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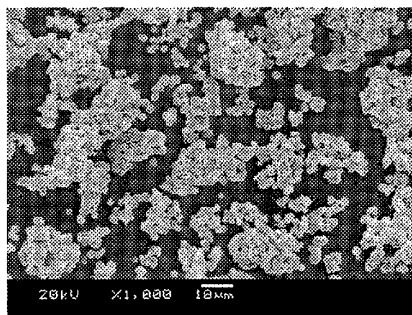
(54) **NICKEL POWDER, METHOD FOR PRODUCING SAME, AND POLYMER PTC DEVICE USING SUCH NICKEL POWDER**

(57) There is provided a nickel powder which is inexpensive, has low electrical resistance when kneaded with a resin, has good weatherability, and can be used as an electrically conductive particles which are used as electrically conductive fillers for an electrically conductive paste.

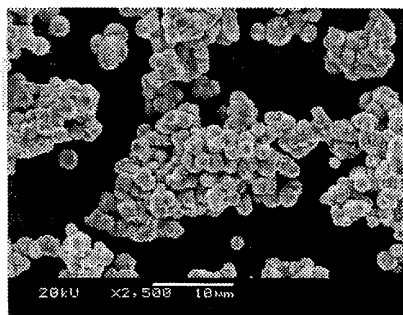
The nickel powder contains 1 - 20 % by mass of cobalt and the balance which comprises nickel and un-

avoidable impurities and which is formed of secondary particles of aggregated primary particles, which powder is **characterized in that** the powder has an average primary particle diameter being in 1.0 - 3.0 μm , a ratio σ/d_1 of a standard deviation σ of a primary particle diameter to the average primary particle diameter d_1 being 0.4 or less, an average secondary particle diameter being 5-60 μm , a tap density being 1.0 - 3.5 g/mL, and a specific surface area being 2.0 m^2/g or less.

[Figure 1]



(a)



(b)

Description

[Technical Field]

[0001] The present invention relates to nickel powder and a process therefor, and a polymer PTC element using said nickel powder. Said nickel powder may be suitably used as conductive particles for an electrically conductive paste and an electrically conductive resin, and in particular may be suitably used as an electrically conductive filler for a polymer PTC element.

[Background Art]

[0002] Heretofore, a tin-lead (Sn-Pb) based solder was used for connections in electronic apparatus, but an electrically conductive paste has recently been considered for the connections in electronic apparatus in response to a move to eliminate Pb. Also, elements utilizing an electrically conductive resin have recently been widely used.

[0003] The electrically conductive paste is a paste in which electrically conductive particles and various resins are kneaded together, and the electrically conductive resin is a formed article which is produced by hardening such paste. Properties required of the electrically conductive particles are that the particles themselves have high electric conductivity, that they show low electrical resistance even when kneaded with a resin, that they have high migration resistance, that they have good weatherability, and the like. Currently, metal powders or carbon powders are used as the electrically conductive particles.

[0004] Of the metal powders, noble metal powders have high conductivity and low electrical resistance, but they have a problem in that they are expensive. Base metal powders, represented by nickel (Ni) or copper (Cu) powders, etc., are inexpensive in their cost and also have high conductivity, but as they have inferior weatherability, so that there is a problem in that the electrical resistance rises when kneaded with resin and used over a long period as the electrically conductive paste or the electrically conductive resin.

[0005] Further, the carbon powders are inexpensive and has high weatherability, but has low conductivity and there is a problem in that the electrical resistance rises when kneaded with a resin.

[0006] In order to solve these problems, powders having the surfaces of Ni particles or Cu particles covered with a noble metal such as silver (Ag), etc., have been proposed in Patent Reference 1 (Japanese Patent Kokai Publication No. 2002-025345) and Patent Reference 2 (Japanese Patent Kokai Publication No. 2002-075057). Since in these powders, Ni particles or Cu particles are covered by the noble metal, the property aspects are generally improved; however, there is a problem with the migration resistance. In particular, the powders covered with Ag are not suitable for the use under environments requiring the migration resistance. Further, covering Ni particles or Cu particles with a noble metal is expensive in cost.

[0007] In Patent Reference 3 (Japanese Patent Kokai Publication No. 2001-043734), an attempt has been made to decrease electrical resistance when kneaded with a resin, by changing the surface shape of the Ni particles, etc., for example by forming semi-spherical nodules on the surface. However, the inferior weatherability of the particles remains, so that stability in long-term use cannot be said to have improved.

[0008] Further, the inventor proposed an Ni powder having a particular shape and with cobalt (Co) added to improve the conductivity and the weatherability (see Patent Reference 4), but further improvements are desired. Consequently, provision is desired of a conductive particle that is inexpensive, has good weatherability, has low electrical resistance when kneaded with a resin, and can be used with stability over a long period.

[0009]

[Patent Reference 1] Japanese Patent Kokai Publication No. 2002-25345

[Patent Reference 2] Japanese Patent Kokai Publication No. 2002-75057

[Patent Reference 3] Japanese Patent Kokai Publication No. 2002-43734

[Patent Reference 4] International Publication No. WO2005/023461

[Disclosure of the Invention]

[Problem to be Solved by the Invention]

[0010] The present invention has been made in view of the above problems, and intends to provide a nickel powder and a process of producing the same, which is inexpensive, has low electrical resistance when kneaded with a resin, has good weatherability, and can be used as an electrically conductive particles which are used as electrically conductive fillers for an electrically conductive paste, an electrically conductive resin, a PTC element, and the like.

[Means to Solve the Problem]

[0011] The nickel powder according to the present invention is characterized by containing 1 - 20 % by mass of cobalt with the balance comprising nickel and unavoidable impurities, further being composed of secondary particles of aggregated primary particles, an average primary particle diameter further being 1.0 - 3.0 μm , a ratio σ/d_1 of a standard deviation σ of a primary particle diameter and the average primary particle diameter d_1 being 0.4 or less, an average secondary particle diameter being 5 - 60 μm , a tap density being 1.0 - 3.5 g/mL, and a specific surface area being 2.0 m^2/g or less.

[0012] A ratio d_2/d_1 of the above average primary particle diameter d_1 and the above average secondary particle diameter d_2 is preferably in the range of 5 - 60.

[0013] Also, a cobalt content of the primary particles present in a surface layer section of the above secondary particles is preferably 1 - 40 % by mass based on a total mass of said surface layer section.

[0014] The process of producing the nickel powder according to the present invention is characterized by comprising a first reduction precipitation step to precipitate nickel by adding a bivalent nickel salt to an aqueous solution containing a reducing agent, and a second reduction precipitation step to further precipitate nickel by adding at least a bivalent nickel salt to the aqueous solution after the first reduction precipitation step, wherein a low hydrophilic surface active agent having an HLB value of 10 or less is added to at least the first reduction precipitation step of the above first and second reduction precipitation steps, and also a bivalent cobalt salt is added to the aqueous solution precipitating the nickel in at least the second reduction precipitation step of the above first and second reduction precipitation steps so as to precipitate nickel and obtain nickel powder, and the nickel powder obtained is dried under an inert atmosphere or vacuum at a temperature of 80 - 230 $^{\circ}\text{C}$ or dried in an air atmosphere at a temperature of 80 - 150 $^{\circ}\text{C}$, and then heat treated under a reducing atmosphere at a temperature of 200 - 400 $^{\circ}\text{C}$.

[0015] Preferably, a cobalt ion content in the aqueous solution having bivalent the bivalent cobalt salt added in the above second reduction precipitation step is 1 - 40 % by mass based on the total amount of nickel ions and cobalt ions in said aqueous solution, and the cobalt ion concentration in said aqueous solution is higher than the cobalt ion concentration in the aqueous solution in the above first reduction precipitation step, and further the nickel powder obtained through the above first and second reduction precipitation steps contains 1 - 20 % by mass of cobalt.

[0016] The bivalent cobalt salt may be added to the aqueous solution in the above first reduction precipitation step such that the cobalt ion content in said aqueous solution is 1 - 20 % by mass based on the total amount of the nickel ions and the cobalt ions in said aqueous solution, and the bivalent cobalt salt may be added to the aqueous solution in the above second reduction precipitation step such that the cobalt ion content in said aqueous solution is 1 - 20 % by mass based on the total amount of the nickel ions and the cobalt ions in said aqueous solution.

[0017] When the above nickel powder is used for the polymer PTC element, the cobalt content in the surface layer section of said secondary particles is preferably 8 - 20 % by mass based on the total mass of said surface layer section, the cobalt content of the nickel powder overall is preferably 4 - 10 % by mass, and the cobalt content in the interior of the nickel powder is preferably 3 - 6 % by mass based on the total mass of said interior. Further, the tap density is preferably 2.3 - 3.0 g/mL, and d_2/d_1 is preferably 8 - 16. It is noted that the polymer PTC element more preferably has one or more of these features, and most preferably has all of these features.

[0018] The polymer PTC element according to the present invention is a polymer PTC element having a polymer PTC component comprising a conductive filler and a polymeric material, and a metal electrode located on at least one of surfaces of the polymer PTC component, and is characterized by using as the conductive filler either the above nickel powder or the nickel powder produced by the above process.

[Effect of the Invention]

[0019] When a formed resin article is prepared by kneading the nickel powder according to the present invention with a resin, it is possible to obtain a formed resin article which has extremely low electrical resistance. The formed resin article thus obtained has good weatherability and may be used stably over a long period. Thus, the nickel powder according to the present invention may be used extremely suitably as the conductive particles used in the electrically conductive paste, the electrically conductive resin and the like. Further, as described below, the nickel powder according to the present invention may be suitably used as the electrically conductive filler of the polymer PTC element.

[0020] Further, the nickel powder according to the present invention is of a low cost because of not using expensive materials and being obtained without requiring complicated steps.

[0021] The nickel powder described in Patent Reference 4 also has good weatherability, but the average primary particle diameter of the present invention is 1.0 - 3.0 μm while the average primary particle diameter of the nickel powder of Patent Reference 4 is 0.2 - 2.0 μm . The tap density of the nickel powder according to the present invention is 1.0 - 3.5 g/mL while the tap density of the nickel powder of Patent Reference 4 is 0.5 - 2.0 g/mL. Moreover, the nickel powder according to the present invention specifies the ratio σ/d_1 of the standard deviation σ of the primary particle diameter to

the average primary particle diameter d_1 to be 0.4 or less, and the specific surface area to be $2.0 \text{ m}^2/\text{g}$ or less. Thus, the nickel powder according to the present invention has the better weatherability than that of the nickel powder of Patent Reference 4.

[0022] Also, the nickel powder according to the present invention may be suitably used in the polymer PTC element. Since the increase in resistivity is small even in harsh environments such as high temperature and dry conditions (such as the environment inside a car in summer), such a PTC element is useful compared with the PTC element in the prior art.

[Brief Description of the Drawings]

[0023]

[Figure 1] Figure 1 shows photographs from a scanning electron microscope (SEM) of the nickel powder obtained in Example 1. The magnification of (b) is higher than the magnification of (a).

[Figure 2] Figure 2 shows photographs from a scanning electron microscope (SEM) of the nickel powder obtained in Comparative Example 2. The magnification of (b) is higher than the magnification of (a).

[Figure 3] Figure 3 shows a graph showing the resistance-temperature curve of the PTC elements of the Examples and the Comparative Examples.

[Figure 4] Figure 4 shows a graph showing the change of resistance over time of the PTC elements of the examples and the Comparative Examples under the high temperature/dry conditions.

[Figure 5] Figure 5 shows a graph showing the change over time in the rate of change of resistance after trip of the PTC elements of the Examples and the Comparative Examples under the high temperature/dry conditions.

[Figure 6] Figure 6 shows a graph showing the change of resistance over time of the PTC elements of the Examples and the Comparative Examples under the room temperature/normal humidity conditions.

[Figure 7] Figure 7 shows a graph showing the change over time in the rate of change of resistance after trip of the PTC elements of the Examples and the Comparative Examples under the room temperature/normal humidity conditions.

[Figure 8] Figure 8 shows a graph showing the change of resistance over time of the PTC elements of the Examples and the Comparative Examples under the accelerated oxidation conditions.

[Figure 9] Figure 9 shows a graph showing the change over time in the rate of change of resistance after trip of the PTC elements of the Examples and the Comparative Examples under the accelerated oxidation conditions. [Figure 10] Figure 10 shows a graph showing the rate of change of resistance in the trip cycle test.

[Embodiments to Carry Out the Invention]

[0024] As a result of carrying on a research related to the electrical resistance of a resin with which a nickel powder is kneaded, the present inventors have discovered that the grain size and the tap density of the nickel powder has a large effect on the electrical resistance of the formed material using the resin with which the nickel powder is kneaded, and that the electrical resistance of the above formed article can be greatly reduced by controlling the grain size and the tap density of the nickel powder within specific ranges.

[0025] It has also been found that, by including a small amount of cobalt in the nickel powder, in particular including cobalt in the surface layer section of the nickel powder, the weatherability of the nickel powder is improved. Further, it has been found that suppressing fluctuations in the primary particle diameter and making the specific surface area a particular value improve the weatherability even more.

[0026] The present invention has been completed based on such findings. The nickel powder according to the present invention will be described in detail below, and the process for the production of the nickel powder according to the present invention will also be described.

[0027] The nickel powder according to the present invention contains 1 - 20 % by mass of cobalt, with the remainder comprising nickel and unavoidable impurities, and is further composed of the secondary particles of the aggregated primary particles, the average primary particle diameter further being $1.0 - 3.0 \mu\text{m}$, the ratio σ/d_1 of the standard deviation σ of the primary particle diameter to the average primary particle diameter d_1 being 0.4 or less, the average secondary particle diameter being $5 - 60 \mu\text{m}$, the tap density being $1.0 - 3.5 \text{ g/mL}$, and the specific surface area being $2.0 \text{ m}^2/\text{g}$ or less.

"Average primary particle diameter, and standard deviation of primary particle diameter"

[0028] The primary particle diameter is a grain size of an individual particle which forms the aggregate and is measured by the SEM observation. Specifically, the nickel powder is affixed to a sample holder with an electrically conductive double-sided tape and observed using JSM-6360LA manufactured by Nippon Denshi (JEOL Ltd.) at 20 kV accelerating voltage and 2500-fold magnification. An image processing software (SmileView) attached to the above equipment is

applied to the SEM image thus obtained to measure the particle diameters of 200 or more primary particles, excluding overlapping particles whose diameters cannot be determined, so as to obtain the average primary particle diameter d_1 . Also, the standard deviation of the primary particle diameter is calculated from the data thus obtained.

