an optical microscope photograph taken before and after current limiting test, showing the dispersion condition of nickel particles, which are the conductive particles of the PTC element according to Comparative Example 6 of the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

The polymeric PTC composition according to the present invention comprises an organic polymer and conductive particles having a melting point of at least 2000 °C that are dispersed in the organic polymer.

When used under large current and high voltage, and even an internal arc is generated, the conductive particles having a melting point as high as at least 2000 °C, are not melted and do not form a local conductive circuit in the PTC composition, or in the element, unlike the PTC composition containing the conventional metal particles, therefore the PTC composition and the element are not electrically destroyed. Also, when large current flows, the temperature of the PTC element increases and the resistance increases as well, the circuit can be protected against the over-current. In addition, the resistivity is low and the resistivity at an ordinary room temperature ( $\rho_L$ ) can be sufficiently decreased.

Therefore, according to the present invention, the conductive particles are not melted under large current and high voltage to locally form a conductive circuit and

the resistivity at an ordinary room temperature ( $\rho_L$ ) can be sufficiently decreased so that good conductivity is exhibited under normal operating conditions and the peak resistance ( $\rho_H$ ) can be increased, that means  $\rho_H/\rho_L$  can be increased, therefore the flow of current can be securely cut-off if large current flows through the device, to protect the circuit; thus a PTC composition having an excellent current limiting performance, high safety and high reliability can be obtained. The element using the same functions well as a self-reset type over-current protection element.

The metal particles having a low resistivity can decrease  $\rho_L$  of the PTC element, but they might cause internal arc phenomenon and present defective conditions. But the finding that the use of a substance having a melting point of at least 2000 °C, as the conductive particles, can provide an excellent PTC composition which is free from internal arc phenomenon, having a big  $\rho_H$  and can make an over-current protection element, has been obtained by the intensive study of the present inventors who have carried out various experiments.

CB is a sublimating substance having no melting point and is not included in the category of the conductive particles according to the present invention.

The average particle size of the conductive particle is preferably 0.01 - 50  $\mu\text{m}$ , and more preferably it is in the range of from 0.1 to 30  $\mu\text{m}$ . The organic polymer cannot be loaded with the conductive particles having a small average particle size in a large amount since the particle size distribution is small and the conductive particles become bulky. Accordingly, the resistivity of the PTC element at an ordinary room temperature is increased. The particles having a large average particle size result in the increase of the resistivity of the PTC element at an ordinary room temperature when the same amount of the particle are loaded in the polymer. FIG. 1 is a characteristic diagram showing the relationship between the particle size of the conductive particle contained in the PTC element, illustratively tungsten, and the resistivity of the PTC element at an ordinary room temperature, and black circle represents the case wherein the tungsten is loaded in an amount of 90 % by weight, white circle represents the case wherein the tungsten is loaded in an amount of 95 % by weight. It is shown that the resistivity of the PTC element at an ordinary room temperature increases with increasing average particle size. By the use of the conductive particles having the above-mentioned average particle size, a PTC composition having a small resistivity at an ordinary room temperature can be obtained. The conductive particles having different particle sizes can be appropriately selected according to the application and the desired characteristics of the PTC composition.

The content of the conductive particles is preferably 50 - 99 % by weight based on the PTC composition and more preferably it is 70 - 97 % by weight. With low content of the conductive particles, the resistivity at an ordi-

nary room temperature is increased. When the content of the conductive particles is increased, the kneading torque during the kneading of the organic polymer with the conductive particles becomes high, and either the kneading becomes impossible or even if the kneading is possible, the resulting PTC element shows low elasticity and provides an element having a weak impact resistance which is not appropriate for a practical application. FIG. 2 is a characteristic diagram showing the relationship between the loading ratio of tungsten and the resistivity of the PTC element at an ordinary room temperature, and it is shown that the resistivity of the PTC element at an ordinary room temperature increases with decreasing loading ratio of tungsten. FIG. 3 is a characteristic diagram showing the relationship between the loading ratio of tungsten and the torque during the kneading, and it is shown that the loading ratio of tungsten increases as the torque during the kneading increases. The measurement was carried out by Laboplastomill equipment under the kneading condition of 200 °C and 50 rpm.

The conductive particles are desired to have a melting point of at least 2000 °C, and their electric conductivity, heat conductivity as well as fusion resistance to micro arc are desired to be good enough for a PTC composition to provide excellent PTC characteristics. Particles of a metal, metal carbide, metal boride, metal silicide and metal nitride are used. These can be used alone or in combination of two or more kinds, and appropriately selected according to the application and the desired characteristics of the PTC composition.

An example of the metal particles includes tungsten (W). Examples of the metal carbide include TiC, ZrC, VC, NbC, TaC, Mo<sub>2</sub>C, and WC. Examples of the metal boride include TiB<sub>2</sub>, ZrB<sub>2</sub>, NbB<sub>2</sub>, TaB<sub>2</sub>, CrB, MoB, and WB. Examples of the metal silicide include TaSi<sub>2</sub>, MoSi<sub>2</sub>, and WSi<sub>2</sub>. Examples of the metal nitride include TiN, ZrN, VN, NbN, TaN, and Cr<sub>2</sub>N. (Ti: titanium, Zr: zirconium, V: vanadium, Nb: niobium, Ta: tantalum, Mo: molybdenum, and Cr: chromium.)

In particular, it is preferable to use particles of tungsten, and the carbide, boride, silicide and nitride thereof. Tungsten is a metal having the highest melting point (3410 °C) among metal particles, besides tungsten and a tungsten compound of a desired particle size are easily available as they are supplied steadily.

As the organic polymer, polyethylene, polyethylene oxide, polybutadiene, polyethylene acrylate, ethylene-ethyl acrylate copolymer, ethylene-acrylic acid copolymer, polyester, polyamide, polyether, polycaprolactam, fluorinated ethylene-propylene copolymer, chlorinated polyethylene, chlorosulphonated ethylene, ethylene-vinyl acetate copolymer, polypropylene, polystyrene, styrene-acrylonitrile copolymer, polyvinyl chloride, polycarbonate, polyacetal, polyalkylene oxide, polyphenylene oxide, polysulphone and a fluororesin are used according to the present invention and these can be used alone or two or more kinds of the compound

selected from these are used in admixture as a blended polymer. The kind, the composition ratio and the molecular weight of the organic polymer can be appropriately selected according to the desired property, and application.

