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## (54) Electroplating on inorganic powdery or granular materials.

(57) Metal(s) is/are electroplated onto an inorganic powdery or granular material by first making the particles of the material electrically conductive and then carrying out electroplating in a plating solution containing the metal(s) with which the material is/are to be plated, between an anode made of graphite or of the said metal(s) and a cathode made of an electrically conductive net-like ot plate-like material, whereby individual particles of the inorganic powdery or granular material intermittently come into direct or indirect contact with the cathode during electroplating.



Croydon Printing Company Ltd.

# ELECTROPLATING ON INORGANIC POWDERY OR GRANULAR MATERIALS

The present invention relates to electroplating on inorganic powdery or granular material.

Electroplating is a method of forming a desired metallic coating on the surface of an electrically conductive material by passing an electric current between a cathode made of the material to be coated and an anode made of the metal that is to form the coating or of graphite in a plating solution containing ions of the metal to form the coating. Consequently, electroplating is widely used industrially, e.g. in decoration and the anti-corrosive field. When the substances plated are electrically nonconductive, such as glass or plastics, they can be plated if electrical conductivity has previously been imparted to their surface, e.g. by electroless plating. However, only an electroless plating method such as that disclosed in Japanese Patent Publication No. 19127/1975 can be applied to inorganic powdery or granular material, since the fine particles used for a cathode cannot be held with a clip. This method is expensive and, applied to such substances, not particularly efficient.

The present invention provides a method of electroplating metal(s) onto an inorganic powdery or granular material, characterized in that electric conductivity is first imparted to the surface of the inorganic powdery or granular material and the subsequent electroplating is carried out with the said material suspended in a plating solution containing the said metal(s) between an anode made of graphite or of the said metal(s) and a cathode made of an electrically conductive net-like or plate-like material, and individual particles of the inorganic powdery or granular material intermittently come into direct or indirect contact with the cathode during electroplating.

By proceeding in accordance with the present invention, a uniform metallic coating can be formed efficiently on inorganic powdery or granular materials. The products can be light and inexpensive inorganic powdery or granular materials having metallic lustre and superior electric conductivity.

Although any powdery or granular natural mineral or any artificial inorganic powdery or granular material can be used as the inorganic powdery or granular material in the present invention, powdery materials such as calcium carbonate, barium sulphate, wollastonite, clay, silicic acid, silicate, basic magnesium carbonate, quartz powder, titanium oxide, aluminium oxide, aluminium hydroxide, sirasu microballoons and glass microballoons (sirasu is a ceramic material derived from volcanic ash); flaky materials such as mica, talc, sericite, glass flake, stratified graphite, vermiculite, bentonite and attapulgite; and fibrous materials such as asbestos, glass fibre, rock wool and ceramic fibre having an average length of 10 mm or less are preferably used for fillers added to resin. In addition, the above described flaky materials are preferably used as electrically conductive inorganic powdery or granular materials for electromagnetic shielding. It is desired that the flaky inorganic powdery or granular materials have an average diameter of 0.1 to 500 μm and an aspect ratio of 10 or more in respect of the moulding and electromagnetic shielding properties. In particular, natural or artificial minerals belonging to the mica group, clintonite group or chlorite group and glass flakes are preferably used for flaky nonmetallic inorganic powdery or granular materials in the present invention. More specifically, these materials include natural muscovite, phlogopite, biotite, vermiculite, fluorine mica, and glass flakes for use in flake lining.

The provision of electric conductivity to the surface of inorganic powdery or granular materials prior to electroplating in accordance with the present invention can be achieved by forming an electrically conductive layer on the surface. Such a layer can be formed by methods such as electroless plating, high-vacuum metallizing, sputtering, ion-plating, electrically conductive painting and coating with electrically conductive corpuscles. The substances used for forming such an electrically conductive layer include silver, copper, iron, nickel, aluminium, tin, chromium, titanium, zinc, gold, platinum and palladium, their alloys, and graphite. It is not always required that the electrically conductive layer be uniformly formed all over the surface of the inorganic powdery or granular materials. It is necessary only to form such an electrically conductive layer so that the volume resistivity may be $1 \times 10^4$ ohm.cm or less after imparting electric conductivity to it.

Although every electrically conductive metal having a volume resistivity of 1 ohm.cm or less can be used for the layer plated on the surface of the inorganic powdery or granular materials obtained by electroplating according to the present invention, silver, copper, iron, nickel, aluminium, tin, chromium, titanium, zinc, gold and platinum or their alloys are preferably used in respect of electrical conductivity, adhesion and cost, with silver, copper and nickel being especially preferred when high electrical conductivity is required. In addition, it is desired that the thickness of the layer plated be 100 A (10 nm) to 1 mm, preferably 0.05 to 100 μm, in respect of various kinds of performance.