[0029] By having the average primary particle diameter in the range of 1.0 - 3.0 μm , the nickel powder agglomerates appropriately to form the secondary particles of complicated shapes such as a chain form. By creating such secondary particles, the nickel powder intertwined with one another to form a network in the formed resin article obtained by kneading with a resin, and said formed resin article exhibits an extremely low electrical resistance as well as excellent weatherability.

[0030] In contrast, the average primary particle diameter of the nickel powder of Patent Reference 4 (International Publication (WO) No. 2005/023461) is 0.2 - 2.0 μm . Even if the average particle diameter of the nickel powder is 0.2 μm or higher and less than 1.0 μm , the weatherability of the nickel powder is good if 1 - 20 % by mass% of cobalt is contained overall. However, when the average particle diameter of the nickel powder is 0.2 μm or higher and less than 1.0, the effect of oxidation of the nickel powder surface becomes greater than when the average primary particle diameter of the nickel powder is 1.0 - 3.0 μm , and the weatherability of the formed article obtained by kneading with the resin gets worse than when the average primary particle diameter is 1.0 - 3.0 μm . Therefore, the average primary particle diameter of the nickel powder is preferably 1.0 μm or higher.

[0031] On the other hand, if the average primary particle diameter exceeds 3.0 μm , the contacts in the nickel powders in the formed article obtained by kneading with the resin are decreased and the resistance of the formed article rises. When the average primary diameter becomes even larger, the agglomeration of the nickel powder itself decreases, approaching mono-dispersion, and the contacts in the nickel powders are further reduced and the resistance of the formed article rises further.

[0032] The ratio σ/d_1 of the standard deviation σ of the primary particle diameter to the average primary particle diameter d_1 shows the degree of fluctuation of the primary particle diameters. Having the ratio σ/d_1 0.4 or less greatly reduces particles whose primary particle diameters are small, so that the average primary particle diameter increases even if the number of particles having a primary particle diameter about or higher than the average value is not changed. By this means, agglomeration is possible even with nickel powder having a larger average primary particle diameter than that of the prior art. Also, with the average primary particle diameter increased, a greater amount of the nickel powder may be kneaded with the resin than in the prior art, which enhances the weatherability. Further, with the decrease of easily oxidizable and fine primary particles, the oxidation of the nickel powder is suppressed and the weatherability is greatly improved.

"Average secondary particle diameter"

[0033] When the Nickel powder agglomerates, they form the secondary particles. The grain size of the secondary particles is measured by laser particle size distribution measurement. Specifically, using MICROTRAC HRA MODEL 9320-X100 manufactured by Nikkiso Co. Ltd., the nickel powder is charged in an aqueous solution of 0.2 % by mass of sodium hexametaphosphate and ultrasonically stirred at 300 W for 10 minutes, after which the average particle dimension (D50) is measured in FRA mode; this becomes the average the secondary particle diameter d_2 .

[0034] By making the average secondary particle diameter in the range of 5 - 60 μm , locations are increase where the nickel powders (particularly, the particles which forms the powder) are in contact with one another after kneading with the resin, considerably reducing the electrical resistance of the formed resin article. However, if the average secondary particle diameter is less than 5 μm , the intertwining locations are decreased as there is less agglomeration, and resistance after kneading with the resin is increased. Also, it is not preferable that the average secondary particle diameter exceeds 60 μm , since there is a danger in that the nickel powder dispersion in the resin becomes non-uniform.

"Tap density"

[0035] The tap density of the nickel powder affects the degree of the nickel powder dispersion in the resin. Shaker type specific gravity measuring machine (tapping machine) KRS-409 manufactured by Kuramochi Kagaku Kikai Seisakusho is used to measure tap density. 15 g of the nickel powder is weighed out and charged in a 20 mL measuring cylinder, and tapping is performed 500 times at a tap speed of 120 times/minute with a tap height of 20 mm. After this, the volume of the nickel powder is read from the calibrations on the measuring cylinder. The mass (g) of the nickel powder is divided by the volume read to calculate the tap density.

[0036] By making the tap density in the range of 1.0 - 3.5 g/mL, the nickel powder is dispersed evenly in the resin and the electrical resistance of the formed resin article is considerably decreased.

[0037] In contrast, the tap density of the nickel powder of Patent Reference 4 is 0.5 - 2.0 g/mL. Even if the tap density of the nickel powder is 0.5 g/mL or higher and less than 1.0 g/mL, the weatherability of the nickel powder is good as long as 1 - 20 % by mass of cobalt is contained overall. However, it is effective to increase the kneaded nickel powder in order to improve the weatherability of the formed resin article. If the tap density is 0.5 g/mL or higher and less than

1.0 g/mL, it is difficult to increase the amount of the nickel powder kneaded into the resin so that the weatherability is decreased compared to when the tap density is 1.0 g/mL. Therefore, the tap density of the nickel powder is preferably 1.0 g/mL or higher.

[0038] On the other hand, if the tap density of the nickel powder exceeds 3.5 g/mL, the nickel powder is not distributed evenly in the resin so that the mutual contact (particularly, the contact between the particles which constitute the powder) is reduced and the electrical resistance of the formed resin article increases.

"Specific Surface Area"

[0039] The specific surface area greatly affects the weatherability of the nickel powder. Multisorb 16 manufactured by Yuasa Ionics is used to measure the specific surface area. After degassing of the nickel powder with nitrogen gas for a degassing time of 15 minutes at a degassing temperature of 200 °C, the specific surface area is measured by BET one-point method by nitrogen 30% - argon mixed gas adsorption.

[0040] If the specific surface area is 2.0 m²/g or less, micropores of the surface are decreased so that surface oxidation is suppressed and weatherability is greatly improved. When the specific surface area is 1.2 m²/g or less, the weatherability enhancement effect is even greater and is therefore preferred.

"Cobalt content"

[0041] The nickel powder according to the present invention contains 1 - 20 % by mass of cobalt overall based on the total mass of the nickel powder, and the weatherability of the nickel powder is greatly improved by such amount of cobalt. This is because cobalt is slightly baser than nickel and, cobalt is preferentially corroded, and in addition to this, the corroded cobalt has electric conductivity. However, there is no weatherability enhancement effect if the cobalt content is less than 1 % by mass of the nickel powder overall, and if more than 20 % by mass of cobalt is added, it increases the cost and is not preferred.

"Cobalt content of primary particles present in surface layer section of secondary particles"

[0042] To ensure sufficient weatherability while keeping the cobalt content as small as possible, it is preferred that much of the cobalt is contained in the surface layer section of the secondary particles of the nickel powder. Here, the surface layer sections of the secondary particles of the nickel powder are sections precipitated by the second stage of the reduction precipitation step when preparing the nickel powder through the two-stage reduction precipitation process.

[0043] The cobalt content in said surface layer section is preferably in the range of 1 - 40 % by mass based on the total mass of said surface layer section. In order to obtain the required weatherability, 1 % by mass or higher of cobalt must be contained in said surface layer section. However, it is difficult to improve the weatherability further even if more than 40 % by mass of cobalt is added to said surface layer section. Also, if more than 40 % by mass of cobalt is added to said surface layer section, the nickel powder becomes ferromagnetic and is not preferred for the use in electronic parts and the like. As is clear from the above description, the present invention does not exclude embodiment wherein cobalt is contained also in the interior of the nickel powder. In other words, cobalt may be contained in the interior of the nickel powder in addition to the surface layer section, and such cases may sometimes be preferred. Such a case, for example, is when the nickel powder is used in the polymer PTC element as described below.

"Average secondary particle diameter (d_2)/average primary particle diameter (d_1)"

[0044] Further, in the nickel powder according to the present invention, the average secondary particle diameter (d_2)/average primary particle diameter (d_1) is preferably in the range of 5 - 60. When the average secondary particle diameter (d_2)/average primary particle diameter (d_1) is in the range of 5 - 60, the contact between the nickel powders (particularly, the contact between the particles which forms the powder) kneaded with resin is facilitated and the electrical resistance of the formed resin article obtained becomes small. When this ratio is less than 5, the contact between nickel powders is difficult, which is not preferred. Also, when this ratio exceeds 60, the agglomerations become larger so that dispersion in the resin is uneven, which is not preferred.

"Process of producing nickel powder"

[0045] Next, the process of producing the nickel powder according to the present invention will be described. The nickel powder of the present invention is produced by a two-stage reduction precipitation step and a drying/heating step.

[0046] In the first reduction precipitation step, an aqueous solution containing a bivalent nickel salt is added to an aqueous solution containing a reducing agent (generally, an excessive amount of the reducing agent are contained) so

as to precipitate virtually all of the nickel. Following this, in the second reduction precipitation step, a bivalent nickel salt containing aqueous solution is added to the aqueous solution containing the nickel powder precipitated through the first reduction precipitation step while a reducing agent as needed is optionally added, so that nickel is further precipitated.

[0047] In the above production, a less hydrophilic surface active agent is added in at least the first reduction precipitation step. For instance, in the case of a modified silicone oil-based surface active agent, one having an HLB value shown in the following Formula 1 of 10 or less is added. By adding the less hydrophilic surface active agent, the nickel ion concentration during the reaction is suppressed to prevent excessive nucleation, so that generation of fine nickel primary particles is suppressed and the primary particles may grow into suitable sizes.

[0048]

[Formula 1]

$$\text{HLB value} = (\text{Inorganic value} / \text{organic value}) \times 10$$

[0049] When the surface active agent is not added, the nucleation would be excessive, creating fine nickel primary particles. Also, since they will not grow into suitably-sized primary particles, the variance in the primary particle diameters would also be large.

[0050] Even when the surface active agent is added, if the HLB value of the added surface active agent exceeds 10, the fluctuation in the primary particle diameters may be suppressed, but fine nickel primary particles would be produced, so that the average primary particle diameter would be decreased.

[0051] A multivalent carboxylic acid such as tartaric acid, a conventionally used complexing agent such as ethylene diamine, sodium hydroxide for the pH adjustment or the like may be added to the aqueous solution containing the reducing agent. There is no particular restriction on the reducing agent as long as it can precipitate nickel by reduction, but a hydrazine-based reducing agent is suitable.

[0052] In the above production process, the nickel particles precipitated through the first reduction precipitation step become the secondary particles of suitably agglomerated primary particles and form the interior of the nickel powder, but the agglomeration force is weak and they are easily separated into individual particles during the separation from the post-reaction solution or kneading with the resin. By following with the second reduction precipitation step, however, the agglomeration becomes stronger by means of the nickel further precipitated and a suitable agglomeration may be maintained without being separated in the operations that follow. It is believed that the nickel precipitated in the second reduction precipitation step agglomerates outside the nickel secondary particles precipitated in the first reduction precipitation step so as to form the surface layer section of the nickel powder, and connects the networks structurally to form high-strength nickel powder. The electrical resistance of the formed article, produced by kneading the nickel thus obtained with the resin, is extremely low.

[0053] By producing through the above two-stage reduction precipitation process as well as adjusting the concentrations of the nickel salt and the reducing agent, the temperatures of the aqueous solutions and other conditions, the nickel powder having the powder properties described above (consisting of the secondary particles from the agglomerated primary particles, the average primary particle diameter 1.0 - 3.0 μm , the ratio σ/d_1 of the standard deviation σ of the primary particle diameter to the average primary particle diameter d_1 of 0.4 or less, the average secondary particle diameter of 5 - 60 μm , the tap density of 1.0 - 3.5 g/mL, and the specific surface area of 2.0 m²/g or less) may be obtained.

[0054] In order to include cobalt in this nickel powder, nickel may be precipitated with a bivalent cobalt salt added to the aqueous solution in only the second reduction precipitation step out of the two-stage reduction precipitation process described above, or both the first reduction precipitation step and the second reduction precipitation step. In order to include cobalt over the entire nickel powder including the interior, the nickel may be precipitated with the bivalent cobalt added to the aqueous solution in both of the first and second reduction precipitation steps. The cobalt ion content in the aqueous solution in either step may be 1 - 20 % by mass based on the total amount of nickel ion and cobalt ion in the aqueous solution. In order to have more cobalt contained in the surface layer sections than in the interior, more bivalent cobalt salt may be added to the second reduction precipitation step than in the first reduction precipitation step, such that the cobalt content in the nickel powder overall is ultimately adjusted to be 1 - 20 % by mass.

[0055] Further, when no cobalt is to be contained in the interior of the nickel powder but cobalt is to be contained only in the surface layer section, the bivalent cobalt salt is added to the aqueous solution only in the second reduction precipitation step and no cobalt salt is added in the aqueous solution in the first reduction precipitation step. The amount of cobalt added in this case may be such that the cobalt ion content in the aqueous solution is 1 - 40 % by mass based on the total amount of nickel ion and cobalt ion in the aqueous solution, and through this the cobalt content in the surface layer sections of the nickel powder may be 1 - 40 % by mass.

[0056] By heating and drying the nickel powder obtained in the two-stage reduction process as described above in

an inert atmosphere or a vacuum at a temperature of 80 - 230 °C, the surface nickel atoms are diffused so that micro-pores are further eliminated to decrease the specific surface area. When the drying temperature is less than 80 °C, the elimination of the micro-pores is not sufficient and the specific surface area will exceed 2.0 m²/g. On the other hand, when the temperature exceeds 230 °C, the nickel hydroxide that has passivated the surface decomposes so that oxidation proceeds after drying and the resistance when kneading with the resin increase. The drying temperature is preferably 120 - 230 °C from the standpoint of sufficiently eliminating the micro-pores.

[0057] The micro-pores may be sufficiently eliminated by drying the nickel powder obtained in the two-stage reduction step described above by drying the nickel powder in atmosphere and then heating it in a reducing atmosphere at 200 - 400 °C. When dried in atmosphere (air), a large amount of hydroxides are produced on the surfaces so that the specific surface area is increased and the resistance after kneading with the resin rises considerably. However, by heating in the reducing atmosphere after drying, the nickel hydroxide may be decomposed except for a small amount of the nickel hydroxide remains so that the specific surface area is smaller. When the heating in the reducing atmosphere is carried out at a temperature of less than 200 °C, the decomposition of nickel hydroxide is insufficient and the specific surface area becomes large and the resistance after kneading with the resin is also high. When the temperature exceeds 400 °C, not only does the nickel hydroxide decompose excessively but the nickel powders get sintered mutually together.

[0058] Thus, the process of producing the nickel powder according to the present invention does not use expensive material such as a noble metal and the like, and no complicated steps are required. Therefore, the nickel powder according to the present invention may be obtained inexpensively.

"Polymer PTC element"

[0059] The nickel powder according to the present invention and the process of producing the same have been described above. The present invention also provides a polymer PTC element in which the nickel powder described above or below is used as an electrically conductive filler. Although said polymer PTC element will be described below, the polymer PTC element itself is well-known and an explanation of the polymer PTC element itself is omitted.