For preparation of the PTC composition, various additives can be mixed, if necessary, with the above-mentioned organic polymers and conductive particles. Examples of the additive include an antioxidant, a stabilizer, and a flame-retardant such as an antimony compound, phosphorus compound, chlorine compound and bromine compound.

The PTC composition is prepared by mixing the organic polymer, conductive particles and other additives at a desired ratio followed by kneading. The conductive particles can be added to the organic polymer, then kneaded, or both materials can be simultaneously mixed and kneaded. The blending ratio of the organic polymer and the conductive particles can be appropriately selected according to the content of the conductive particles in the desired composition, the kind of the organic polymer, and the kind of the kneaders such as Banbury type mixer, pressure kneader and roll mill, and the loading ratio of the conductive particles is preferably in the range of from 50 to 99 % by weight of the PTC composition.

The PTC composition of the present invention can be used for various uses. When it is used as a PTC element, the PTC composition can be molded into, illustratively, a film form and metal foil electrodes are bonded on the front and the back surfaces of the film by thermo-compression bonding to form a laminate, then the laminate is cut to a desired size and lead wires are welded on the electrode surface by soldering, brazing, or spot welding and the like to provide a PTC element.

Particularly useful is a circuit protection device comprising the above-mentioned PTC element and at least two electrodes electrically connected thereto by pressure welding.

In such a circuit protection device, the PTC element and the electrodes are electrically connected by pressure welding electrode system, the current limiting peak value ( $I_P$ ) can be decreased as described above and the device has excellent current limiting performance and works with high repeat stability.

According to the first viewpoint of the polymeric PTC composition of the present invention, there is an advantage that the polymeric PTC composition shows a low resistance and good conductivity under normal operating conditions, and even under large current and high voltage, the conductive particles are not melted to locally form a conductive circuit, but the resistance is increased due to the PTC characteristics to protect the circuit against the over-current by dispersing the conductive particles having a melting point of at least 2000 °C in the organic polymer. Accordingly, there is an advantage that a polymeric PTC composition having excellent PTC characteristics, and current limiting per-

formance, high safety and reliability can be obtained.

According to the second viewpoint of the polymeric PTC composition of the present invention, there is an advantage that a polymeric PTC composition having a small resistivity at an ordinary room temperature can be obtained by the use of conductive particles having an average particle size of 0.01 - 50  $\mu\text{m}$ ,

According to the third viewpoint of the polymeric PTC composition of the present invention, there is an advantage that a polymeric PTC composition having a small resistivity at an ordinary room temperature which is suited for practical use can be obtained by incorporating the conductive particles in the composition in an amount of 50 - 99 % by weight.

According to the fourth viewpoint of the polymeric PTC composition of the present invention, there is an advantage that a polymeric PTC composition having excellent PTC characteristics and current limiting performance can be obtained by employing particles containing at least one kind of a metal, metal carbide, metal boride, metal silicide and metal nitride as conductive particles.

According to the fifth viewpoint of the polymeric PTC composition of the present invention, there is an advantage that a polymeric PTC composition having even more excellent PTC characteristics and current limiting performance can be obtained by employing particles of at least one of tungsten, carbide, boride, silicide and nitride thereof as conductive particles.

According to the sixth viewpoint of the polymeric PTC composition of the present invention, there is an advantage that a polymeric PTC composition having higher safety and reliability, excellent PTC characteristics and current limiting performance can be obtained by employing tungsten as conductive particles.

The circuit protection device according to the present invention employs an element comprising the above-mentioned polymeric PTC composition, and comprises at least two electrodes that are electrically connected to the PTC element by pressure welding, accordingly the device acquires useful effects owned by the composition, and shows a low resistivity and good conductivity under normal operating conditions, has excellent current limiting performance and works with high repeat stability, therefore it is of high safety and high reliability.

## EXAMPLES

To further illustrate this invention, and not by way of limitation, the following examples are given.

### Example 1

10 parts by weight of high density polyethylene (abbreviated as HDPE, available from Mitsubishi Chemical Co., Ltd., under the trade name of HJ560) as an organic polymer, 90 parts by weight of tungsten (having

an average particle size of 0.88  $\mu\text{m}$ , a melting point of 3410 °C, available from Nippon Shinkinzoku Co., Ltd., under the trade name of W-1) as conductive particles, and 2 parts by weight of a phenol type antioxidant (available from Ciba-Geigy Co., Ltd., under the trade name of Irganox 1010) were kneaded in Laboplastomill equipment (manufactured by Toyo Seiki Co., Ltd.) at 200 °C for 15 minutes to prepare a PTC composition. The produced PTC composition was molded into a plate of 40 x 60 x 1 mm by hot-press and used for producing a PTC element. A polyethylene frame was produced by injection molding on the periphery of the PTC element for 20 mm to carry out insulation at the cut-off. Then the PTC element with the frame was sandwiched between electrodes and pressed from both sides to electrically connect the element and the electrodes (pressure welding electrode system) to provide a circuit protection device body, and the obtained device body was subjected to over-current cut-off test. The characteristic diagram of FIG. 4 illustrates the PTC curve showing the relationship between the temperature of the circuit protection device body and the resistivity. The resistivity at an ordinary room temperature ( $\rho_L$ ) was 0.01  $\Omega\text{cm}$ , peak resistivity ( $\rho_H$ ) was  $10^5 \Omega\text{cm}$ ,  $\rho_H/\rho_L$  was  $10^7$ . It showed very good characteristics; when the initial resistance was 1.2 m $\Omega$ , the cut-off current for the over-current of 50 kA at 300 V was 7.5 kA, when the initial resistance was 3.5 m $\Omega$ , the cut-off current was 4 kA.

