

DESCRIPTION

Title of Invention

PARTICLES COATED WITH CUPROUS OXIDE, METHOD FOR PRODUCING
THE SAME, AND ANTIFOULING COATING MATERIAL CONTAINING THE
PARTICLES COATED WITH CUPROUS OXIDE

Technical Field

[0001] The present invention relates to particles coated with cuprous oxide in which the surface of a core material is coated with cuprous oxide, and a method for producing the same. The particles coated with cuprous oxide of the invention are particularly useful as a pigment for an antifouling coating material.

Background Art

[0002] Cuprous oxide has been known as an antifouling pigment, and is made into a coating material and used as a coating material for ship bottoms to prevent attachment of shellfishes or algae in the sea. Cuprous oxide has a large absolute specific gravity of 6.0, and in a case in which cuprous oxide is made into a coating material for ship bottoms, there is a problem in that cuprous oxide settles due to the difference in the specific gravity between the vehicle and the cuprous oxide. In addition,

due to the recent increase in the price of metallic raw materials, reduction of the amount used has become an issue in the field.

[0003] Coating the surface of a core material with cuprous oxide can be considered as a method for decreasing the specific gravity. For example, a method for producing a composite pigment for an antifouling coating material is proposed in which a fluid having powder including at least SiO_2 and Al_2O_3 suspended in an aqueous solution including chlorine ions is used as an electrolytic solution, and a copper plate is electrolyzed as the anode (refer to Patent Document 1).

[0004] However, powder coated with cuprous oxide which is obtained by the production method of Patent Document 1 has practicality problems, such as poor adhesion of cuprous oxide, poor dispersion-in-the antifouling coating material, poor storage stability of the antifouling coating agent, and the like.

Citation List

[0005] [PTL 1] JP-A-1-213368

Summary of Invention

Technical Problem

[0006] The object of the invention is to provide

particles coated with cuprous oxide which can solve the variety of problems of the related art, a method for producing the same, and an antifouling coating material containing the particles coated with cuprous oxide.

Solution to Problem

[0007] The invention is to provide particles coated with cuprous oxide made by coating the surface of a core material with a cuprous oxide layer, in which the cuprous oxide layer completely coats the surface of the core material, and is configured with an assembly of octahedral cuprous oxide particles.

[0008] In addition, the invention is to provide a method for producing the particles coated with cuprous oxide having a surface treatment process in which a core material is brought into contact with one or two or more of the surface treatment aqueous solutions: an aqueous solution of stannous salt, an aqueous solution of silver salt, and an aqueous solution of palladium salt, thereby producing a surface-treated core material; and an electrodeposition process in which the surface-treated core material is dispersed in an aqueous electrolytic solution containing an electrolyte and an antioxidant, and electrolysis is carried out using metallic copper as the anode so that the cuprous oxide is electrodeposited on the

surface of the surface-treated core material, thereby producing the particles coated with cuprous oxide, in which the electrodeposition of cuprous oxide is carried out while maintaining the pH of the aqueous electrolytic solution between 7 to 13 during the electrodeposition process.

[0009] Furthermore, the invention provides an antifouling coating material including the particles coated with cuprous oxide as a pigment for an antifouling coating material.

Advantageous Effects of Invention

[0010] According to the invention, particles coated with cuprous oxide having high adhesion between a core material and a cuprous oxide layer, favorable dispersion in an antifouling coating material, and high storage stability of an antifouling coating material are provided.

Brief Description of Drawings

[0011] Fig. 1 is a scanning electron microscope image of particles coated with cuprous oxide B1 obtained in Example 1.

Fig. 2 is a scanning electron microscope image of particles coated with cuprous oxide b1 obtained in Comparative Example 1.