[0060] Specifically, the PTC element according to the present invention comprises (A) a polymer PTC component comprising (a1) an electrically conductive filler, and (a2) a polymeric material, and (B) a metal electrode located on at least one surface of the polymer PTC component, wherein the nickel powder according to the present invention is used as the electrically conductive filler. The considerations on the nickel powder physical properties, in particular the considerations on their effects on the weatherability, the electrical conductivity and the like are applicable likewise to the nickel powder as the electrically conductive filler in the polymer PTC element.

[0061] The polymer material used in the polymer PTC element according to the present invention may be a known polymer material used in a conventional PTC element which polymer provides with the PTC property. Such a polymer material is a thermoplastic crystalline polymer, examples being a polyethylene, an ethylene copolymer, a fluorine-containing polymer, a polyamide and a polyester, which may be used singly or combined.

[0062] More specifically, for the polyethylene, a high density polyethylene, a low density polyethylene and the like may be used; for the ethylene copolymer, an ethylene-ethyl acrylate copolymer, an ethylene-butyl acrylate copolymer, an ethylene-vinyl acetate copolymer, an ethylene-polyoxymethylene copolymer and the like may be used; for the fluorine-containing polymer, a polyvinylidene fluoride, an ethylene difluoride-ethylene tetrafluoride-propylene hexafluoride copolymer and the like may be used; for the polyamide, a 6-Nylon, a 6,6-Nylon, a 12-Nylon and the like may be used; and for the polyester, a polybutylene terephthalate (PBT), a polyethylene terephthalate (PET) and the like may be used.

[0063] The metal electrode used for the polymer PTC element according to the present invention may be composed of any known metal material used in the conventional polymer PTC element. The metal electrode may, for instance, be in a plate form or a foil. As long as the PTC element that the present invention intends can be obtained, the metal electrode is not restricted in particular. Specifically, a surface-roughened metal plate, a surface-roughened metal foil and the like may be given as examples. When using a metal electrode whose surface is roughened, the roughened surface is in contact with the PTC component. For example, commercially available electrodeposited copper foil, or nickel-plated electrodeposited copper foil may be used.

[0064] Such "metal electrode" is placed on at least one of the main surfaces of the PTC component, and is preferably placed on the two opposing main surfaces of the PTC component. The placement of the metal electrode may be performed in the same way as the conventional methods for the production of a PTC element. For example, placement may be made by thermally compressing a metal electrode on a plate-form or sheet-form PTC component obtained by extrusion. In another embodiment, a blend of the polymer material and the electrically conductive filler may be extruded on the metal electrode. After this, a small PTC element may be obtained by cutting as needed.

[0065] In addition, the present invention provides a PTC device wherein a metal lead is electrically connected to at least one of the metal electrodes of the above-described PTC element according to the present invention, and further provides an electrical apparatus (for example a cell-phone) wherein such a PTC device is electrically connected to a wiring or an electronic component.

[0066] The nickel powder of the present invention that is particularly preferred for the use in the PTC element according to the present invention is, for example, as follows:

(Cobalt content)

[0067] 2 - 20 % by mass, preferably 3 - 18 % by mass, more preferably 3 - 15 % by mass, for example 4 - 10 % by mass, in particular 5 - 7 % by mass (for example 6 % by mass) of cobalt, based on the total mass of the nickel powder overall, is contained.

[0068] In the surface layer section of the nickel powder, 3 - 40 % by mass, preferably 8 - 30 % by mass, more preferably 8 - 20 % by mass, for example 9 - 15 % by mass, in particular 10 % by mass of cobalt, based on the total mass of said surface layer section, is contained.

[0069] Further, the nickel powder preferred for the use in the PTC device may contain cobalt in the interior, which is inside the surface layer section, in addition to the surface layer section; this is preferred but it is not necessarily required that cobalt be contained in the interior. When cobalt is contained in the interior, the amount of cobalt in the interior is, for example, preferably 2 - 7 % by mass (in particular 3 - 6 % by mass), based on the total mass of the interior.

[0070] Specific examples of the nickel powder of the present invention that is particularly preferred for the use in the PTC device according to the present invention are any of the various combinations that may be made in the range of the three types of the cobalt contents described above and an example may be as follows: 5 - 7 % by mass as the amount of cobalt overall, 9 - 12 % by mass as the amount of cobalt in the surface layer section, and 4 - 5 % by mass as the amount of cobalt in the interior.

(Tap density)

[0071] For example, 2.0 - 3.5 g/mL, preferably 2.3 - 3.0 g/mL.

(Average primary particle diameter)

[0072] For example 1.5 - 2.5 μm , preferably 1.7 - 2.2 μm .

(Primary particle diameter standard deviation/average primary particle diameter)

[0073] For example 0.3 or less, preferably 0.25 or less.

(Average secondary particle diameter)

[0074] For example, 10 - 40 μm , preferably 15 - 30 μm .

(Average secondary particle diameter/average primary particle diameter)

[0075] For example 5 - 20, preferably 8 - 16, more preferably 10-15.

(Specific surface area)

[0076] For example 2 or less, preferably 1.7 or less.

[0077] In the polymer PTC component of the polymer PTC element according to the present invention, the ratio between the polymer material and the electrically conductive filler may be of any suitable ratio as long as prescribed functions as the PTC element are exhibited. For example, the conductive filler is 65 - 90 % by mass, preferably 70 - 80 % by mass on a mass basis.

[0078] In the PTC element according to the present invention as described above, containing the nickel powder according to the present invention, the increase in resistance is greatly suppressed compared with the PTC element in the prior art, even when used over a long period in an environment where it may be exposed to a high temperature and dry condition.

[Examples]

[0079] The present inventions will further be described through examples and comparative examples. The examples and the comparative examples as to the nickel powder are Examples 1 - 12 and Comparative Examples 1 - 6. The examples and the comparative examples as to the polymer PTC element are Examples A - D and Comparative Examples

A and B.

"Examples and comparative examples as to nickel powder (Examples 1 - 12 and Comparative Examples 1 - 6)

(Example 1)

[0080] 37.8 L of an aqueous solution of 25 % sodium hydroxide and 1209 g of tartaric acid was added to 138 L of pure water and heated to 70 °C while stirring. 28.8 L of 60 % hydrazine hydrate and a modified silicone oil-based surface active agent having an HLB value of 9 were added to this aqueous solution. 3.7 kg, in an Ni + Co converted mass, of an aqueous blend solution of a cobalt chloride aqueous solution and a nickel chloride aqueous solution (an aqueous solution blended such that the Co content is 5 % by mass based on the Ni + Co amount) was further added, so that nickel powder was precipitated through the first reduction precipitation step. Next, 4.8 L of 60 % hydrazine hydrate and 3.7 kg, in an Ni + Co converted mass (total mass of Ni and Co obtained by converting salts contained in the aqueous solution to metals), of an aqueous blend solution of a cobalt chloride aqueous solution and a nickel chloride aqueous solution (an aqueous solution blended such that the Co content is 10 % by mass based on the Ni + Co amount) was added to the aqueous solution that had completed the nickel powder precipitation through the first reduction precipitation step, so that nickel powder was further precipitated through the second reduction precipitation step. The nickel powder was then obtained by filtering off, cleaning with water, and drying in vacuum at a temperature of 80 °C.

[0081] The Co content of the nickel powder thus obtained was 6.6 % by mass. Powder properties of the nickel powder are shown below in Table 1. It is noted that the Co content in the nickel powder overall is an analyzed value, but the Co content in the surface layer section was calculated from an Ni amount and a Co amount to which the salt amounts in the aqueous solution in the second reduction precipitation step is converted. Specifically, it was calculated as the ratio of the above Co converted value to the total of the above Ni converted value and the above Co converted value.

[0082] The " d_1 " in Table 1 denotes the average primary particle diameter; this was measured by the SEM observation. Specifically, the nickel powder was affixed to a sample holder with an electrically conductive double-sided adhesive tape and observed using JSM-6360LA manufactured by Nippon Denshi (JEOL Ltd.) at 20kV accelerating voltage and 2500-fold magnification. An image processing software (SmileView) attached to the above apparatus was applied to the SEM image thus obtained to measure the particle diameters of 200 or more primary particles, excluding overlapping particles whose diameters cannot be determined, to obtain the average particle diameter d_1 . Also, the standard deviation of the primary particle diameters was calculated from the data obtained.

[0083] The " d_2 " in Table 1 denotes the average secondary particle diameter. The grain size of the secondary particles was measured by the laser particle size distribution measurement. Specifically, using MICROTRAC HRA MODEL 9320-X100 manufactured by Nikkiso Co. Ltd., the nickel powder was charged in an aqueous solution of 0.2 % by mass of sodium hexametaphosphate and ultrasonically stirred at 300W for 10 minutes, after which the average particle dimension (D50) was measured in the FRA mode; this became the average secondary particle diameter d_2 .

[0084] The " σ " in Table 1 represents the standard deviation of the average primary particle diameter d_1 , and " σ/d_1 " represents the ratio between the standard deviation σ of the primary particle diameter and the average primary particle diameter d_1 .

[0085] Tapping machine KRS-409 manufactured by Kuramochi Kagaku Kikai Seisakusho was used to measure the tap density in Table 1. 15 g of the nickel powder was weighed out and put in a 20 mL measuring cylinder, and tapping was performed 500 times at a tap speed of 120 times/minute with a tap height of 20 mm. After this, the volume of the nickel powder was read from the calibrations on the measuring cylinder. The mass (g) of the nickel powder was divided by the volume read to calculate the tap density.

[0086] Multisorb 16 manufactured by Yuasa Ionics was used to measure the specific surface area in Table 1. After degassing with nitrogen gas for a degassing time of 15 minutes, the specific surface area was measured by BET one-point method through nitrogen 30% - argon mixed gas adsorption.

[0087] Next, the above nickel powder was blended with a polyethylene resin such that the nickel powder content was 35 % volume and also 43 % by volume based on the nickel powder + polyethylene resin, followed by kneading at a temperature at or above the melting point of the polyethylene resin and forming into a sheet.

[0088] The formed sheet sample was cut out into 25 mm (W) x 60 mm (L) materials and a surface resistivity thereof was measured in accordance with JIS K 7194. The initial surface resistivity of the 35 % by volume kneaded material was 0.209 $\Omega/\square$ (ohm/square), and 0.036 $\Omega/\square$ for the 43 % volume kneaded material. It is noted that this measurement was carried out using a low resistivity meter (Loresta GP, manufactured by Dia Instruments).

[0089] Further, in order to evaluate the weatherability, a humidity resistance test was performed, maintaining the sheet sample for 168 hours in a constant temperature and constant humidity vessel set up at 85 °C - 85 % RH, after which the surface resistivity was measured in the same way as above. The 35 % by volume kneaded material showed 0.217 $\Omega/\square$, and the 43 % by volume kneaded material showed 0.033 $\Omega/\square$. These results are shown in Table 2.

(Example 2)

[0090] The reduction precipitation of nickel was carried out in the two steps in the same way as in Example 1, through the two-stage reduction precipitation process. 25.2 L of an aqueous solution of 25 % sodium hydroxide and 806 g of tartaric acid was added to 138 L of pure water and heated to 70 °C while stirring. 19.2 L of 60 % hydrazine hydrate and a modified silicone oil-based surface active agent having an HLB value of 9 were added to this aqueous solution. An aqueous solution of cobalt chloride was not added to this solution; only 2.5 kg, in an Ni converted mass, of nickel chloride aqueous solution was added to perform the first reduction precipitation step. 2.5 kg, in the Ni + Co converted mass, of an aqueous blend solution of a cobalt chloride aqueous solution and a nickel chloride aqueous solution (an aqueous solution blended such that the Co content is 5 % by mass based on the Ni + Co amount) was added, so that nickel powder was further precipitated through the second reduction precipitation step. The nickel powder was then obtained by filtering off, cleaning with water, and drying in vacuum at a temperature of 80 °C.

[0091] The nickel powder thus obtained contained Co only in the surface layer sections, and the Co content overall was 5.0 % by mass. The powder properties are shown in Table 1. When this nickel powder was evaluated in the same way as in Example 1, the initial surface resistivity of the 35 % volume kneaded material (that is, a material obtained as in the above with blending 35 % by volume) was 0.711 $\Omega/\square$, and the 43 % by volume kneaded material (that is, a material obtained as in the above with blending 43 % by volume) was 0.194 $\Omega/\square$. When the surface resistivity was measured after the humidity resistance test, the 35 % by volume kneaded material showed 0.706 $\Omega/\square$, and the 43 % by volume kneaded material showed 0.160 $\Omega/\square$. The results are shown in Table 2.

(Example 3)

[0092] 94.8 g of sodium hydroxide and 12.6 g of tartaric acid was added to 2280 ml of pure water and heated to 65 °C while stirring. 180 ml of hydrazine and a modified silicone oil-based surface active agent having an HLB value of 9 were added to this aqueous solution. 39 g, in an Ni + Co converted mass, of an aqueous blend solution of a cobalt chloride aqueous solution and a nickel chloride aqueous solution (an aqueous solution blended such that the Co content is 1 % by mass based on the Ni + Co amount) was further added, so that nickel powder was precipitated through the first reduction precipitation step. Next, 45 ml of hydrazine and 39 g, in an Ni + Co converted mass (total mass of Ni and Co obtained by converting from salts contained in the aqueous solution to metals), of an aqueous blend solution of a cobalt chloride aqueous solution and a nickel chloride aqueous solution (an aqueous solution blended such that the Co content is 1.5 % by mass based on the Ni + Co amount) was added to the aqueous solution that had completed the nickel powder precipitation through the first reduction precipitation step, so that nickel powder was further precipitated through the second reduction precipitation step. The nickel powder was then obtained by filtering off, cleaning with water, and drying in vacuum at a temperature of 80 °C.

[0093] The Co cobalt content of the overall nickel powder thus obtained was 1.2 % by mass. The powder properties are shown in Table 1. When this nickel powder was evaluated in the same way as in Example 1, the initial surface resistivity of the 35 % by volume kneaded material was 0.725 $\Omega/\square$, and the 43 % by volume kneaded material was 0.203 $\Omega/\square$. When the surface resistivity was measured after the humidity resistance test, the 35 % by volume kneaded material showed 0.720 $\Omega/\square$, and the 43 % by volume kneaded material showed 0.173 $\Omega/\square$. The results are shown in Table 2.