Using PTC elements having different sizes, therefore having different initial resistances, the relationship between the resistance of the PTC element and the peak current (current limiting peak value:  $I_P$ ) of the circuit protection device body at the cut-off of the over-current was examined. The results are shown by the characteristic curve a of the characteristic diagram of FIG. 5. The results of the later-described Comparative Examples in which the fusion bond electrode system was used or CB was used as the conductive particles are also shown. In the FIG. 5, when the initial resistance is small, the smaller the  $I_P$  (the line heads for down left direction in FIG. 5), the better the current limiting performance. This figure shows that the current limiting performance of the circuit protection device of the Example 1 of the present invention is superior.

FIG. 6 is a schematic illustration of an optical microscope photograph showing the dispersion condition of tungsten particles, which are the conductive particles of the PTC element constituting this circuit protection device, and FIG. 6 (a) shows the condition before the cut-off (current limiting) test, and FIG. 6 (b) shows the condition after the cut-off test. The FIGs. show that there was no change between the conditions before and after the cut-off test, i.e. tungsten particles were similarly and homogeneously dispersed in the organic polymer 1.

## Example 2

5 parts by weight of HDPE (available from Mitsubishi Chemical Co., Ltd., under the trade name of HJ560) and 5 parts by weight of polypropylene (available from Mitsubishi Chemical Co., Ltd., under the trade name of MA03) were mixed and used as organic polymers, 90 parts by weight of a metal carbide, WC, (having an average particle size of 0.7  $\mu\text{m}$ , a melting point of 2785 °C, available from Nippon Shinkinzoku Co., Ltd. under the trade name of WC-10) as conductive particles, and 2 parts by weight of a phenol type antioxidant (available from Ciba-Geigy Ltd., under the trade name of Irganox 1010) were kneaded in Laboplastomill equipment (manufactured by Toyo Seiki Co., Ltd.) at 200 °C for 15 minutes to prepare a PTC composition. The produced PTC composition was molded into a plate of 40 x 60 x 1 mm by hot-press and used for producing a PTC element. A polyethylene frame was produced by injection molding on the periphery of the PTC element for 20 mm to carry out insulation at the cut-off. Then the PTC element with the frame was sandwiched between electrodes and pressed from both sides (pressure welding electrode system) to provide a circuit protection device, and the obtained device was subjected to over-current cut-off test in the way analogous to that of Example 1. When the initial resistance of the circuit protection device body was 1.5 m $\Omega$ , the cut-off current for the over-current of 50 kA at 300 V was 8 kA.

When the above-mentioned Example 2 was repeated by using 10 parts by weight of HDPE alone as an organic polymer, similar PTC characteristics were observed.

## Example 3

10 parts by weight of ethylene vinyl acetate copolymer as an organic polymer, 90 parts by weight of a metal oxide, ZrN (having an average particle size of 1  $\mu\text{m}$ , a melting point of 2980 °C, manufactured by from Nippon Shinkinzoku Co., Ltd.) as conductive particles, and 2 parts by weight of a phenol type antioxidant (available from Ciba-Geigy Ltd., under the trade name of Irganox 1010) were kneaded in Laboplastomill equipment (manufactured by Toyo Seiki Co., Ltd.) at 200 °C for 15 minutes to prepare a PTC composition. The produced PTC composition was molded into a plate of 40 x 60 x 1 mm by hot-press and used for producing a PTC element. A polyethylene frame was produced by injection molding on the periphery of the PTC element for 20 mm to carry out insulation at the cut-off. Then the PTC element with the frame was sandwiched between electrodes and pressed from both sides (pressure welding electrode system) to provide a circuit protection device, and the obtained device was subjected to over-current cut-off test in the way analogous to that of Example 1. When the initial resistance of the circuit protection device body was 1.1 m $\Omega$ , the cut-off current for the over-

current of 50 kA at 300 V was 8.5 kA.

When the above-mentioned Example 3 was repeated by changing the organic polymer to 10 parts by weight of HDPE, similar PTC characteristics were observed.

## Example 4

10 parts by weight of HDPE (available from Mitsubishi Chemical Co., Ltd., under the trade name of HJ560), 90 parts by weight of a metal silicide, WSi<sub>2</sub> (having an average particle size of 1  $\mu\text{m}$ , a melting point of 2160 °C, manufactured by Nippon Shinkinzoku Co., Ltd.) as conductive particles, and 2 parts by weight of a phenol type antioxidant (available from Ciba-Geigy Ltd., under the trade name of Irganox 1010) were kneaded in Laboplastomill equipment (manufactured by Toyo Seiki Co., Ltd.) at 200 °C for 15 minutes to prepare a PTC composition. The produced PTC composition was molded into a plate of 40 x 60 x 1 mm by hot-press and used for producing a PTC element. A polyethylene frame was produced by injection molding on the periphery of the PTC element for 20 mm to carry out insulation at the cut-off. Then the PTC element with the frame was sandwiched between electrodes and pressed from both sides (pressure welding electrode system) to provide a circuit protection device, and the obtained device was subjected to over-current cut-off test in the way analogous to that of Example 1. When the initial resistance of the circuit protection device body was 1.3 m $\Omega$ , the cut-off current for the over-current of 50 kA at 300 V was 8 kA.

## Example 5

10 parts by weight of HDPE (available from Mitsubishi Chemical Co., Ltd., under the trade name of HJ560), 90 parts by weight of a metal boride, WB (having an average particle size of 1  $\mu\text{m}$ , a melting point of 3700 °C, manufactured by Nippon Shinkinzoku Co., Ltd.) as conductive particles, and 2 parts by weight of a phenol type antioxidant (available from Ciba-Geigy Ltd., under the trade name of Irganox 1010) were kneaded in Laboplastomill equipment (manufactured by Toyo Seiki Co., Ltd.) at 200 °C for 15 minutes to prepare a PTC composition. The produced PTC composition was molded into a plate of 40 x 60 x 1 mm by hot-press and used for producing a PTC element. A polyethylene frame was produced by injection molding on the periphery of the PTC element for 20 mm to carry out insulation at the cut-off. Then the PTC element with the frame was sandwiched between electrodes and pressed from both sides (pressure welding electrode system) to provide a circuit protection device, and the obtained device was subjected to over-current cut-off test in the way analogous to that of Example 1. When the initial resistance of the circuit protection device body was 1.2 m $\Omega$ , the cut-off current for the over-current of 50 kA at 300 V was 8 kA.