The composition of the electroplating solution used in the present invention is not different in any way from that of an electroplating solution used in electroplating of general metallic products and plastics products. That is to say, the electroplating solution used in the present invention is an aqueous solution of salts or acid compounds of the metals to be plated. For example, a copper sulphate bath or a copper pyrophosphate bath can be used for copper plating, a nickel sulphate or nickel chloride bath for nickel plating, and a chromic acid bath for chromium plating. Compounds for ionizing these metals, chelating agents, buffering agents, lustre-giving agents, reducing agents and pH adjusters are added if necessary to prepare the electroplating solution.

Rods or plates of the metals to be plated or of graphite are used as anode in the present invention, as in conventional electroplating methods. However, the invention differs in that the cathode is not a product to which electric conductivity has been imparted: electrically conductive net-like or plate-like substances are used for cathode. Although the electrically conductive inorganic powdery or granular materials are suspended in a plating solution, the metals to be plated are not stuck to the cathode but uniformly and efficiently stuck to the electrically conductive inorganic powdery or granular materials, since an individual powdery or granular particle comes into direct contact with the cathode or comes into indirect and intermittent contact with the cathode through other particles. Although any electrically conductive net-like material or plate-like material can be used for the cathode, such material is preferably arranged all over the bottom surface of the plating tank in order to heighten the efficiency. The mesh of the net-like materials used for the cathode must be smaller than the diameter of the inorganic powdery or granular materials. A plate-like cathode is used when the electrically conductive inorganic powdery or granular materials are in corpuscular form. The cathode is preferably made of a corrosion-resistant metal such as platinum depending upon the properties of the plating solution. However, stainless steel is most usual.

Although the surface of the inorganic powdery or granular materials can be uniformly and efficiently plated owing to the above described mechanism of plating, the structure of the plating tank and the stirring method are also important in order to further heighten the efficiency. The usual inorganic powdery or granular materials have a true specific gravity larger than that of the plating solution, thereby being liable to settle when the plating solution is gently stirred. The above described desired condition of the inorganic powdery or granular materials coming into contact with the cathode can be achieved by suitably selecting the stirring conditions with the anode arranged in the upper portion of the plating tank and immersed in the plating solution and the cathode arranged in the bottom portion of the plating tank. On the other hand, it is necessary only to reverse the anode and the cathode in position for light inorganic powdery or granular materials such as sirasu and glass microballoons and perlite. In addition, in the case when the plating solution is circulated, the inorganic powdery or granular materials contained in the plating solution are pressed against the net-like cathode installed on the bottom portion of the plating tank by supplying the plating solution from the upper portion of the tank and discharging it from the bottom of the tank, so that plating can proceed more efficiently. Although a cathodic current density of 2 to 6 ampere/square decimeter is usual, it is desirable that the current be reduced in the initial stage of electroplating, during which electric conductivity is not sufficiently imparted, and then gradually increased. It is best to control the current by varying the voltage.

Although the plating condition of inorganic powdery or granular materials plated according to the present invention can be directly observed by scanning electron microscopy, its electric conductivity can be measured by determining its volume resistivity as follows. A cylindrical container made of insulating materials is filled with the electrically conductive powdery or granular materials to be tested, the materials are compressed under a definite load, a definite strength of current is passed between the two outside electrodes of four electrodes linearly inserted into the compressed electrically conductive powdery or granular materials, and the voltage measured between the two inside electrodes.

The plated inorganic powdery or granular materials obtained according to the present invention can be blended with a liquid resin to use in, for example, electrode materials of piezoelectric elements, electromagnetic shielding coating to be coated on the housing of electronic instruments, antistatic materials of products requiring earthing, or in heating resistors such as a defroster for glass, or can be blended with plastics and moulded into a computer housing to be used as an electromagnetic shielding material, since they are uniformly coated with metals, have a metallic lustre, are light and have superior electric conductivity. Further, they can be used as a coating having a metallic lustre, to reinforce metals, and as radio scattering materials for radar.

The present invention will be illustrated below with reference to the non-limiting Examples, in which "parts" are by weight unless the contrary is stated.

Example 1

Fine powdery or granular commercial barium sulphate (average diameter 10 µm) is thinly distributed over the base plate of a vacuum metallizer of tungsten coil heater type and metallized with copper under vacuum of (1.3 mPa). It is subjected to vacuum metallizing for 15 minutes in all with stirring about every 3 minutes. Then an electroplating solution containing 10 g/l of copper pyrophosphate, 27 g/l of potassium pyrophosphate and 0.5 ml/l of 20% aqueous ammonia is prepared. A plating tank is provided with an anode made of copper plate at its upper portion and a cathode made of stainless steel plate at its bottom portion. 10 g/l of the barium sulphate to which electric conductivity has been imparted is dispersed in the prepared electroplating solution. Electroplating is carried out for 200 minutes at an average cathodic current density of 3 ampere/square decimeter, maintaining the solution temperature at about 40 °C and the pH at about 8.5. After washing and drying, the powdery or granular copper-plated barium sulphate has a coppery lustre. The thickness of the copper-plated layer is about 0.7 µm observed by scanning electron microscopy and the quantity of copper adhering is 48% by weight. In addition, the volume resistivity under a pressure of 50 g/cm$^2$ is

$10^{-2}$ ohm.cm or less, which shows superior electric conductivity. Then a paste-like electrically conductive adhesive is prepared by blending 100 parts of the powdery or granular copper-plated barium sulphate with 50 parts of a two-pack commercially available epoxy resin containing amine as a curing agent. The prepared paste-like electrically conductive adhesive shows superior conductivity when used in an electrode terminal.