(Example 4)

[0094] The reduction precipitation of nickel was performed in two stages in the same way as in Example 3 through the two-stage reduction precipitation process. Although heating was up to 65°C in Example 3, Example 4 was heated to 60°C, and 39g, in the Ni + Co converted mass, of an aqueous blend solution of a cobalt chloride aqueous solution and a nickel chloride aqueous solution (an aqueous solution blended such that the Co content is 20 mass% based on the Ni + Co amount (in Example 3, the Co content was 1 mass% based on the Ni + Co amount in the first reduction precipitation step and the Co content was 1.5 mass% based on the Ni + Co amount in the second reduction precipitation step)) was added in both the first reduction precipitation step and the second reduction precipitation step to precipitate the nickel powder. The nickel powder was then obtained by filtering off, cleaning with water, and drying in vacuum at 80°C.

[0095] The Co content of the overall nickel powder thus obtained was 19.4 % by mass. The powder properties are shown in Table 1. When this nickel powder was evaluated in the same way as in Example 1, the initial surface resistivity of the 35 % by volume kneaded material was 0.097 $\Omega/\square$, and the 43 % by volume kneaded material was 0.033 $\Omega/\square$. When the surface resistivity was measured after a humidity resistance test, the 35 % by volume kneaded material showed 0.115 $\Omega/\square$, and the 43 % by volume kneaded material showed 0.035 $\Omega/\square$. The results are shown in Table 2.

(Example 5)

[0096] The reduction precipitation of nickel was performed in two stages in the same way as in Example 3 through the two-stage reduction precipitation process. A cobalt chloride aqueous solution was not added to the solution to be added in the first reduction precipitation step; 39 g, in the Ni converted mass, of only a nickel chloride aqueous solution was added to perform the first reduction precipitation step. In the second reduction precipitation step, 39g in the Ni + Co converted mass of an aqueous blend solution of a cobalt chloride aqueous solution and a nickel chloride aqueous solution (an aqueous solution blended such that the Co content is 40 % by mass based on the Ni + Co amount (the Co content was 1.5 mass% based on the Ni + Co amount in Example 3)) was added and the nickel powder precipitated. The nickel powder was then obtained by filtering off, cleaning with water, and drying in vacuum at 80°C.

[0097] The nickel powder thus obtained contains Co in the surface layer section only, and the Co content of the overall nickel powder obtained was 18.7 % by mass. The powder properties are shown in Table 1. When this nickel powder was evaluated in the same way as in Example 1, the initial surface resistivity of the 35 % by volume kneaded material was 0.539 $\Omega/\square$, and the 43 % by volume kneaded material was 0.178 $\Omega/\square$. When the surface resistivity was measured after the humidity resistance test, the 35 % by volume kneaded material showed 0.609 $\Omega/\square$, and the 43 % by volume kneaded material showed 0.176 $\Omega/\square$. The results are shown in Table 2.

(Example 6)

[0098] The reduction precipitation of nickel was performed in two stages in the same way as in Example 1 through the two-stage reduction precipitation process. The nickel powder was then obtained by filtering off, cleaning with water, and drying in vacuum at 150°C. This Example 6 differs from Example 1 only in that the drying temperature in vacuum is 150°C (the temperature in Example 1 is 80°C).

[0099] The Co content of the overall nickel powder thus obtained was 6.5 % by mass, and the specific surface area was 0.94 m²/g. The powder properties are shown in Table 1.

[0100] Next, when the surface resistivity was measured in the same way as in Example 1, the initial surface resistivity was 0.147 $\Omega/\square$. The surface resistivity after a humidity resistance test, showed 0.112 $\Omega/\square$. The results are shown in Table 2.

(Example 7)

[0101] The reduction precipitation of nickel was performed in two stages in the same way as in Working Example 1 through the two-stage reduction precipitation process. In the first reduction precipitation step, 3.7 kg, in the Ni + Co converted mass, of an aqueous blend solution of a cobalt chloride aqueous solution and a nickel chloride aqueous solution (an aqueous solution blended such that the Co content is 4 % by mass based on the Ni + Co amount (the Co content was 5 % by mass based on the Ni + Co amount in Example 1)) was added to precipitate the nickel powder. Next, in the second reduction precipitation step, additional 60% hydrazine hydrate and the aqueous blend solution of a cobalt chloride aqueous solution and a nickel chloride aqueous solution (aqueous solution blended such that the Co content is 10 % by mass based on the Ni + Co amount) were added, 35 minutes after starting the addition of 60% hydrazine hydrate in the first reduction precipitation step, to precipitate the nickel powder. The nickel powder was then obtained by filtering off, cleaning with water, and drying in vacuum at 200°C.

[0102] The Co content of the overall nickel powder thus obtained was 6.2 % by mass, and the specific surface area was 0.65 m²/g. The powder properties are shown in Table 1. Further, when this nickel powder was evaluated in the same way as in Example 1, the initial surface resistivity was 0.151 $\Omega/\square$. The surface resistivity after a humidity resistance test showed 0.122 $\Omega/\square$. The results are shown in Table 2.

(Example 8)

[0103] The reduction precipitation of nickel was performed in two stages in the same way as in Example 1 through the two-stage reduction precipitation process. 25.2 L of an aqueous solution of 25 % sodium hydroxide and 806 g of tartaric acid was added to 138 L of pure water and heated to 75 °C while stirring. 19.2 L of 60 % hydrazine hydrate was added to this aqueous solution. A cobalt chloride aqueous solution was not added in the first reduction precipitation step; 2.5 kg, in an Ni converted mass, of only a nickel chloride aqueous solution was added to precipitate the nickel powder. Next, in the second reduction precipitation step, more 60% hydrazine hydrate and 2.5 kg, in the Ni + Co converted mass, of an aqueous blend solution of a cobalt chloride aqueous solution and a nickel chloride aqueous solution (an aqueous solution blended such that the Co content is 10 % by mass based on the Ni + Co amount) were added, 50 minutes after starting the addition of 60 % hydrazine hydrate in the first reduction precipitation step, so as to precipitate the nickel powder. The nickel powder was then obtained by filtering off, cleaning with water, and drying in vacuum at 220 °C.

[0104] The nickel powder thus obtained contains Co in the surface layer section only, and the Co content of the overall nickel powder obtained was 4.6 % by mass and the specific surface area was 0.97 m²/g. The powder properties are shown in Table 1. When this nickel powder was evaluated in the same way as in Example 1, the initial surface resistivity was 0.209 Ω/□. The surface resistivity after a humidity resistance test showed 0.190 Ω/□. The results are shown in Table 2.

(Example 9)

[0105] The reduction precipitation of nickel was performed in two stages in the same way as in Example 1 through the two-stage reduction precipitation process. In the first reduction precipitation step, 25.2 L of an aqueous solution of 25 % sodium hydroxide and 806g of tartaric acid was added to 138L of pure water and heated to 70 °C while stirring. 19.2 L of 60 % hydrazine hydrate was added to this aqueous solution. Further, in the first reduction precipitation step, 2.5 kg, in the Ni + Co converted mass, of an aqueous blend solution of a cobalt chloride aqueous solution and a nickel chloride aqueous solution (an aqueous solution blended such that the Co content is 1.5 % by mass of the Ni + Co amount) was added to precipitate the nickel powder. Next, in the second reduction precipitation step, additional 60 % hydrazine hydrate and 2.5 kg, in the Ni + Co converted mass, of an aqueous blend solution of a cobalt chloride aqueous solution and a nickel chloride aqueous solution (an aqueous solution blended such that the Co content is 1.5 % by mass of the Ni + Co amount) were added, 40 minutes after starting the addition of 60 % hydrazine hydrate in the first reduction precipitation step, to precipitate the nickel powder. The nickel powder was then obtained by filtering off, cleaning with water, and drying in vacuum at 120 °C.

[0106] The Co content of the overall nickel powder thus obtained was 1.3 % by mass, and the specific surface area was 0.85 m²/g. The powder properties are shown in Table 1. Further, when this nickel powder was evaluated in the same way as in Example 1, the initial surface resistivity was 0.361 Ω/□. The surface resistivity after a humidity resistance test was 0.318 Ω/□. The results are shown in Table 2.

(Example 10)

[0107] 94.8 g of sodium hydroxide and 12.6 g of tartaric acid was added to 2280 mL of pure water and heated to 55 °C while stirring. 180 mL of hydrazine and a modified silicone oil-based surface active agent having an HLB value of 9 were added to this aqueous solution. 39 g, in the Ni + Co converted mass, of an aqueous blend solution of a cobalt chloride aqueous solution and a nickel chloride aqueous solution (an aqueous solution blended such that the Co content is 20 % by mass based on the Ni + Co amount) was further added, and the nickel powder was precipitated through the first reduction precipitation step. Next, in the second reduction precipitation step, 45 mL of hydrazine and 39 g, in the Ni + Co converted mass, of an aqueous blend solution of a cobalt chloride aqueous solution and a nickel chloride aqueous solution (an aqueous solution blended such that the Co content is 20 % by mass based on the Ni + Co amount) were further added to the aqueous solution, 30 minutes after starting the addition of hydrazine in the first reduction precipitation step, so as to further precipitate the nickel powder. The nickel powder was then obtained by filtering off, cleaning with water, and drying in vacuum at 200 °C.

[0108] The Co content of the overall nickel powder thus obtained was 18.8 % by mass, and the specific surface area was 1.09 m²/g. The powder properties are shown in Table 1. Further, when this nickel powder was evaluated in the same way as in Example 1, the initial surface resistivity was 0.085 Ω/□. The surface resistivity after a humidity resistance test was 0.081 Ω/□. The results are shown in Table 2.

(Example 11)

[0109] The reduction precipitation of nickel was performed in two stages in the same way as in Example 10 through the two-stage reduction precipitation process, but heating was up to 70 °C. An aqueous solution of cobalt chloride was not added in the first reduction precipitation step, but 39 g, in the Ni converted mass, of a nickel chloride aqueous solution only was added to precipitate the nickel powder. Next, in the second reduction precipitation step, 45 mL of hydrazine and 39 g, in the Ni + Co converted mass, of an aqueous blend solution of a cobalt chloride aqueous solution and a nickel chloride aqueous solution (an aqueous solution blended such that the Co content is 40 % by mass of the Ni + Co amount) were further added 45 minutes after starting the addition of hydrazine in the first reduction precipitation step, so as to further precipitate the nickel powder. The nickel powder was then obtained by filtering off, cleaning with water, and drying in vacuum at 220 °C.

[0110] The nickel powder thus obtained contains Co in the surface layer section only, and the Co content of the overall nickel powder obtained was 19.1 % by mass and the specific surface area was 1.15 m²/g. The powder properties are shown in Table 1. When this nickel powder was evaluated in the same way as in Example 1, the initial surface resistivity was 0.406 Ω/□. The surface resistivity after a humidity resistance test showed 0.369 Ω/□. The results are shown in

Table 2.

(Example 12)

[0111] The reduction precipitation of nickel was performed in two stages in the same way as in Example 7 through the two-stage reduction precipitation process. Then, after filtering off and cleaning with water, the nickel powder was further heated for 2 hours in nitrogen - hydrogen (10%) at a temperature of 350 °C. The Co content of the overall nickel powder thus obtained was 5.9 % by mass, and the specific surface area was so small as 0.35 m²/g. The powder properties are shown in Table 1. Further, when this nickel powder was evaluated in the same way as in Example 1, the initial surface resistivity was 0.205 Ω/□. The surface resistivity after the humidity resistance test was 0.196 Ω/□. The results are shown in Table 2.

(Comparative Example 1)

[0112] The reduction precipitation of nickel was performed in two stages in the same way as in Example 2 through the two-stage reduction precipitation process; however, in the first reduction precipitation step, a modified silicone oil-based surface active agent having an HLB value of 11 was added to obtain the nickel powder.

[0113] The nickel powder thus obtained contained Co in the surface layer section only, and the Co content of the overall nickel powder obtained was 4.8 % by mass. The powder properties are shown in Table 1. Because the modified silicone oil-based surface active agent having an HLB value of 11 was used, the average primary particle diameter d_1 was smaller. Further, when this nickel powder was evaluated in the same way as in Example 1, the initial surface resistivity when 35 % by volume of the nickel powder was kneaded was 0.043 Ω/□, but when 43 % by volume was kneaded, the resin was absorbed between the nickel powders (particularly, between the particles forming the nickel powder) and kneading was not possible. Further, when the surface resistivity was measured after the humidity resistance test, the 35 % by volume kneaded material was 0.059 Ω/□. These results are shown in Table 2.

(Comparative Example 2)

[0114] Other than obtaining the nickel powder by a milling processing after the vacuum drying step, the reduction precipitation of nickel was performed in two stages in the same way as in Example 2 through the two-stage reduction precipitation process so as to obtain the nickel powder. Because the milling processing had been performed, the tap density became larger, at 3.61 g/mL.

[0115] The nickel powder thus obtained contained Co in the surface layer section only, and the Co content of the overall nickel powder obtained was 4.6 % by mass. The powder properties are shown in Table 1. Further, when this nickel powder was evaluated in the same way as in Example 1, the initial surface resistivity of the 35 % by volume kneaded material was 356 Ω/□ and the 43 % by volume kneaded material was 129 Ω/□. Since the initial surface resistivity was high, the humidity resistance test was not performed on these sample materials. These results are shown in Table 2.

(Comparative Example 3)

[0116] 164 g of sodium hydroxide and 21 g of ethylene diamine were added to 3800 mL of pure water and heated to 85°C while stirring. 300 mL of hydrazine and 130 g, in the Ni converted mass, of a nickel chloride aqueous solution were added (no cobalt chloride aqueous solution was added), and the nickel powder was precipitated with only a one-stage reduction precipitation process. The nickel powder was then obtained by filtering off and cleaning with water, and drying in vacuum at 80°C.

[0117] The nickel powder thus obtained does not contain Co. The powder properties are shown in Table 1. When a polyethylene resin was kneaded with this nickel powder in the same way as in Example 1, kneading was not possible since the resin was absorbed between the nickel powders even when 35 % by volume of the nickel powder was kneaded.

(Comparative Example 4)

[0118] The powder properties of a typical filler-form nickel powder (manufactured by INCO) commercially available for the electrically conductive paste and the electrically conductive resin are shown in Table 1. This nickel powder does not contain Co.

[0119] When this nickel powder was evaluated in the same way as in Example 1, the initial surface resistivity of the 35 % by volume kneaded material was 0.124 Ω/□ and the 43 % by volume kneaded material was 0.043 Ω/□. Further, when the surface resistivity was measured after a humidity resistance test, the 35 % by volume kneaded material was 0.406 Ω/□ and the 43 % by volume kneaded material was 0.068 Ω/□. These results are shown in Table 2.