Description of Embodiments

[0012] Hereinafter, the invention will be described based on preferred embodiments. The particles coated with cuprous oxide of the invention are configured with a core material and a cuprous oxide (Cu_2O) layer that coats the surface of the core material. In the particles coated with cuprous oxide of the invention, the cuprous oxide layer completely coats the surface of the core material. The complete coating refers to the fact that the cuprous oxide layer covers the surface of the core material so that exposure of the surface of the core material is not observed in a case in which the particles coated with cuprous oxide are observed using an electron microscope (for example, in a case in which the particles coated with cuprous oxide are observed at a magnification of 2000 times).

[0013] The particles coated with cuprous oxide of the invention not only have the cuprous oxide layer completely coating the surface of the core material, but also have a specific structure. In detail, the cuprous oxide layer is configured with an assembly of octahedral cuprous oxide particles. A plurality of the cuprous oxide particles are densely assembled so as to form a layer having a predetermined thickness. It is considered that, because

the cuprous oxide layer has the above structure, the adhesion between the core material and the cuprous oxide layer is increased in the particles coated with cuprous oxide of the invention. In addition, it is considered that the dispersibility in an antifouling coating material is favorable, and the storage stability of the antifouling coating agent is improved. Meanwhile, it is still required to carry out additional studies regarding technical reasons why the above advantageous effects are exhibited due to the fact that the cuprous oxide particles have an octahedral shape.

[0014] While it is ideal that each and every cuprous oxide particle that configures the cuprous oxide layer has an octahedral shape, it is not necessary that all of the cuprous oxide particles have an octahedral shape. As a result of studies by the inventors, the above advantageous effects are exhibited as long as preferably 50 or more cuprous oxide particles, and more preferably 60 or more cuprous oxide particles have an octahedral shape out of 100 cuprous oxide particles, which are observation targets, in a case in which the cuprous oxide layer is observed using an electron microscope.

[0015] A layer including octahedral cuprous oxide particles can be successfully formed by generating cuprous oxide by, for example, the electrolytic reduction method

as described below. In contrast to the above, when cuprous oxide is generated by the electroless reduction method, a layer composed of cubic cuprous oxide particles is formed as shown in Comparative Example 1 as described below. For particles coated with cuprous oxide having a layer with the above structure, the adhesion between the core material and the cuprous oxide layer is not sufficiently strong, and the dispersibility or storage stability in an antifouling coating material is poor in the case in which the particles coated with cuprous oxide are used as a pigment for an antifouling coating material.

[0016] The cuprous oxide particles having an octahedral shape preferably have a particle diameter of 0.1 μm to 3 μm , and particularly preferably 0.5 μm to 2 μm . When the particle diameter is in the above range, the layer composed of the cuprous oxide particles becomes sufficiently dense, and the dispersibility or storage stability in an antifouling coating material is improved. The particle diameter of the cuprous oxide particles is measured by scanning electron microscope observation.

[0017] The thickness of the cuprous oxide layer is not particularly limited as long as the cuprous oxide layer is thick enough to completely coat the surface of the core material. The thickness of the cuprous oxide layer can be measured by, for example, observing the cross section of

the layer using a scanning electron microscope.

[0018] The octahedral cuprous oxide particles may be either regularly accumulated so as to form a layer, or randomly accumulated so as to form a layer.

[0019] Regarding the thickness of the cuprous oxide particle layer, the ratio of the core material to the cuprous oxide, when expressed by the mass ratio, can be preferably set in a wide range of 95/5 to 10/90 (core material/cuprous oxide), and more preferably 80/20 to 20/80. The mass ratio may be appropriately set so that the specific gravity of the target particles coated with cuprous oxide falls within the desired range.