When the above-mentioned Example 5 was

repeated by changing the organic polymer from HDPE alone to a mixture of HDPE and polypropylene, polypropylene alone, or a mixture of polyethylene and polypropylene, similar PTC characteristics were observed.

#### Example 6

10 parts by weight of polypropylene (available from Mitsubishi Chemical Co., Ltd., under the trade name of MA03), 90 parts by weight of tungsten (having an average particle size of 0.88  $\mu\text{m}$ , a melting point of 3410  $^{\circ}\text{C}$ , available from Nippon Shinkinzo Co., Ltd. under the trade name of W-1) as conductive particles, and 2 parts by weight of a phenol type antioxidant (available from Ciba-Geigy Ltd., under the trade name of Irganox 1010) were kneaded in Laboplastomill equipment (manufactured by Toyo Seiki Co., Ltd.) at 200  $^{\circ}\text{C}$  for 15 minutes to prepare a PTC composition. The produced PTC composition was molded into a plate of 40 x 60 x 1 mm by hot-press and used for producing a PTC element. A polyethylene frame was produced by injection molding on the periphery of the PTC element for 20 mm to carry out insulation at the cut-off. Then the PTC element with the frame was sandwiched between electrodes and pressed from both sides (pressure welding electrode system) to provide a circuit protection device, and the obtained device was subjected to over-current cut-off test in the way analogous to that of Example 1. The PTC characteristics of this circuit protection device body were such that the resistivity at an ordinary room temperature ( $\rho_L$ ) was 0.01  $\Omega\text{cm}$ , the peak resistivity ( $\rho_H$ ) was  $10^5 \Omega\text{cm}$ ,  $\rho_H/\rho_L$  was  $10^7$ . When the initial resistance was 1.2 m $\Omega$ , the cut-off current for the over-current of 50 kA at 300 V was 7.5 kA as well.

In the above-mentioned Examples, only one kind of metal or metal composite was used as conductive particles, but two or more kinds can be appropriately combined and used.

#### Comparative Example 1

40 parts by weight of HDPE (available from Mitsubishi Chemical Co., Ltd., under the trade name of HJ560) as an organic polymer, 60 parts by weight of CB (having an average particle size of 0.095  $\mu\text{m}$ , available from Degusa Co., under the trade name of Lampblack 101), and 2 parts by weight of a phenol type antioxidant (available from Ciba-Geigy Ltd., under the trade name of Irganox 1010) were kneaded to prepare a PTC composition. The produced polymeric PTC composition was sandwiched between two nickel plated copper foils having a thickness of 35  $\mu\text{m}$ , and hot pressed (140  $^{\circ}\text{C}$  for 1 minute) by thermo-compression bonding (fusion bond electrode system) into a size of 40 x 60 x 1 mm (overall thickness), then a polyethylene frame was produced by injection molding on the periphery of the PTC element for 20 mm to carry out insulation at the cut-off, and a circuit protection device was prepared. Then the obtained

circuit protection device was sandwiched between the electrodes for testing and over-current cut-off test was carried out in a way analogous to that used in Examples. The relationship between the resistance (R) of the PTC element and the peak current (current limiting peak value:  $I_P$ ) of the circuit protection device body at the cut-off of the over-current was examined using PTC elements having different sizes thus different initial resistances. The results are shown by the characteristic curve b in the characteristic diagram of FIG. 5. The diagram shows that the current limiting performance is considerably poor. When the resistance of the circuit protection device body at a room temperature was 1.2 m $\Omega$ , the cut-off current for 300 V and 50 kA was 28 kA, and when the resistivity at an ordinary room temperature was 2.8 m $\Omega$ , it was 9 kA and the characteristics were much worse than those obtained with the PTC element containing tungsten (Example 1).

#### Comparative Example 2

40 parts by weight of HDPE (available from Mitsubishi Chemical Co., Ltd., under the trade name of HJ560), 60 parts by weight of CB (having an average particle size of 0.095  $\mu\text{m}$ , available from Degusa Co., under the trade name of Lampblack 101) as conductive particles, and 2 parts by weight of a phenol type antioxidant (available from Ciba-Geigy Ltd., under the trade name of Irganox 1010) were kneaded to prepare a PTC composition. The polymeric PTC composition was hot pressed and molded into a plate having a size of 40 x 60 x 1 mm (overall thickness) to prepare a PTC element, then a polyethylene frame was produced by injection molding on the periphery of the PTC element for 20 mm to carry out insulation at the cut-off, and a circuit protection device was produced by pressure welding of electrodes on both sides of the PTC element (pressure welding electrode system) in a process analogous to that used in the above-mentioned Examples and the circuit protection device was subjected to over-current cut-off test. The relationship between the resistance (R) of the PTC element and the peak current ( $I_P$ ) of the circuit protection device body at the cut-off of the over-current was examined using PTC elements having different sizes and different initial resistances. The results are shown by the characteristic curve c in the characteristic diagram of FIG. 5. When the resistance of the circuit protection device body at a room temperature was 1.3 m $\Omega$ , the cut-off current for 300 V and 50 kA was 15 kA, and when the resistivity at an ordinary room temperature was 2.3 m $\Omega$ , it was 9 kA and when the resistivity at an ordinary room temperature was 3.8 m $\Omega$ , it was 7 kA and the characteristics were worse than those obtained with the PTC element containing tungsten (Example 1).