(Comparative Example 5)

[0120] The reduction precipitation of nickel was performed in two stages in the same way as in Example 2 through the two-stage reduction precipitation process, but heating was up to 70°C. In the first reduction precipitation step, a modified silicone oil-based surface active agent having an HLB value of 11 was added to obtain the nickel powder. Next, in the second reduction precipitation step, additional 60 % hydrazine hydrate and 2.5 kg, in the Ni + Co converted mass, of an aqueous blend solution of a cobalt chloride aqueous solution and a nickel chloride aqueous solution (an aqueous solution blended such that the Co content is 10 % by mass of the Ni + Co amount) were further added 25 minutes after starting the addition of the hydrazine hydrate in the first reduction precipitation step, to precipitate the nickel powder. The nickel powder was then obtained by filtering off, cleaning with water, and drying in vacuum at 80°C.

[0121] The nickel powder thus obtained contained Co in the surface layer section only, and the Co content of the overall nickel powder obtained was 5.0 % by mass and the specific surface area thereof was 2.26 m²/g. The powder properties are shown in Table 1. Further, when this nickel powder was evaluated in the same way as in Example 1, the initial surface resistivity was 0.039 Ω/□, and the surface resistivity after a humidity resistance test was 0.051 Ω/□. These results are shown in Table 2.

(Comparative Example 6)

[0122] The reduction precipitation of nickel was performed in two stages in the same way as in Example 2 through the two-stage reduction precipitation process. 32.9 L of an aqueous solution of 25 % sodium hydroxide and 1617 g of tartaric acid were added to 160 L of pure water and heated to 60°C while stirring. 38.5 L of 60% hydrazine hydrate was added to this aqueous solution. No Cobalt chloride aqueous solution was added in the first reduction precipitation step; and only 4.8 kg, in the Ni converted mass, of a nickel chloride aqueous solution was added so as to precipitate the nickel powder. Next, in the second reduction precipitation step, 4.8 kg, in the Ni + Co converted mass, of an aqueous blend solution of a cobalt chloride aqueous solution and a nickel chloride aqueous solution (an aqueous solution blended such that the Co content is 10 % by mass based on the Ni + Co amount) was added 30 minutes after starting the addition of the 60% hydrazine hydrate in the first reduction precipitation step, to further precipitate the nickel powder. The nickel powder was then obtained by filtering off, cleaning with water, drying in atmosphere at 100°C, and further performing heat treatment for 2 hours in nitrogen - 10% hydrogen at 350°C.

[0123] The nickel powder thus obtained contained Co in the surface layer section only, and the Co content of the overall nickel powder obtained was 5.0 % by mass and the specific surface area was 1.13 m²/g. The powder properties are shown in Table 1. Further, when this nickel powder was evaluated in the same way as in Example 1, the initial surface resistivity was 0.046 Ω/□, and the surface resistivity after a humidity resistance test was 0.066 Ω/□. These results are shown in Table 2.

[0124]

[Table 1]

Sample	Co Content (% by mass)		d ₁ (μm)	σ/d ₁	d ₂ (μm)	d ₂ /d ₁	Tap Density (g/mL)	Specific Surface Area (m ² /g)
	Overall	Surface Layer Section						
Example 1	6.6	10	1.7	0.22	19.9	11.7	2.67	1.70
Example 2	5.0	10	2.3	0.40	11.0	5.2	2.86	1.33
Example 3	1.2	1.5	2.6	0.21	16.3	6.3	3.41	1.26
Example 4	19.4	20	1.1	0.35	58.5	53.2	1.13	1.95
Example 5	18.7	40	1.3	0.25	6.6	5.1	2.34	1.87
Example 6	6.5	10	2.1	0.24	24.6	11.7	2.83	0.94
Example 7	6.2	10	1.8	0.20	26.7	14.8	2.56	0.65
Example 8	4.6	10	1.8	0.24	16.5	9.2	2.78	0.97
Example 9	1.3	1.5	2.7	0.37	19.8	7.3	3.35	0.85
Example 10	18.8	20	1.2	0.33	56.9	47.4	1.07	1.09
Example 11	19.1	40	1.4	0.29	7.5	5.4	2.19	1.15

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(continued)

Sample	Co Content (% by mass)		d_1 (μm)	σ/d_1	d_2 (μm)	d_2/d_1	Tap Density (g/mL)	Specific Surface Area (m^2/g)
	Overall	Surface Layer Section						
Example 12	5.9	10	2.1	0.20	30.5	14.5	2.73	0.35
Comparative Example 1	4.8	10	0.9	0.35	40.5	45.0	1.21	2.03
Comparative Example 2	4.6	10	2.5	0.31	6.9	2.8	3.61	1.41
Comparative Example 3	<0.01	-	0.6	0.29	1.8	3.0	0.61	3.85
Comparative Example 4	<0.01	-	1.4	0.40	19.5	13.9	1.25	0.65
Comparative Example 5	5.0	10	0.5	0.48	38.8	77.6	1.21	2.48
Comparative Example 6	4.9	10	0.8	0.42	56.0	70.0	1.43	1.13

[0125]

[Table 2]

Sample	Kneaded Ratio of Ni Powder (% by volume)	Kneadability	Surface Resistivity when Kneaded with Resin ($\Omega/\square$)		Surface Resistivity Increase Rate (times)
			Initial Value	After Humidity Resistance Test	
Example 1	35	○	0.209	0.217	1.04
	43	○	0.036	0.033	0.92
Example 2	35	○	0.711 1	0.706	0.99
	43	○	0.194	0.160	0.82
Example 3	35	○	0.725	0.720	0.99
	43	○	0.203	0.173	0.85
Example 4	35	○	0.097	0.115	1.19
	43	○	0.033	0.035	1.06
Example 5	35	○	0.539	0.609	1.13
	43	○	0.178	0.176	0.99
Example 6	35	○	0.147	0.112	0.76
Example 7	35	○	0.151	0.122	0.81
Example 8	35	○	0.209	0.190	0.91
Example 9	35	○	0.361	0.318	0.88
Example 10	35	○	0.085	0.081	0.95
Example 11	35	○	0.406	0.369	0.91
Example 12	35	○	0.205	0.196	0.96

(continued)

Sample	Kneaded Ratio of Ni Powder (% by volume)	Kneadability	Surface Resistivity when Kneaded with Resin ($\Omega/\square$)		Surface Resistivity Increase Rate (times)
			Initial Value	After Humidity Resistance Test	
Comparative Example 1	35	○	0.043	0.059	1.36
	43	×	-	-	-
Comparative Example 2	35	○	356	-	-
	43	○	129	-	-
Comparative Example 3	35	×	-	-	-
Comparative Example 4	35	○	0.124	0.406	3.28
	43	○	0.043	0.068	1.59
Comparative Example 5	35	○	0.039	0.051	1.31
Comparative Example 6	35	○	0.046	0.066	1.43

[0126] Examples 1 - 5, which are within the scope of the present invention, could be kneaded with the polyethylene resin, either at a 35 % by volume kneading ratio or a 43 % by volume kneading ratio of the Ni powder; while for Examples 6 - 12, kneading with the polyethylene resin was possible at a 35 % by volume kneading ratio of the Ni powder. The surface resistivities of the sheet-form sample formed after kneading with the resin were small at $0.8 \Omega/\square$ or less, both before and after the humidity resistance test. Further, the rates of increase of said surface resistivity before and after the humidity resistance test (surface resistivity after humidity resistance test/surface resistivity before humidity resistance test) were a maximum of 1.19, and it is believed that the Examples 1 - 12, which are within the scope of the present invention, have superior weatherability and can be used stably over a long period.

[0127] In Comparative Example 1, by contrast, since the modified silicone oil-based surface active agent having an HLB value of 11 was added, the average primary particle diameter was, at $0.9 \mu\text{m}$, below the lower limit of $1.0 \mu\text{m}$ of the present invention, and could not be kneaded with the polyethylene resin when the kneading ratio of the Ni powder was 43 % by volume. Kneading with the polyethylene resin was possible when the kneading ratio of the Ni powder was 35 % by volume, but since the specific surface area of the Ni powder was $2.03 \text{ m}^2/\text{g}$, exceeding the upper limit of the present invention of $2.0 \text{ m}^2/\text{g}$, the rate of increase of the surface resistivity before and after the humidity resistance test (surface resistivity after humidity resistance test/surface resistivity before humidity resistance test) was large at 1.36 (35 % by volume kneading ratio of the Ni powder) so that the weatherability is inferior.

[0128] In Comparative Example 2, since the tap density, at 3.61 g/mL , exceeds the 3.5 g/mL upper limit of the present invention, it is believed that the nickel powder is locally distributed in the resin so that the mutual contact of the particles forming the powder is reduced; the initial surface resistivity when the kneading ratio of the Ni powder was 35 % by volume reached $356 \Omega/\square$, while the initial surface resistivity when the kneading ratio of the Ni powder was 43 % by volume was $129 \Omega/\square$. In both cases, the surface resistivity of the sheet-form sample, formed after kneading with the resin, was extremely high.

[0129] The tap density of Comparative Example 3, at 0.61 g/mL , was lower than the lower limit of 1.0 g/mL of the present invention; and because of this, it was difficult to increase an amount of the nickel powder to be kneaded into the resin and it was not possible to knead with the polyethylene resin even when the Ni powder kneading ratio was 35 % by volume.

[0130] Comparative Example 4 was nickel powder without containing Co, so that the rates of the increase of surface resistivity before and after the humidity resistance test (surface resistivity after humidity resistance test/surface resistivity before humidity resistance test) were large, at 3.28 (35 % by volume Ni powder kneading ratio) and 1.59 (43 % by volume Ni powder kneading ratio) and the weatherability was inferior.

[0131] In Comparative Example 5, the average primary particle diameter was lower than that of the present invention, and the standard deviation of the primary particle diameters was also great; further, since the specific surface area was large, the rate of increase of the surface resistivity was great, at 1.31, and the weatherability was inferior.

[0132] With Comparative Example 6, although the specific surface area was in the scope of the invention, the average

primary particle diameter was lower than that of the present invention, the standard deviation of the primary particle diameters was also great at 1.43, and the weatherability was inferior.

[0133] Figures 1(a) and (b) show scanning electron microscope (SEM) photographs of the nickel powder obtained in Example 1, and Figures 2(a) and (b) show scanning electron microscope (SEM) photographs of the nickel powder obtained in Comparative Example 2.

[0134] As can be seen from Figures 1(a) and (b), the primary particle diameters in the nickel powder obtained in Example 1 are even around 1.8 μm . In contrast, as can be seen from Figures 2(a) and (b), the nickel powder obtained in Comparative Example 2 contains particles of uneven sizes in primary particle diameter together, and there are many fine primary particles which are thought to cause the degradation of the weatherability.

"Examples and Comparative Examples relating to polymer PTC elements (Examples A - D and Comparative Examples A and B"

[0135] Next, Examples of manufacturing PTC elements according to the present invention using the nickel powder according to the present invention will be described. Comparative Examples will also be described for the purpose of comparison.

(1) Electrically conductive filler

[0136] Nickel-cobalt alloy filler (i.e. the nickel powder according to the present invention or nickel powder for the comparison) was used as the electrically conductive filler, a high density polyethylene was used as the polymer material, and a surface roughened nickel foil (manufactured by Fukuda Metal Foil & Powder Industry Co. Ltd., thickness: approx. 25 μm) was used as the metal electrodes to manufacture the PTC elements.

[0137] The nickel powders used were those manufactured in the above Example 1, Example 6, Example 7, and Example 12, and these were used to manufacture the PTC elements. These PTC elements will be called PTC elements of Example A, Example B, Example C, and Example D, respectively. Also, for comparison, nickel powders in the above Comparative Example 6 and Comparative Example 5 were used as the electrically conductive filler. These PTC elements will be called PTC elements in Comparative Example A and Comparative Example B.

[0138] The Co contents in the nickel powders used are as shown in Table 3 below.

[0139]

[Table 3]

	Co Content in Nickel Powder (% by mass)
Example A	5
Example B	5
Example C	4
Example D	4
Comparative Example A	0
Comparative Example B	0

[0140] The Co content was calculated on the assumption that substantially all the nickel salt and the cobalt salt in the aqueous solutions used in manufacturing had been precipitated.

(2) Polymer material

[0141] Commercially available high density polyethylene (manufactured by EQUISTAR, PETROTHENE LB832, density: 0.957 - 0.964 g/ml, melt index: 0.23 - 0.30 g/10 minutes, melting point $135 \pm 3^\circ\text{C}$) was used as the polymer material.

(3) Metal electrode

[0142] Nickel metal foil (manufactured by Fukuda Metal Foil & Powder Co., Ltd., electrolytic nickel foil, thickness: approx. 25 μm) was used as the metal electrode.

(4) Manufacture of PTC element

(4 - 1) Production of PTC composition

[0143] A coupling agent (manufactured by KENRICH PETROCHEMICALS, NZ-33) was added to the polymer material in powder form at a ratio of 2 % by mass of the polyethylene mass; these were mixed for 30 seconds in a kitchen blender (manufactured by Sun KK, MILL MIXER MODEL FM-50) to obtain a polymer blend. The nickel powder and Mg(OH)₂ (manufactured by Albemarle, H10) were added in the amounts shown below in Table 4 and mixed for 30 seconds with the kitchen blended so as to obtain the electrically conductive polymer composition.

[0144]

[Table 4]

	Nickel powder (% by volume)	Mg(OH) ₂ (% by volume)	Polymer Blend
Example A	43	10	balance
Example B	43	10	balance
Example C	43	10	balance
Example D	43	10	balance
Comparative Example A	35	10	balance
Comparative Example B	35	10	balance

[0145] 45 mL of the electrically conductive polymer composition thus obtained was charged in a mill (manufactured by Toyo Seiki Seisaku-sho, Ltd. Labo Plastomill Model 50C150, blade R60B) and kneaded for 15 minutes at a set temperature of 160 °C and a blade rotation of 60 rpm so as to obtain the PTC composition.

(4 - 2) Preparation of PTC component base sheet

[0146] The PTC composition obtained in (4-1) is made into a stacked sandwich structure of iron plate/Teflon (registered trademark) sheet/thickness adjusting spacer (SUS with 0.5 mm thickness) + PTC composition/Teflon (registered trademark) sheet/ iron plate; this structure was pre-pressed with a thermal pressure pressing machine (manufactured by Toho Press Seisakusho, hydraulic forming machine: Model T-1) for 3 minutes at a temperature of 180 - 200 °C and pressure of 0.5 MPa, after which main pressing was performed for 4 minutes at a pressure of 5 MPa. Then, a cooling pressing machine (manufactured by Toho Press Seisakusho, hydraulic forming machine: Model T-1) circulating water set to 22 °C in a chiller was used to press for 4 minutes at 0.5 MPa to prepare a polymer PTC component in sheet form (PTC component base sheet).