[0020] An appropriate material is selected as the core material depending on the specific use of the particles coated with cuprous oxide. Specifically, a silicic acid-containing inorganic compound, an alkali earth metal compound, alumina, an organic compound, or the like can be used as the core material. Examples of the silicic acid-containing inorganic compound include crystalline silica, such as silica stone, quartz sand, and quartz, non-crystalline silica, such as fused silica accordingly and appropriately formed by heating and fusing crystalline silica, diatomaceous earth, a variety of zeolites, talc, clay, fly ash, glass beads, glass balloons, Shirasu balloons, and the like. Examples of the alkali earth

metal compound include alkali earth metal salts, such as barium sulfate and calcium carbonate. Examples of the organic compound include polymer materials, such as thermoplastic resins and thermosetting resins. Specific examples thereof include polyethylene, polypropylene, acrylic resins, polystyrene, polyester, fluororesins, silicon resins, phenol resins, urea resins, melamine resins, epoxy resins, and the like.

[0021] The particle diameter of the core material is appropriately selected depending on the specific use of the particles coated with cuprous oxide. In a case in which the particles coated with cuprous oxide are used as a pigment, for example, as an antifouling coating material, it is preferable to use a core material having an average particle diameter D_{50} in the volume standard particle size distribution of 0.5 μm to 100 μm , and particularly 2 μm to 50 μm from the standpoint of ship bottom coating properties. Particularly, in a case in which the thickness of the cuprous oxide layer is in the above range, when a core material having a particle diameter in the above range is used, the adhesion between the two becomes more favorable, which is preferred. D_{50} is measured using a particle size distribution measuring apparatus.

[0022] With regard to the particle diameter, the shape of the core material can be also appropriately selected

depending on the specific use of the particles coated with cuprous oxide. For example, spherical, cubic, plate-shaped, lump-like, and other-shaped core materials can be used. Generally, when a spherical core material is used, satisfactory effects can be obtained. In addition, the core material may be solid or hollow.

[0023] Next, a preferred method for producing particles coated with cuprous oxide of the invention will be described. Particles coated with cuprous oxide can be obtained by generating cuprous oxide particles on the surface of a core material through electrolysis, and accumulating a plurality of the particles so as to form a layer. The present production method is roughly classified into (A) a surface treatment process of a core material, (B) an electrodeposition process of cuprous oxide through electrolysis, and (C) a water washing process of particles coated with cuprous oxide.

Hereinafter, the respective processes will be described.

[0024] In the surface treatment process of a core material of (A), a core material is brought into contact with one or two or more of the surface treatment aqueous solutions: an aqueous solution of stannous salt, an aqueous solution of silver salt, and an aqueous solution of palladium salt, thereby producing a surface treated core material. In a case in which the core material is a

thermoplastic resin, a thermosetting resin, or the like, specifically, polyethylene, polypropylene, an acrylic resin, polystyrene, polyester, a fluororesin, a silicon resin, a phenol resin, an urea resin, a melamine resin, an epoxy resin, or the like, alkali washing and surface roughening by an acid can be carried out prior to the surface treatment process. That is, the alkali washing and surface roughening by an acid of the core material may be carried out before carrying out the surface treatment process. Examples of an alkali that is used for the alkali washing include sodium hydroxide, sodium carbonate, sodium orthosilicate, sodium pyrophosphate, and the like. Meanwhile, examples of an acid that is used for surface roughening by an acid include mixed acids of one or two or more of sulfuric acid, nitric acid, phosphoric acid, chromic acid, chloric acid, acetic acid, hydrofluoric acid, and the like.

[0025] The surface treatment aqueous solution that is used in the surface treatment process is one or two or more of an aqueous solution of stannous salt, an aqueous solution of silver salt, and an aqueous solution of palladium salt as described above. In a case in which a combination of two or more aqueous solutions is used, a mixed aqueous solution of silver salt and palladium salt is preferably used.

[0026] Examples of the aqueous solution of stannous salt according to the surface treatment aqueous solution include aqueous solutions of halogenated tin, such as a stannous fluoride aqueous solution and stannous chloride aqueous solution, an aqueous solution of stannous sulfate, and the like. In addition, examples of the aqueous solution of silver salt according to the surface treatment aqueous solution include aqueous solutions of silver nitrate, silver acetate, and silver sulfate. Examples of the aqueous solution of palladium salt according to the surface treatment aqueous solution include an aqueous solution of palladium chloride.