Example 2

Phlogopite powder having an average diameter of 250 µm and an average aspect ratio of 50 is coated with nickel by electroless plating to impart an electric conductivity to its surface. The quantity of nickel stuck to the resulting nickel-plated phlogopite powders is 2.3% by weight and the volume resistivity is $3.5 \times 10^2$ ohm.cm. Then an electroplating solution containing 30 g/l of nickel sulphate, 5 g/l or nickel chloride and 5 g/l of boric acid is prepared. A plating tank is provided with an anode of graphite rod inserted in its upper portion and a stainless steel net of 200 mesh (wire diameter, 53 µm, sieve opening, 74 µm) placed at the bottom. 15 g/l of phlogopite powders to which electric conductivity has been imparted are dispersed in the prepared electroplating solution. Electroplating is carried out for 180 minutes at a cathodic current density of about 3 ampere/square decimeter maintaining the solution at a temperature about 50 °C and a pH of 4.0. After washing and drying, the nickel-plated phlogopite powders are silvery-black in colour. It is found from observation by scanning electron microscopy that the quantity of nickel stuck is 39% by weight and the thickness of the nickel-plated layer is 0.5 µm. In addition, the volume resistivity is $10^{-2}$ ohm.cm or less, which shows superior electric conductivity. Then sheet-like test pieces 3 mm thick are prepared by blending 100 parts of the nickel-plated phlogopite powders with 100 parts of commercially available polypropylene resin, melting the resulting blend at 250 °C in a kneader (Labo Plasto Mill, Toyo Seiki Seisakusho Ltd), and hot pressing. The prepared test pieces are tested for electromagnetic shielding effect in accordance with a method described in "Engineering Materials", 29 (12) 38. The electromagnetic shielding effect is 38 db for a frequency of 10 MHz, 35 db for a frequency of 100 MHz and 41 db for a frequency of 1 GHz which shows superior electromagnetic shielding.

## CLAIMS

1. A method of electroplating metal(s) onto an inorganic powdery or granular material, characterized in that electric conductivity is first imparted to the surface of the inorganic powdery or granular material and the subsequent electroplating is carried out with the said material suspended in a plating solution containing the said metal(s) between an anode made of graphite or of the said metal(s) and a cathode made of an electrically conductive net-like or plate-like material, and individual particles of the inorganic powdery or granular material intermittently come into direct or indirect contact with the cathode during electroplating.

2. A method as claimed in claim 1, in which the inorganic powdery or granular material is granular, flaky or fibrous having an average length of 10 mm or less.

3. A method as claimed in claim 1 or 2, in which the inorganic powdery or granular material is flaky or granular and has an average aspect ratio (a ratio of diameter to thickness) of 10 or more.

4. A method as claimed in any preceding claim, in which the inorganic powdery or granular material is a natural or artificial mineral belonging to the mica group, the clintonite group or the chlorite group or is in the form of glass flakes.

5. A method as claimed in any preceding claim in which electric conductivity is imparted to the surface of the particles of the inorganic powdery or granular material by the use of at least one of silver, aluminium, copper, nickel, chromium, titanium, tin, antimony, zinc, gold, platinum and iron, alloys thereof and graphite.

6. A method as claimed in any preceding claim, in which the plated layer obtained on the surface of the particles of the inorganic powdery or granular material by electroplating is composed of at least one of silver, aluminium, copper, nickel, chromium, titanium, tin, antimony, zinc, gold, platinum and iron, or an alloy thereof.

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# EUROPEAN SEARCH REPORT

0119030

Application number

EP 84 30 1271

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl. ³) |
|---|---|---|---|
| X | FR-A-2 090 221 (DE BEERS INDUSTRIAL DIAMOND DIVISION LTD.) * Page 2, lines 1-5; page 3, line 32 * | 1-3,5,6 | C 25 D 7/00 |
| X | PLATING & SURFACE FINISHING, vol. 65, no. 3, March 1978, pages 42-46 A. MAYER et al.: "Plating discrete microparticles for laser-fusion targets" * Page 44, right-hand column, lines 16-17 * | 1-6 | |
| X | GB-A-1 387 444 (DE BEERS INDUSTRIAL DIAMOND DIVISION LTD.) * Page 2, lines 86-91 * | 1-3,5,6 | TECHNICAL FIELDS SEARCHED (Int. Cl. ³) |
| X | FR-A-1 561 827 (NATIONAL RESEARCH DEVELOPMENT CORP.) * Page 1, lines 33-36 * | 1-6 | C 25 D |

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 01-06-1984 | NGUYEN THE NGHIEP |

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