[0147] (4 - 3) Manufacture of PTC element plaque base sheet Using the PTC component base sheet prepared in (4 - 2) and metal electrodes, a stacked sandwich structure was made consisting of iron plate/Teflon (registered trademark) sheet/silicone rubber/Teflon (registered trademark) sheet/metal electrode/thickness adjusting spacer (SUS with 0.5mm thickness) + PTC component base sheet/metal electrode/Teflon (registered trademark) sheet/silicone rubber/Teflon (registered trademark) sheet/iron plate; this was subjected to main pressing with the above thermal pressure pressing machine for 4 minutes at a temperature of 220 - 230 °C and pressing pressure of 9 MPa. After this, the above cooling pressing machine with circulating water set to 22 °C in a chiller was used to cool-press the structure for 4 minutes at 9 MPa so as to prepare the PTC element plaque base sheet (PTC element aggregation before cutting) having a metal electrode thermally compressed on each of main surfaces of the polymer PTC component (PTC component base sheet).

(4 - 4) Production of PTC element

[0148] 1000 kGy of electron beam was irradiated on the PTC element plaque base sheet prepared in (4 - 3), and then a manual punch was used to punch out a 3 x 4 mm piece to obtain sample specimens of the polymer PTC element.

(4 - 5) Production of PTC device

[0149] A 4 mm x 5.2 mm piece of a pure Ni lead having a thickness of 0.125 mm and a hardness of 1/4 H was soldered to each side of the 3 x 4 mm specimen punched out in (4 - 4) to obtain a test sample of a PTC device having a strap form as a whole. For soldering, approximately 2.0 mg per one side of a paste solder (manufactured by Senju Metal

Industry Co., Ltd., M705-728C) was used, and a reflow oven (manufactured by Nippon Avionics, Model TCW-118N, auxiliary heating temperature controlled at 360 °C, preheating temperature controlled at 250 °C, reflow temperature (1) controlled at 240 °C, reflow temperature (2) controlled at 370 °C, belt speed of 370 mm/minute) was used in a nitrogen atmosphere.

(5) Measurement of initial resistance

[0150] Two days after the production of the samples, the resistance (resistance between the two leads) were measured on the test samples obtained. Since the resistance of the lead is far lower than the resistance of the PTC element, this resistance can be called the initial resistance of the PTC element. For the measurement of the initial resistance and resistances of the PTC element under various conditions as described below, a milliohmmeter (manufactured by Hewlett Packard, 4263A) was used. The measurement results for the initial resistance are shown in Table 5 (unit: Ω).

[0151]

[Table 5]

	Example A	Example B	Example C	Example D	Comparative Example A	Comparative Example B
Average	0.004931	0.004838	0.005035	0.004996	0.005834	0.006345
Standard Deviation	0.000753	0.000681	0.000808	0.000869	0.000896	0.0006345
Maximum	0.00670	0.00640	0.00660	0.00665	0.00875	0.00820
Minimum	0.00360	0.00370	0.00350	0.00360	0.00390	0.00450

[0152] From these results, it can be seen that, although the test samples of the Examples have slightly lower resistances, all test samples, including the samples of the comparative examples, have low resistance as is normal.

(6) Confirmation of PTC properties

[0153] Next, an R (resistance) - T (temperature) test was performed on each of the 5 test samples of the Examples and Comparative Examples by measuring the resistance-temperature property. The test temperature range was 20 °C -150 °C, and the ambient humidity of the test samples were 60 % or below. The ambient temperature of the test samples was raised in increments of 5 °C and maintained at that temperature for 10 minutes, after which the resistance of the PTC element was measured. Figure 3 shows the ratios of the resistance value measured at each temperature to the resistance at the initial temperature (21 °C) (in other words, the rate of resistance change).

[0154] From the results in Figure 3, the elements of the Examples and the Comparative Examples have threshold temperatures (which is also called trip temperatures at which the resistance of the PTC element increases rapidly after the temperature of the PTC elements increases from room temperature) in the range of 120 °C - 130 °C; and in each element, the resistance after such a range is at least approximately 1015 times or higher of the previous resistance. Thus, it is clear that all the test samples have a switching function as a PTC element. Generally, it may be assumed that elements have the function as a PTC element if the resistance thereof increases by at least approximately 103 times.

(7) Measurement of resistance change over time under high temperature/dry condition

[0155] The test samples of the Examples and the Comparative Examples were placed and kept in a constant temperature oven (manufactured by Yamato, constant temperature oven DK600) controlled at a high temperature/dry condition (85 °C $\pm$ 3 °C and relative humidity of 10 % or below); and after being maintained for 24 hours, 165 hours, 502 hours, and 1336 hours, 5 pieces of each of the Examples and the Comparative Examples were removed from the constant temperature oven and left at room temperature for 1 hour, after which the resistance was measured with a milliohmmeter (resistance before trip). After measuring the resistance, a DC regulated power supply (manufactured by Kikusui Electronic Industry, PAD35-60L) was used to apply a voltage set at 6 V/50 A for 5 minutes so as to trip the element. After this, the test sample was left in room temperature again for 1 hour and the resistance (resistance after trip) was measured using the milliohmmeter. The measurement results are shown in Table 6 and Table 7 below. The results are also shown against maintained time in Figure 4 (resistance when maintained at 85 °C) and Figure 5 (trip jump when maintained at 85 °C). The figures in Table 6 are resistance values before trip and the unit is m Ω Table 7 shows the ratio of the resistance after trip for each time elapsed to the resistance before trip when maintained at 85 °C

for 0 hour, in other words the rate of resistance change.

[0156]

[Table 6]

	Initial		After 24 hours		After 165 hours		After 502 hours		After 1336 hours	
	Average	SD	Average	SD	Average	SD	Average	SD	Average	SD
Comparative Example A	6.61	0.60	5.68	0.44	6.21	0.69	7.77	0.92	7.73	0.98
Comparative Example B	7.03	0.56	6.25	0.44	6.16	0.54	7.75	0.71	9.49	0.57
Example A	5.60	0.44	5.07	0.38	4.66	0.27	5.01	0.41	6.72	0.68
Example B	5.40	0.41	4.78	0.49	4.50	0.40	4.61	0.28	5.66	0.21
Example C	5.86	0.32	5.18	0.41	5.09	0.35	6.92	0.48	8.99	0.78
Example D	5.90	0.37	5.11	0.41	5.45	0.45	8.77	1.08	8.45	0.45
SD: standard deviation										

[0157]

[Table 7]

	Initial		After 24 hours		After 165 hours		After 502 hours		After 1336 hours	
	Avg.	SD	Avg.	SD	Avg.	SD	Avg.	SD	Avg.	SD
Comparative Example A	1.16	0.0737	0.99	0.0480	1.29	0.101	3.13	0.459	6.01	0.848
Comparative Example B	1.11	0.658	1.07	0.0357	1.24	0.076	1.96	0.182	5.54	0.757
Example A	0.99	0.0765	0.96	0.0797	0.93	0.071	1.58	0.071	2.98	0.179
Example B	1.04	0.0620	0.91	0.0314	0.91	0.073	1.49	0.156	2.26	0.336
Example C	0.93	0.0676	0.94	0.791	0.99	0.068	2.57	0.532	4.36	0.544
Example D	0.96	0.0469	0.84	0.0179	0.99	0.060	2.89	0.591	3.49	1.192
Avg.: average SD: standard deviation										

[0158] Under the high temperature/dry condition, the change over time of the resistance before trip is not so large in any of the samples of the Examples and the Comparative Examples; however, with respect to the resistance after trip, the samples of the Comparative Examples clearly have a larger rate of resistance increase.

(8) Measurement of resistance change over time under room temperature/normal humidity condition

[0159] The same tests as in the above (7) were performed on the PTC elements as the test samples of the Examples and the Comparative Examples which were kept in a room temperature controlled at 23 ± 5 °C and relative humidity of 20 - 60 % (which corresponds to a normal humidity when the humidity is not controlled). The number of the samples used was 20 each; and 5 each were removed after 1002 hours and 1863 hours to measure the resistance (resistance before trip). The resistance after trip was similarly measured. The measurement results are shown in Table 8 and Table 9 below. The results are shown against maintained time in Figure 6 (resistance when maintained at room temperature) and Figure 7 (trip jump when maintained at room temperature). The figures in Table 8 are resistance values before trip and the unit is mΩ. Table 9 shows the ratio of the resistance after trip for the times elapsed to the resistance before trip when maintained at room temperature for 0 hour, in other words the rate of resistance change.

[0160]

[Table 8]

	Initial		After 1002 hours		After 1863 hours	
	Average	SD	Average	SD	Average	SD
Comparative Example A	5.37	0.46	5.22	0.46	4.87	0.45
Comparative Example B	5.79	0.63	6.16	0.27	5.67	0.33
Example A	4.66	0.50	3.87	0.36	4.28	0.20
Example B	4.66	0.50	3.75	0.42	4.26	0.35
Example C	4.48	0.49	4.01	0.32	4.36	0.36
Example D	4.32	0.41	3.96	0.34	4.45	0.32
SD: standard deviation						

[0161]

[Table 9]

	Initial		After 1002 hours		After 1863 hours	
	Average	SD	Average	SD	Average	SD
Comparative Example A	1.16453	0.07367	1.27203	0.13667	1.380	0.159
Comparative Example B	1.10595	0.06582	1.20820	0.09800	1.460	0.127
Example A	0.98501	0.07650	1.03980	0.14126	10.60	0.248
Example B	1.04034	0.06195	0.90125	0.06262	1.129	0.053
Example C	0.92925	0.6765	1.09836	0.16574	1.414	0.092
Example D	0.96403	0.01688	1.10407	0.12894	1.427	0.131
SD: standard deviation						

[0162] Under the room temperature/normal humidity condition, the change over time of the resistance before trip as well as the resistance after trip is not so large in any of the samples of the Examples and the Comparative Examples; however, the samples of the Comparative Examples have a relatively larger rate of increase of the resistance after trip.

(9) Accelerated oxidation test under pressure

[0163] The test samples were placed in a pressure vessel; compressed air was supplied to the vessel so that there was a pressurized ambient of 40 atm pressure to set up a condition wherein the oxidation of the electrically conductive filler in the PTC element could be accelerated. The test samples were kept in this pressurized ambient for 14 days and 28 days, after which they were maintained in air atmosphere/room temperature for 1 hour; the resistance was then measured as before (these measurements are shown in Figure 8 as "2 week" and "4 week" respectively. Measurements before maintaining under the pressure is shown as "initial". After this, the PTC element was tripped in the same way as before, then left at room temperature for 1 hour as before and the resistance measured. The measurement results are shown in Table 10 and Table 11 below. The results are shown against the maintained time in Figure 8 (resistance after 40 atm. pressurized test) and Figure 9 (trip jump after 40 atm. pressurized test). The figures in Table 10 are resistance values before trip and the unit is mΩ. Table 11 shows the ratio of the resistance after trip for the times elapsed to the resistance before trip when maintained at 40 atm for 0 hour, in other words the rate of resistance change.

[0164]

[Table 10]

	Initial		After 14 days		After 28 days	
	Average	SD	Average	SD	Average	SD
Comparative Example A	5.16	0.73	5.66	0.74	5.07	0.29

(continued)

	Initial		After 14 days		After 28 days	
	Average	SD	Average	SD	Average	SD
Comparative Example B	5.95	0.68	6.24	0.57	6.59	0.94
Example A	4.17	0.38	4.48	0.16	4.33	0.46
Example B	4.14	0.40	3.92	0.13	4.22	0.52
Example C	4.41	0.35	5.19	0.59	4.50	0.44
Example D	4.39	0.42	4.50	0.21	4.75	0.45
SD: standard deviation						

[0165]

[Table 11]

	Initial		After 14 days		After 28 days	
	Average	SD	Average	SD	Average	SD
Comparative Example A	1.16	0.0737	3.37	0.335	9.61	3.425
Comparative Example B	1.11	0.0658	3.30	0.660	8.14	3.374
Example A	0.99	0.0765	20.8	0.377	4.39	1.223
Example B	1.04	0.0620	1.70	0.114	5.22	1.067
Example C	0.93	0.0676	2.97	0.567	7.16	1.712
Example D	0.96	0.0469	2.70	0.394	7.20	1.85
SD: standard deviance						

[0166] According to these results, under the pressurized condition, the effect of time elapsed on the resistance before trip is not so large in any of the samples of the Examples and the Comparative Examples; however, with respect to the resistance after trip, it can be seen that in the samples of the Comparative Examples, the increase in resistance becomes remarkable with the time elapsed. Particularly good results were obtained on the samples of Example A and Example B with respect to the increase in resistance after trip.

(10) Trip cycle test

[0167] At room temperature and using the milliohmmeter, the resistance before testing was measured on the samples of the Examples and the Comparative Examples. The samples were then set in a trip cycle machine. The testing machine uses Model Pad 35-60L manufactured by Kikusui Electronics as a power supply, and the setting voltage was 6 V DC with a test current of 50 A.

[0168] 50A of current was applied for 6 seconds to each sample. Samples tripped within such time applied, and for the remainder of the time, a voltage of 6V was applied to the samples.

[0169] After the 6 seconds of applied time was completed, the application of the current/voltage was stopped for 54 seconds to be a non-applied state. This current/voltage On/Off was controlled by a sequencer and defined as one trip cycle. 200 trip cycles were performed on each sample.

[0170] After the prescribed number of cycles has been completed, the samples are removed from the testing machine. After an hour has elapsed after completion of the prescribed number of cycles, the resistance of the samples was measured, and then the samples were set again in the testing machine and the trip cycle test was continued. The prescribed number of cycles was 50 cycles, 100 cycles, and 200 cycles. Table 12 and Figure 10 show the results of the resistance measurement. The figures in the Table and the Figure show the ratio of the resistance after completion of each cycle to the resistance at initial value (0 cycle), in other words the rate of resistance change.

[0171]

[Table 12]

	50 Cycles		100 Cycles		200 Cycles	
	Average	SD	Average	SD	Average	SD
Comparative Example A	2.71	0.408	4.37	0.637	5.69	0.281
Comparative Example B	2.22	0.274	3.11	0.673	3.52	0.586
Example A	1.95	0.058	2.62	0.203	2.90	0.112
Example B	1.62	0.131	1.92	0.181	2.22	0.170
Example C	2.25	0.140	3.19	0.209	3.86	0.230
Example D	2.16	0.353	2.69	0.154	3.27	0.559
SD: standard deviation						

[0172] In the sample of Comparative Example A, the resistance increased considerably after completing 200 cycles; on the other hand, the increase in resistance was not so large in the samples of the Examples.