[0027] The individual concentrations of the stannous salt, the silver salt, or the palladium salt in the surface treatment aqueous solution is preferably 0.1 g/L to 40 g/L, and particularly preferably 0.5 g/L to 30 g/L respectively.

[0028] In the surface treatment process, examples of the method for bringing the core material and the surface treatment aqueous solution into contact include a method in which the core material is added to and stirred into the surface treatment aqueous solution, but are not limited thereto.

[0029] The temperature of the surface treatment aqueous solution when the surface treatment process is

carried out is not particularly limited, but is preferably set to 0°C to 70°C, and particularly to 10°C to 50°C.

[0030] In the surface treatment process, the core material is brought into contact with the surface treatment aqueous solution, and then separated from the surface treatment aqueous solution, thereby producing the surface-treated core material. In this case, the core material may be brought into contact with only one kind of surface treatment aqueous solution, or may be brought into sequential contact with two or more kinds of surface treatment aqueous solutions so that the core material is brought into contact with a surface treatment aqueous solution, then separated from the surface treatment aqueous solution, furthermore, brought into contact with another surface treatment aqueous solution, and separated from the surface treatment aqueous solution.

[0031] The method for separating the surface treatment aqueous solution and the core material after carrying out the surface treatment includes Buchner filtration, centrifugation, and the like. The surface-treated core material separated from the surface treatment aqueous solution may be dried if necessary.

[0032] The surface-treated core material obtained in the above manner is subsequently subjected to the electrodeposition process of cuprous oxide by electrolysis

of (B). In the present process, the surface-treated core material is dispersed in an aqueous electrolytic solution, and cuprous oxide is electrodeposited on the surface of the surface-treated core material using metallic copper as the anode, thereby producing particles coated with cuprous oxide.

[0033] The aqueous electrolytic solution contains an electrolyte and an antioxidant. Examples of the electrolyte that can be used include chlorides, such as sodium chloride and potassium chloride. Meanwhile, examples of the antioxidant that can be used include glycerin, citric acid, saccharides, and the like.

[0034] The concentration of the chloride in the aqueous electrolytic solution is preferably 20 g/L to 200 g/L, and more preferably 20 g/L to 150 g/L when expressed by the concentration of chlorine ions. Meanwhile, the concentration of the antioxidant is preferably 0.3 g/L to 60 g/L, and more preferably 0.5 g/L to 40 g/L.

[0035] The amount of the surface-treated core material dispersed in the aqueous electrolytic solution is preferably 1 g/L to 80 g/L and more preferably 1 g/L to 60 g/L with respect to the aqueous electrolytic solution. When the amount is set in the above range, the efficiency of the electrodeposition can be increased while agglomeration between the core materials during the

electrodeposition is suppressed.

[0036] In the electrodeposition process, metallic copper is used as the anode as described above. An ordinary metallic copper plate may be used as the metallic copper. The metallic copper may have any purity of 99% or more. Meanwhile, a plate-shaped metallic copper or stainless steel can be used as the cathode.

[0037] In the electrodeposition process, the surface-treated core material is added to the aqueous electrolytic solution, the aqueous electrolytic solution is stirred, and an electrical current is made to flow in a state in which the surface-treated core is dispersed, thereby electrodepositing cuprous oxide on the surface of the surface-treated core material.

[0038] The electrodeposition temperature is preferably 10°C to 70°C. When the temperature is set in the above range, the electrodeposition rate can be increased while generation of gas due to the electrodeposition and degradation of the adhesion between the cuprous oxide and the core material due to the generation of gas are suppressed. In addition, the current density during the electrodeposition is preferably 1 A/dm² to 30 A/dm², and more preferably 1 A/dm² to 10 A/dm². When the current density is set within the above range, the electrodeposition can be efficiently carried out while the

generation of gas and the like are suppressed.