#### Comparative Example 3

10 parts by weight of HDPE (available from Mitsubi-



shi Chemical Co., Ltd., under the trade name of HJ560), 90 parts by weight of tungsten (having an average particle size of 0.88  $\mu\text{m}$ , a melting point of 3410  $^{\circ}\text{C}$ , available from Nippon Shinkinzoku Co., Ltd. under the trade name of W-1) as conductive particles, and 2 parts by weight of a phenol type antioxidant (available from Ciba-Geigy Ltd., under the trade name of Irganox 1010) were kneaded in Laboplastomill equipment (manufactured by Toyo Seiki Co., Ltd.) at 200  $^{\circ}\text{C}$  for 15 minutes to prepare a PTC composition. The produced PTC composition was sandwiched between two nickel plated copper foils having a thickness of 35  $\mu\text{m}$ , and hot pressed (140  $^{\circ}\text{C}$  for 1 minute) to carry out thermo-compression bonding (fusion-bond electrode system) into a size 40 x 60 x 1 mm (overall thickness) to prepare a circuit protection device. A polyethylene frame was produced by injection molding on the periphery of this device body for 20 mm to carry out insulation at the cut-off, then the device was sandwiched between the electrodes for testing and over-current cut-off test was carried out. When the initial resistance of the circuit protection device body was 0.9 m $\Omega$ , the cut-off current for 300 V and 50 kA was 13 kA, and when the resistance at a room temperature was 2.2 m $\Omega$ , the cut-off current was 8 kA. The results are better than those obtained with the PTC element containing CB, but worse than those obtained with the PTC element containing tungsten, using pressure welding electrode system (Examples 1 and 6). The relationship between the resistance of the PTC element and the peak current ( $I_p$ ) of the circuit protection device body obtained at the cut-off of the over-current using PTC elements having different sizes and different initial resistances is shown by the characteristic curve d in the FIG. 5.

#### Comparative Example 4

90 parts by weight of silver particles (having a melting point of 960.5  $^{\circ}\text{C}$ , available from Novamet Co.) as conductive particles, 10 parts by weight of HDPE and 2 parts by weight of a phenol type antioxidant (available from Ciba-Geigy Ltd., under the trade name of Irganox 1010) were kneaded in Laboplastomill equipment (manufactured by Toyo Seiki Co., Ltd.) at 200  $^{\circ}\text{C}$  for 15 minutes to prepare a PTC composition. The obtained PTC composition was hot pressed and molded into a plate having a size of 40 x 60 x 1 mm to prepare a PTC element, then a polyethylene frame was produced by injection molding on the periphery of the PTC element for 20 mm to carry out insulation at the cut-off. Then the PTC element having the frame was sandwiched between electrodes and pressed from both sides to electrically connect the element and the electrodes (pressure welding electrode system) to prepare a circuit protection device body and it was subjected to over-current cut-off test. When the resistance of the circuit protection device body at an ordinary room temperature was 1 m $\Omega$ , current limiting effect was not exhibited for high voltage and

large current of 300 V and 50 kA, and the flow of current could not be cut off. We understand that the reason why the cut-off was impossible was that silver particles having a low melting point were loaded in the PTC element constituting the Comparative Example 4, and when the element was used under large current and high voltage, it caused internal arc phenomenon (micro arc was generated among the conductive particles) and the PTC element was subjected to electric destruction. It is deemed that, the heat generated by the internal arc phenomenon melts the silver particles in the PTC element, then the silver particles are bonded together and large current flows through the bonded part and that causes the electric destruction of the composition.

#### Comparative Example 5

85 parts by weight of copper particles (having a melting point of 1083  $^{\circ}\text{C}$ , an average particle size of 1.0  $\mu\text{m}$ , available from Fukuda Kinzokuhaku Kogyo Co., Ltd.) as conductive particles, 15 parts by weight of HDPE and 2 parts by weight of a phenol type antioxidant (available from Ciba-Geigy Ltd., under the trade name of Irganox 1010) were kneaded in Laboplastomill equipment (manufactured by Toyo Seiki Co., Ltd.) at 200  $^{\circ}\text{C}$  for 15 minutes to prepare a PTC composition. A circuit protection device was produced from the PTC composition in the manner similar to that used in Comparative Example 4, and the device was subjected to over-current cut-off test. When the resistance of the circuit protection device body at an ordinary room temperature was 3 m $\Omega$ , current limiting effect was not exhibited for high voltage and large current of 300 V and 50 kA, and the flow of current could not be cut off.

The reason why the cut-off was impossible is deemed to be that copper particles having a low melting point in the PTC composition were melted to form a conductive circuit locally as is the case with Comparative Example 4.

#### Comparative Example 6

85 parts by weight of nickel particles (having a melting point of 1452  $^{\circ}\text{C}$ , available from Novamet Co.) as conductive particles, 15 parts by weight of HDPE and 2 parts by weight of a phenol type antioxidant (available from Ciba-Geigy Ltd., under the trade name of Irganox 1010) were kneaded in Laboplastomill equipment (manufactured by Toyo Seiki Co., Ltd.) at 200  $^{\circ}\text{C}$  for 15 minutes to prepare a PTC composition. A circuit protection device was produced from the PTC composition in the manner similar to that used in Comparative Example 4, and the device was subjected to over-current cut-off test. When the resistance of the circuit protection device body at an ordinary room temperature was 1 m $\Omega$ , current limiting effect was not exhibited for high voltage and large current of 300 V and 50 kA, and the flow of current could not be cut off.

FIG. 7 is a schematic illustration of an optical microscope photograph showing the dispersion condition of nickel particles, which are the conductive particles of the PTC element constituting the Comparative Example 6, and FIG. 7 (a) illustrates the condition prior to the cut-off (current limiting) test, and FIG. 7 (b) illustrates the condition after the cut-off test in which the device was destroyed. Prior to the cut-off test, the nickel particles 3 were homogeneously dispersed in the organic polymer 1, but after the cut-off test, the nickel particles 3 were melted and bonded each other to form a nickel particle bonded part 3a. It is deemed that since the nickel particles 3 in the PTC element were melted to form the nickel particle bonded part 3a (i.e. a conductive circuit), the over-current could not be cut-off like Comparative Examples 4 and 5, and the element was led to destruction.