[0173] From the results of the Examples and the Comparative Examples related to the PTC elements described above, it has been confirmed that the samples of the Examples, in particular the samples of Example A and Example B, maintained the good performances, compared to the samples of the Comparative Examples, under the high temperature/dry maintained conditions, the room temperature/normal humidity maintained conditions, the maintained conditions under the accelerated ambient and in the trip cycle test. Thus, when the nickel powder according to the present invention which is used to producing such samples is used as the electrically conductive filler, preferred PTC elements can be produced. It is contemplated that this is because the nickel powder according to the present invention is selected for having the specific characteristics among the nickel powders containing cobalt. That is, this is believed to be caused by, in addition to the properties of the cobalt-containing nickel powder itself, selecting the specific ranges from viewpoints of the primary particle diameter distribution and the morphology of the secondary particle diameter which are more controlled.

[0174] A point to be particularly noted is that, although the resistance after trip of the PTC element increases when exposed to the high temperature/dry conditions, in the case of the PTC element of the present invention, the ratio of increase is relatively small. Hitherto, evaluation of the PTC element was performed under the room temperature/normal humidity conditions. As can be seen from the results in Figure 6 and Figure 7, the increase in the element resistance is not remarkable in such evaluations. However, in the evaluation under the high temperature/dry conditions, the difference in the resistance increases of the PTC elements is clear. There are various environments in which the PTC elements are used, and they may be used under the high temperature and dry conditions (for example an environment inside a car during daytime in summer). With the PTC element according to the present invention, the increase in the resistivity is small even in such harsh environments, so that it is more useful than the PTC element in the prior art.

[Industrial Applicability]

[0175] The nickel powder according to the present invention may be suitably used as the electrically conductive particles for the electrically conductive paste and the electrically conductive resin as well as the electrically conductive filler for the polymer PTC element.

[0176] Further, the PTC element according to the present invention has the same level of the switching property as that of the PTC element using the nickel powder containing only nickel as the electrically conductive filler, and the improved performance exhibits in change over time for a long period, so that it may be used widely for longer periods in the electrical equipment in the same way as with the PTC element of the prior art.

Claims

1. Nickel powder which contains 1 - 20 % by mass of cobalt and the balance which comprises nickel and unavoidable impurities and which is formed of secondary particles of aggregated primary particles, which powder is **characterized in that** the powder has
an average primary particle diameter being in 1.0 - 3.0 μm ,
a ratio σ/d_1 of a standard deviation σ of a primary particle diameter to the average primary particle diameter d_1 being 0.4 or less,

an average secondary particle diameter being 5 - 60 μm , a tap density being 1.0 - 3.5 g/ml, and a specific surface area being 2.0 m^2/g or less.

2. The nickel powder according to Claim 1 **characterized in that** a ratio d_2/d_1 of the above average primary particle diameter d_1 to the above average secondary particle diameter d_2 is in the range of 5 - 60.
3. The nickel powder according to Claim 1 or 2 **characterized in that** a cobalt content of the primary particles present in surface layer sections of the above secondary particles is 1 - 40 % by mass based on a total mass of said surface layer section.
4. A process of producing nickel powder, **characterized in that** the process comprises a first reduction precipitation step to precipitate nickel by adding a bivalent nickel salt to an aqueous solution containing a reducing agent, and a second reduction precipitation step to further precipitate nickel by adding at least a bivalent nickel salt to the aqueous solution after the first reduction precipitation step wherein of the above first and second reduction precipitation steps, a low hydrophilic surface active agent having an HLB value of 10 or less is added to at least the first reduction precipitation step, and a bivalent cobalt salt is added to the aqueous solution in which nickel is precipitated in at least the second reduction precipitation step so as to precipitate nickel and obtain nickel powder, the nickel powder obtained is dried under an inert atmosphere or a vacuum atmosphere at 80 - 230 $^{\circ}\text{C}$, or dried in atmosphere at 80 - 150 $^{\circ}\text{C}$ followed by being heat treated under a reducing atmosphere at 200 - 400 $^{\circ}\text{C}$.
5. The process of producing the nickel powder according to Claim 4, **characterized in that** a cobalt ion content in the aqueous solution having the bivalent cobalt salt added in said second reduction precipitation step is 1 - 40 % by mass based on the total amount of nickel ion and cobalt ion in said aqueous solution, and a cobalt ion concentration in said aqueous solution is higher than the cobalt ion concentration in the aqueous solution in said first reduction precipitation step, and the nickel powder obtained through said first and second reduction precipitation steps contains 1 - 20 % by mass of cobalt.
6. The process of producing nickel the powder according to Claim 4, **characterized in that** the bivalent cobalt salt is added to the aqueous solution in said first reduction precipitation step such that a cobalt ion content in said aqueous solution is 1 - 20 % by mass based on the total amount of nickel ion and cobalt ion in said aqueous solution, and the bivalent cobalt salt is added to the aqueous solution in said second reduction precipitation step such that the cobalt ion content in said aqueous solution is 1 - 20 % by mass of the total amount of nickel ion and cobalt ion in said aqueous solution.
7. The nickel powder according to Claim 3 **characterized in that** the cobalt content in the surface layer section of said secondary particles is 8 - 20 % by mass based on the total mass of said surface layer section.
8. The nickel powder according to any one of Claims 1 - 3 and Claim 7 **characterized in that** the cobalt content of the nickel powder as a whole is 4 - 10 % by mass.
9. The nickel powder according to any one of Claims 1 - 3 and Claims 7 and 8 **characterized in that** the cobalt content in the interior of the nickel powder is 3 - 6 % by mass based on the total mass of said interior.
10. The nickel powder according to any one of Claims 1 - 3 and Claims 7 - 9 **characterized in that** a tap density of the nickel powder is 2.3 - 3.0 g/ml.
11. The nickel powder according to any one of Claims 1 - 3 and Claims 7 - 10 **characterized in that** said ratio d_2/d_1 is within the range of 8 - 16.
12. A polymer PTC element comprising:
 - (A) a polymer PTC component comprising:
 - (a1) an electrically conductive filler, and
 - (a2) a polymeric material; and
 - (B) a metal electrode located on at least one surface of the polymer PTC component,

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characterized in that the nickel powder according to any one of Claims 1 - 3 and Claims 7 - 11 or the nickel powder produced by the process according to any one of Claims 4 - 6 is used as the electrically conductive filler.

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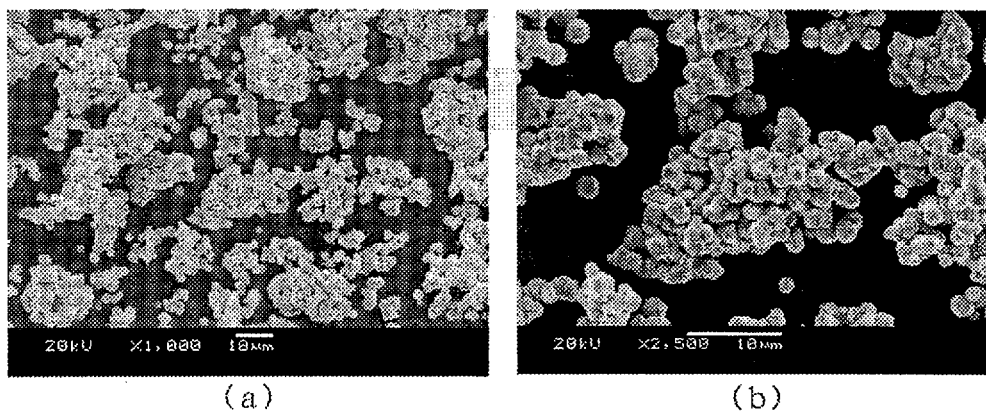
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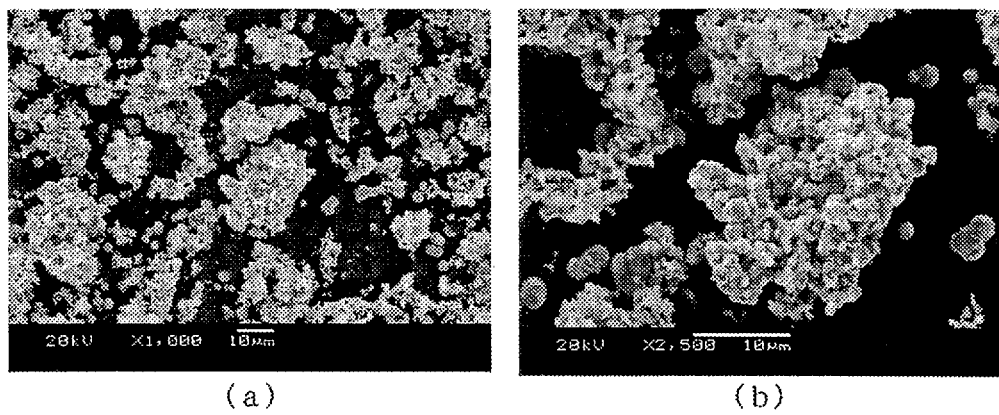
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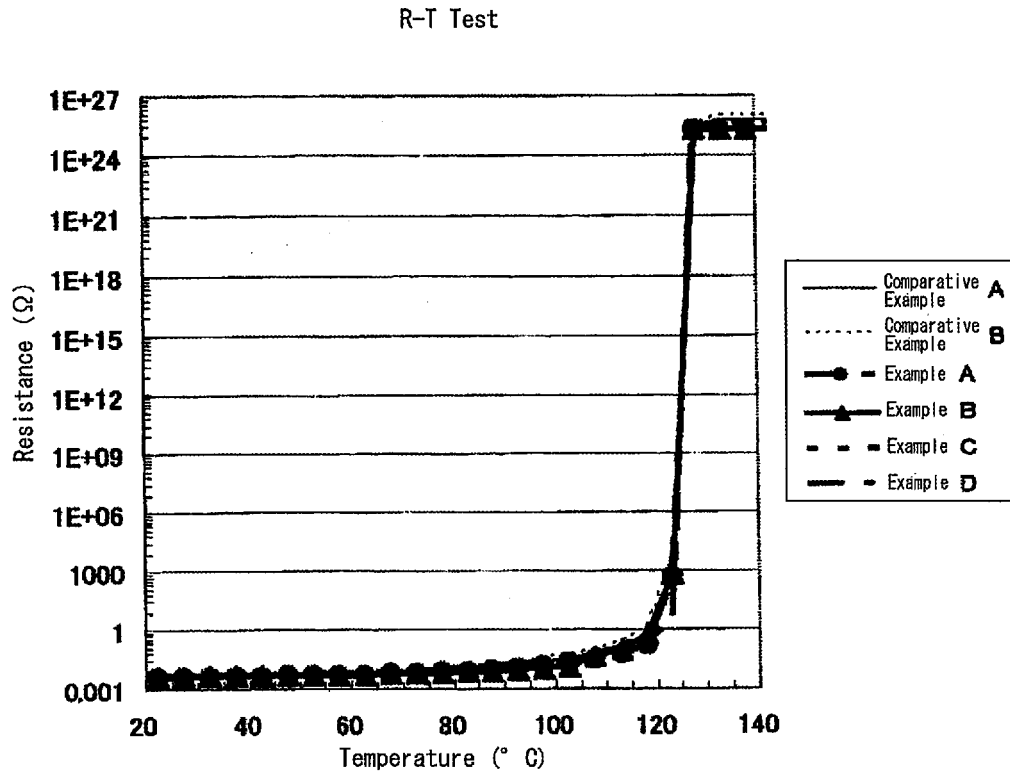
[Figure 1]



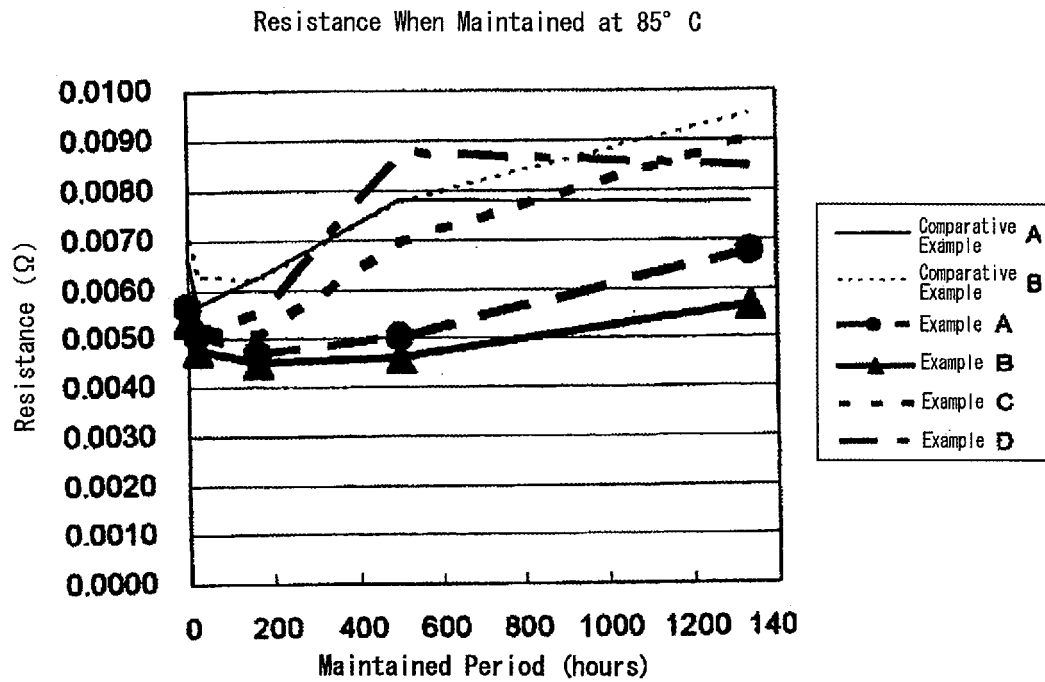
[Figure 2]