### Claims

1. A polymeric PTC composition comprising an organic polymer and conductive particles having a melting point of at least 2000 °C dispersed therein.
2. The polymeric PTC composition according to claim 1, wherein the average particle size of the conductive particle is 0.01 - 50  $\mu\text{m}$ .
3. The polymeric PTC composition according to claim 1, wherein the conductive particles are contained in an amount of 50 - 99 % by weight based on the composition.
4. The polymeric PTC composition according to claim 1, wherein the conductive particles are particles containing at least one kind of substance selected from the group consisting of a metal, a metal carbide, a metal boride, a metal silicide and a metal nitride.
5. The polymeric PTC composition according to claim 4, wherein the conductive particles are particles containing at least one kind substance selected from the group consisting of tungsten, a carbide, a boride, a silicide and a nitride thereof.
6. The polymeric PTC composition according to claim 5, wherein the conductive particles are tungsten.
7. A circuit protection device having a PTC element consisting of the polymeric PTC composition comprising an organic polymer and conductive particles having a melting point of at least 2000°C dispersed therein, and at least two electrodes which are pressure welded to the PTC element and electrically connected thereto.

FIG. 1

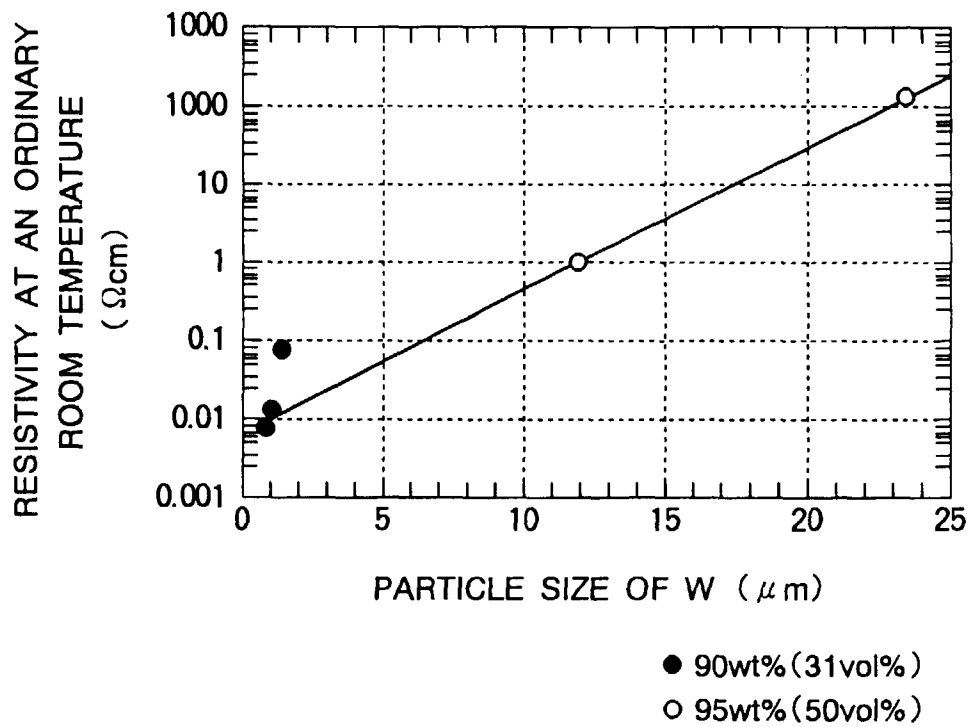


FIG. 2

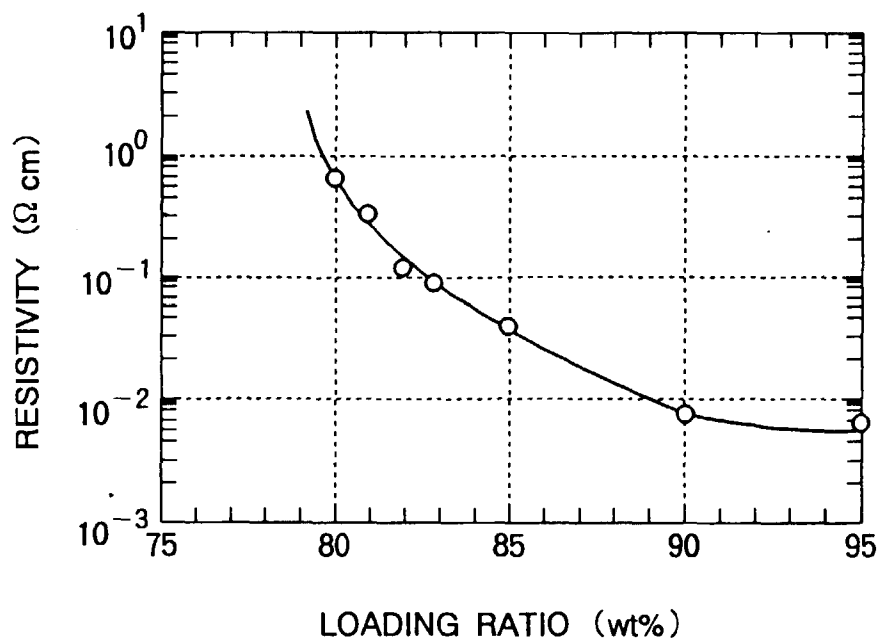


FIG. 3

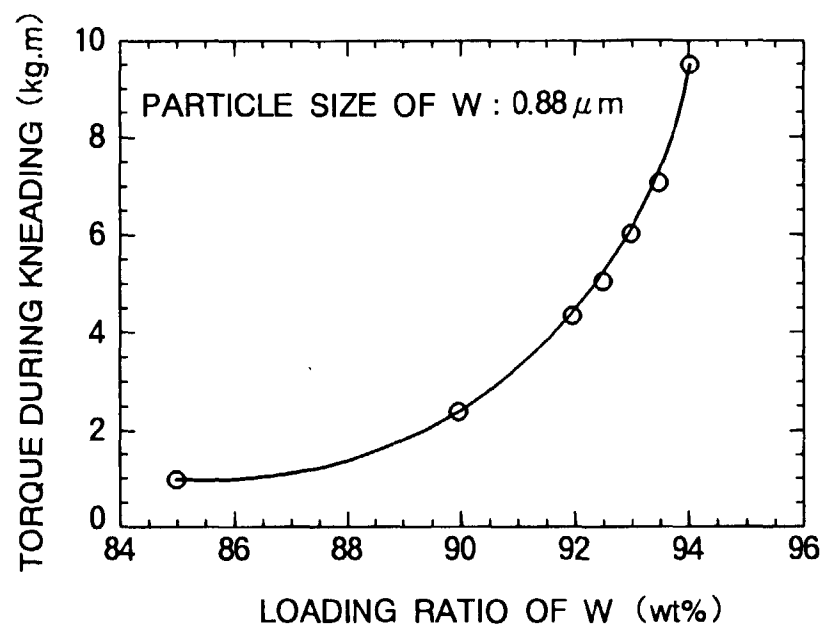


FIG. 4

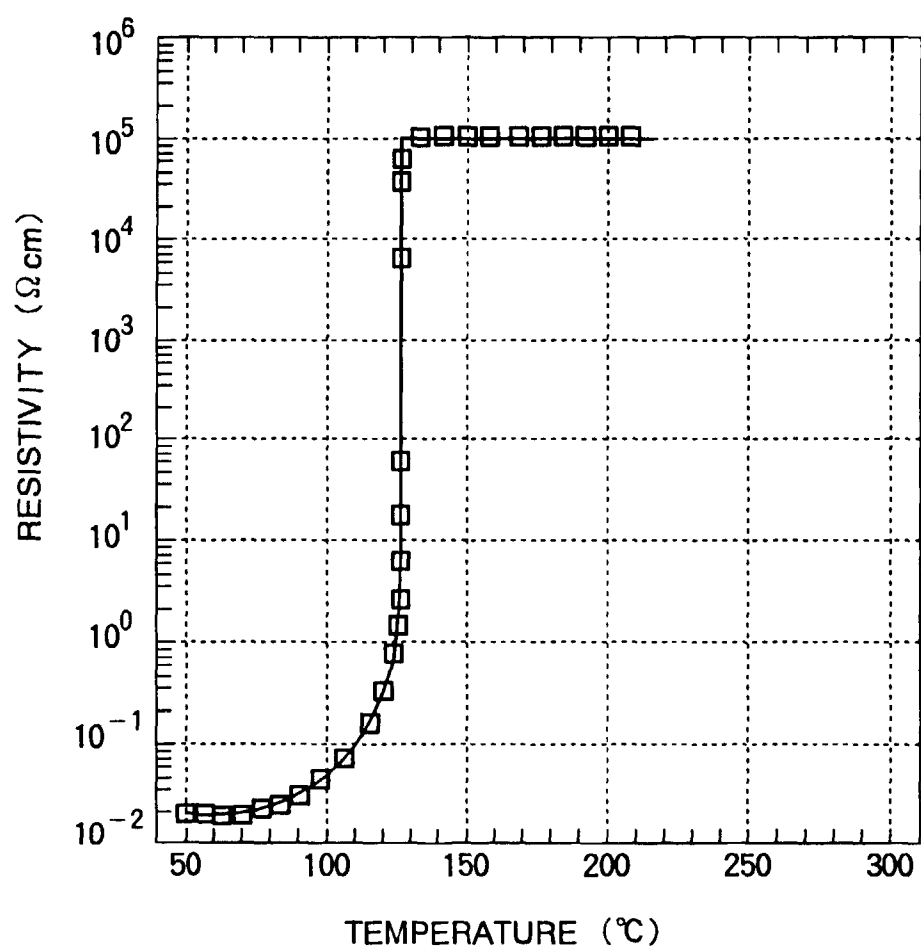
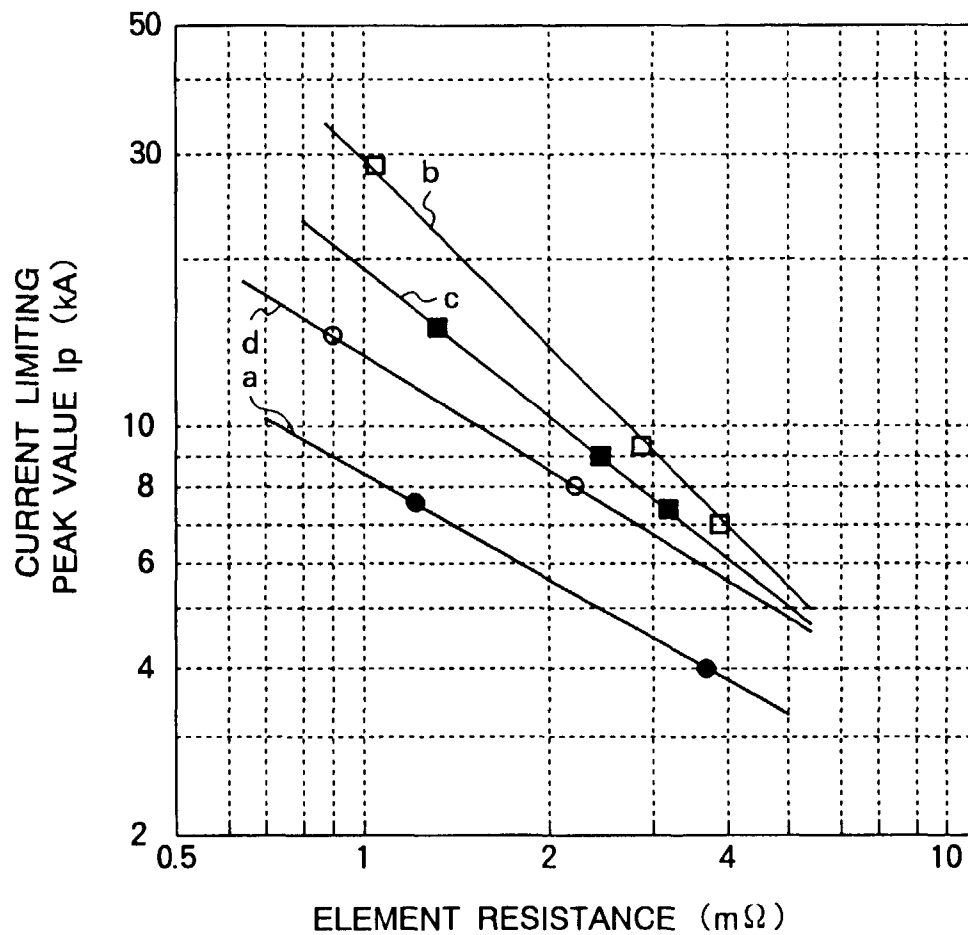