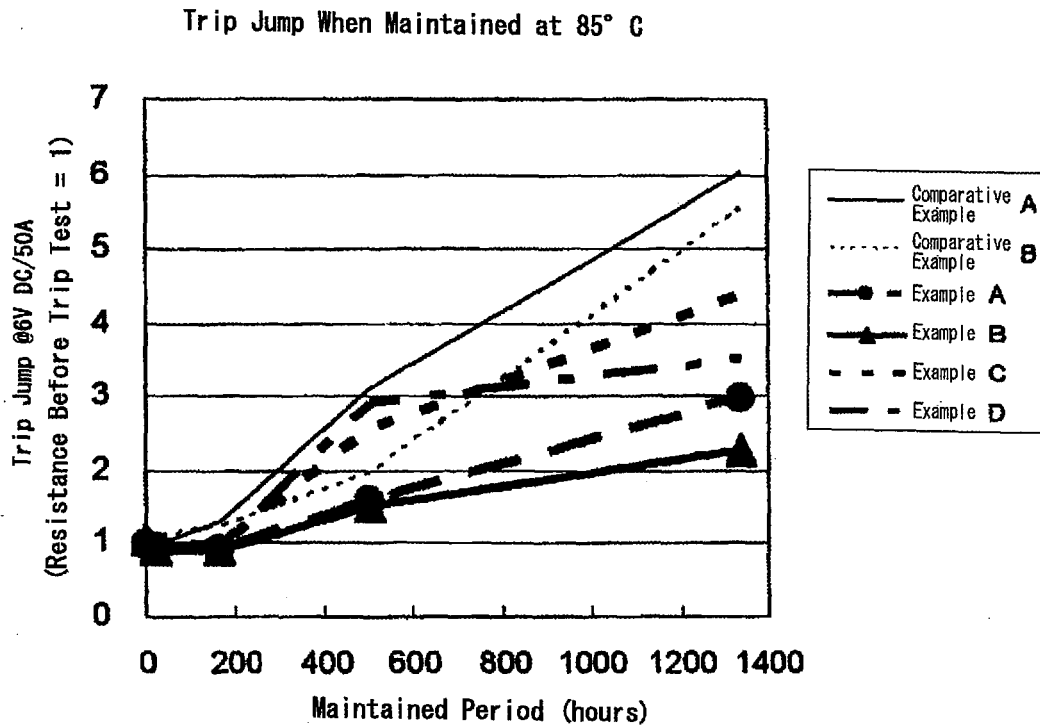
[Figure 3]



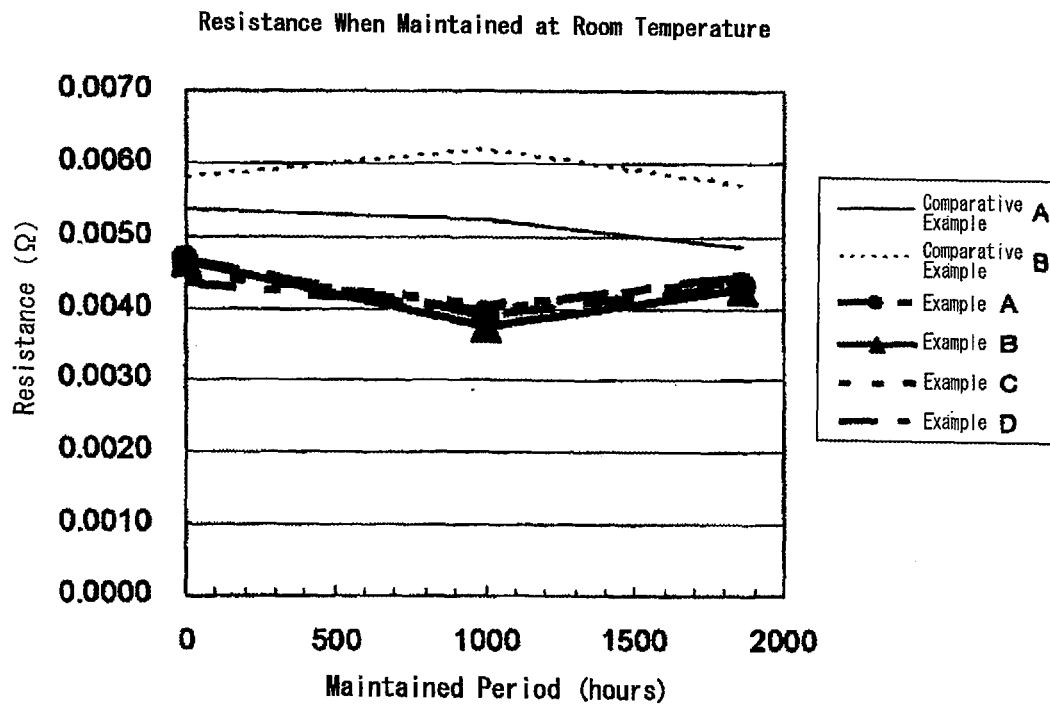
[Figure 4]



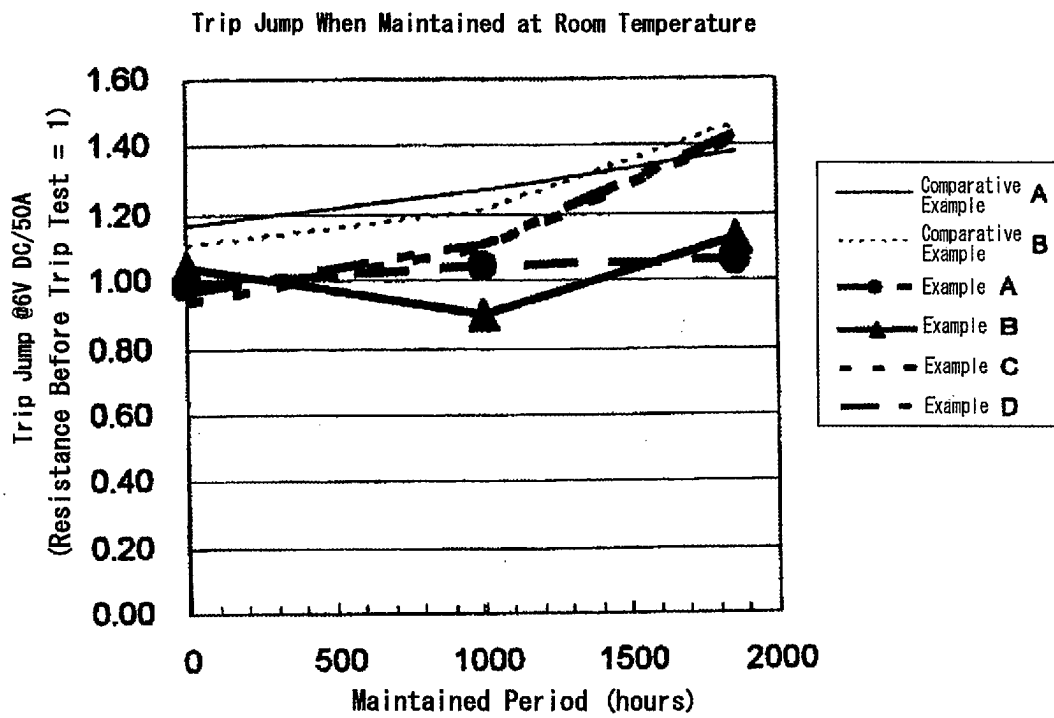
[Figure 5]



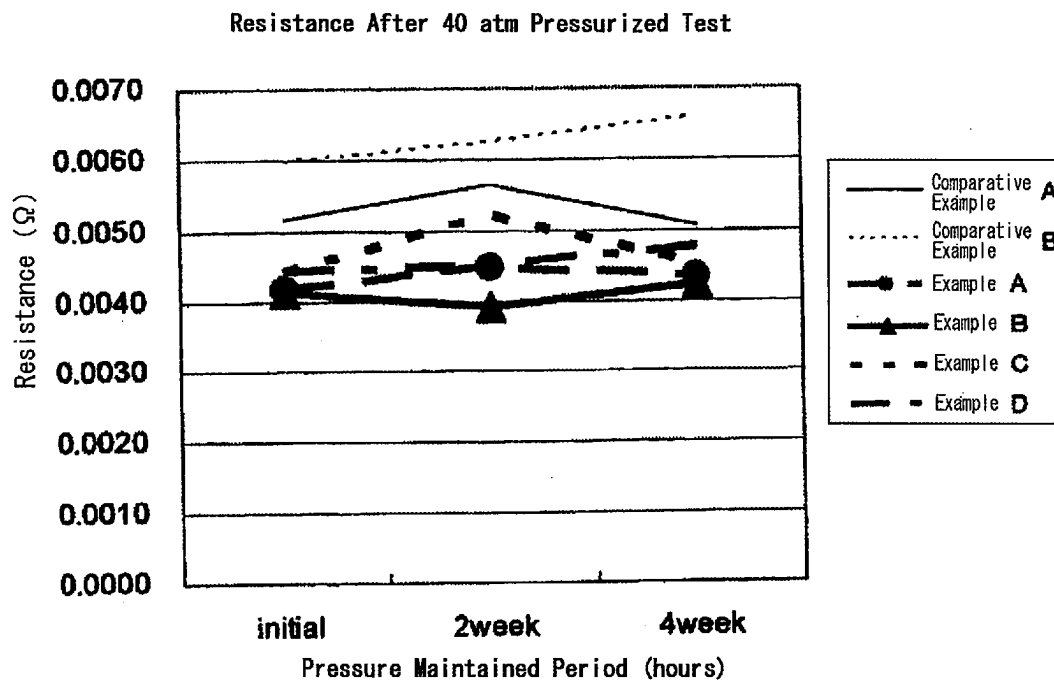
[Figure 6]



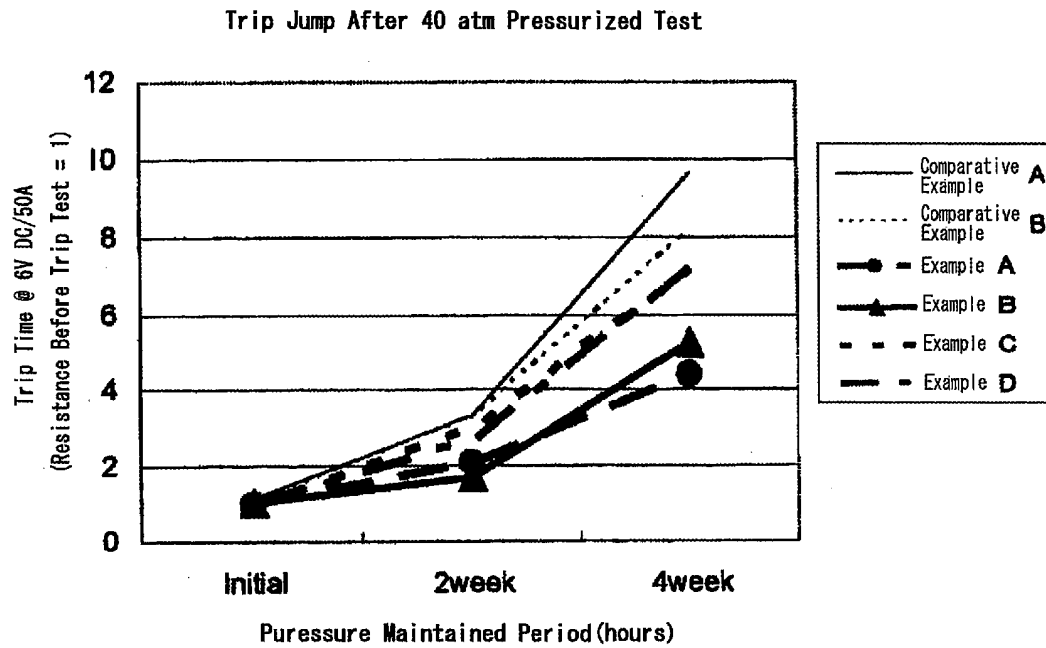
[Figure 7]



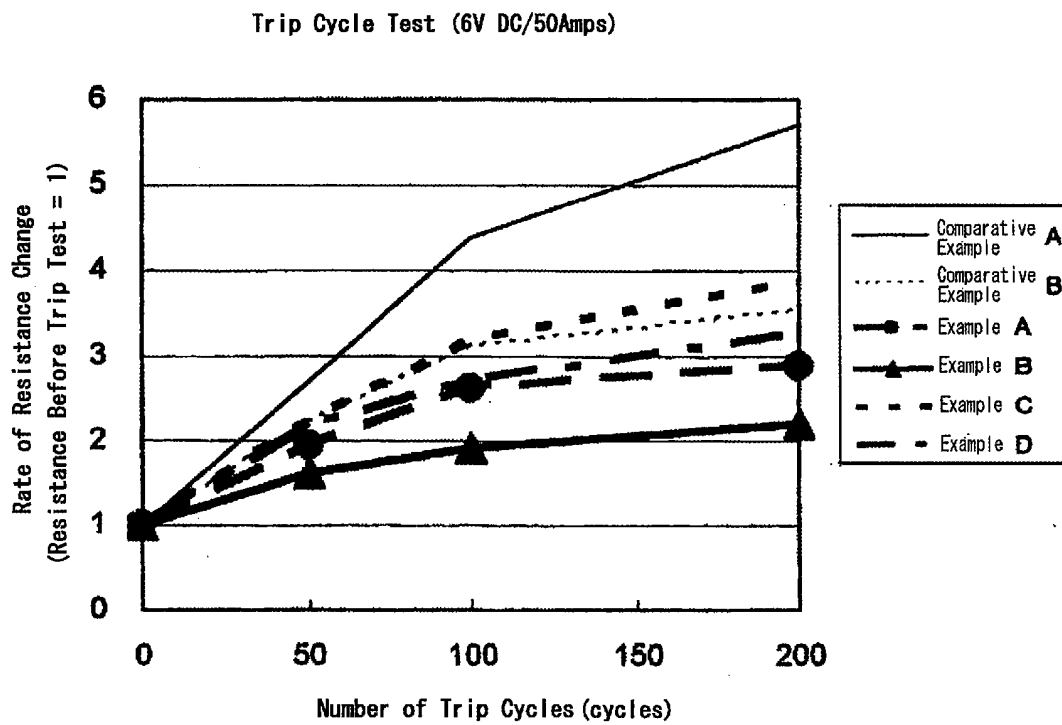
[Figure 8]



[Figure 9]



[Figure 10]



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2006/323720

A. CLASSIFICATION OF SUBJECT MATTER

B22F1/00(2006.01)i, B22F9/24(2006.01)i, C22C19/03(2006.01)i, H01B1/22(2006.01)i, H01B5/00(2006.01)i, H01C7/02(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B22F1/00, B22F9/24, C22C19/03, H01B1/22, H01B5/00, H01C7/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2007
Kokai Jitsuyo Shinan Koho 1971-2007 Toroku Jitsuyo Shinan Koho 1994-2007

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2005/023461 A1 (Sumitomo Metal Mining Co., Ltd.), 17 March, 2005 (17.03.05), Claims (Family: none)	1-12
A	JP 2005-048191 A (Raychem Corp.), 24 February, 2005 (24.02.05), Claims & WO 1993/026014 A1 & US 5378407 A & EP 0643869 A1 & CA 2134561 A	12

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search
13 February, 2007 (13.02.07)

Date of mailing of the international search report
20 February, 2007 (20.02.07)

Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2006/323720

Although claims 1-11 include every "nickel powder", only nickel powders used as conductive particles for conductive pastes or conductive resins are disclosed within the meaning of PCT Article 5. Consequently, claims 1-11 are not fully supported within the meaning of PCT Article 6.

This international search report therefore covers those supported and disclosed by the description, namely nickel powders used as conductive particles for conductive pastes or conductive resins which are specifically mentioned in the description.

REFERENCES CITED IN THE DESCRIPTION

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