FIG. 5



- a : EXAMPLE 1 (TUNGSTEN, PRESSURE WELDING,  
ELECTRODE SYSTEM)
- b : COMPARATIVE EXAMPLE 1  
(CB,FUSION BOND ELECTRODE SYSTEM)
- c : COMPARATIVE EXAMPLE 2  
(CB,PRESSURE WELDING  
ELECTRODE SYSTEM)
- d : COMPARATIVE EXAMPLE 3  
(TUNGSTEN,FUSION BOND  
ELECTRODE SYSTEM)

FIG. 6

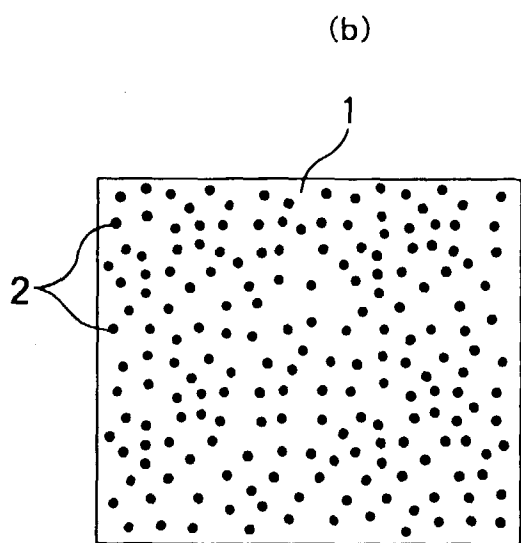
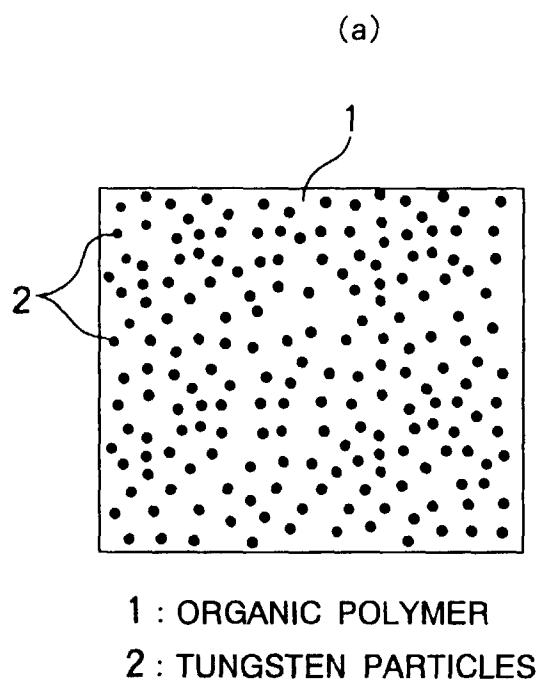
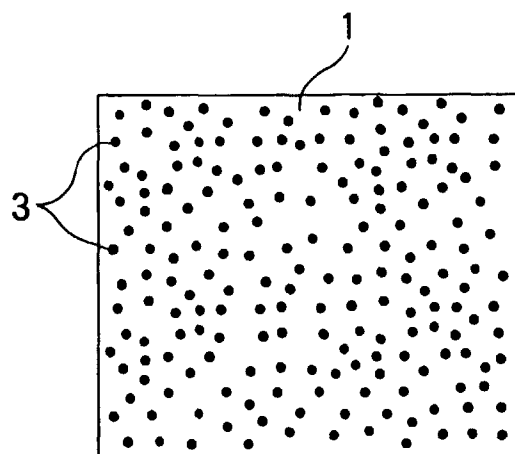


FIG. 7

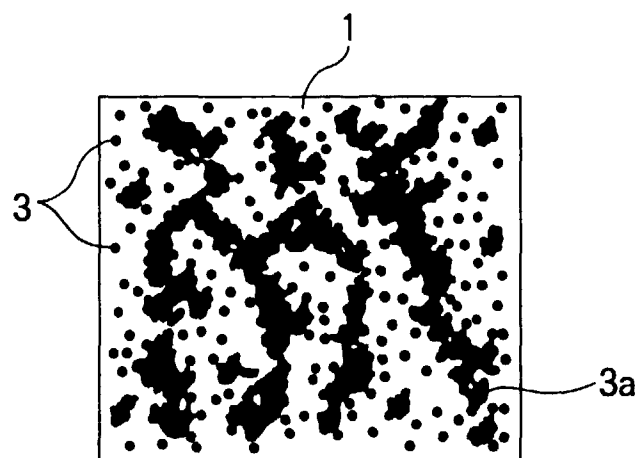
(a)



3 : NICKEL PARTICLES

3a : NICKEL PARTICLES BONDED PART

(b)







European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 97 11 6074

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP 0 696 036 A (ABB RESEARCH LTD) 7 February 1996 * abstract; claims * * page 3, line 9 - line 29 * * page 4, line 7 - line 13 * ---	1-6	H01C7/02 H01C1/14
X	EP 0 758 131 A (TDK CORP) 12 February 1997 * abstract; claims; tables * * page 3, line 45 - line 49 * * page 4, line 27 - line 31 * ---	1,2,4,5	
A	PATENT ABSTRACTS OF JAPAN vol. 096, no. 002, 29 February 1996 & JP 07 263202 A (TDK CORP), 13 October 1995, * abstract * ---	1,3-5,7	
A	VERESHCHAGIN L F, FATEEVA N S, AND MAGNITSKAYA M V: "Pressure dependence of the melting temperature of tungsten carbide up to 80 kbar" JETP LETT., AMERICAN INSTITUTE OF PHYSICS, vol. 26, no. 4, 20 August 1977, USA, pages 207-209, XP002071339 * figure 1 * ---	1,7	TECHNICAL FIELDS SEARCHED (Int.Cl.6) H01C
P,X	PATENT ABSTRACTS OF JAPAN vol. 097, no. 010, 31 October 1997 & JP 09 153402 A (TDK CORP), 10 June 1997, * abstract * -----	1,4-6	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 13 July 1998	Examiner Wirner, C
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... &amp; : member of the same patent family, corresponding document</p>			

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