[0039] In the electrodeposition process, it is important to carry out the electrodeposition of the cuprous oxide while maintaining the pH of the aqueous electrolytic solution between 7 to 13, preferably between 8 to 12, and more preferably between 9 to 11 by monitoring the pH during the electrodeposition. Thereby, particles coated with cuprous oxide having an octahedral shape can be successfully generated. Since the electrodeposition gradually increases the pH of the aqueous electrolytic solution, the pH of the aqueous electrolytic solution is maintained in the above range by, for example, adding an acid to lower the pH. Examples of the acid that can be used for adjustment of the pH include chloric acid, sulfuric acid, nitric acid, bromic acid, and the like. Meanwhile, the pH of the aqueous electrolytic solution before starting the electrodeposition is preferably 2 to 12, and particularly 4 to 10.

[0040] The thickness of the cuprous oxide layer formed on the surface of the core material, that is, the amount of cuprous oxide coated can be adjusted by the electrodeposition duration. While being dependent on the specific use of the target particles coated with cuprous oxide, generally, the electrodeposition duration that is employed is preferably approximately 10 minutes to 4 hours

in a case in which the particles are used as a pigment for an antifouling coating material.

[0041] When the electrodeposition is completed in the above manner, the particles coated with cuprous oxide are separated from the aqueous electrolytic solution using means, such as Buchner filtration or centrifugation. Next, the particles are subjected to the water washing process of (C). Generally, repulp washing is used as the method for water-washing the particles coated with cuprous oxide. In a case in which repulp washing is carried out, the concentration of the particles coated with cuprous oxide in a mixed slurry of the particles coated with cuprous oxide and water is preferably 5% by mass to 20% by mass. A sufficient washing duration is 10 minutes to 60 minutes. Warm water of 10°C to 70°C can be used as the washing water.

[0042] In the water washing process, the particles coated with cuprous oxide are preferably washed with washing water containing an antioxidant since the cuprous oxide is prevented from being oxidized. Examples of the antioxidant that can be used include glycerin, saccharides, and the like. The concentration of the antioxidant in the washing water is preferably 0.3 g/L to 60 g/L, and particularly preferably 0.5 g/L to 40 g/L.

[0043] When the water washing is completed, the particles coated with cuprous oxide are separated from the

washing water, and dried. Target particles coated with cuprous oxide are obtained in the above manner.

[0044] When the particles coated with cuprous oxide are produced by the above method, since the throwing and adhesion of the cuprous oxide are improved, the adhesion of the cuprous oxide layer is improved, and pure cuprous oxide particles or agglomerates of particles coated with cuprous oxide can be extremely decreased.

[0045] The particles coated with cuprous oxide that are obtained in the above manner are particularly preferably used as, for example, a pigment for an antifouling coating material. The antifouling coating material is used to prevent aquatic organisms from attaching to ship bottoms, underwater structures, fishing nets, and the like. Specifically, when the particles coated with cuprous oxide are coated once or plural times on the surfaces of a variety of base materials, such as underwater structures, such as ships, fishing equipment (example: ropes, fishing nets, floats, and buoys), supply and exhaust openings in thermal power and nuclear power plants; anti-pollution dispersion films used in a variety of marine civil engineering works, such as seashore roads, underwater tunnels, seaport facilities, canals, and water channels; and the like, antifouling properties are exhibited.

[0046] Generally, the antifouling coating material contains an encapsulating polymer and a pigment, and the particles coated with cuprous oxide of the invention are used as the pigment. Encapsulating polymers that have thus far been used in the corresponding field can be used as the encapsulating polymer. Examples thereof include polymers including a component unit that is derived from a trialkylsilyl ester in a polymeric unsaturated carboxylic acid, such as trimethylsilyl (meth)acrylate, triethylsilyl (meth)acrylate, tripropylsilyl (meth)acrylate, tributylsilyl (meth)acrylate, dimethyl propylsilyl (meth)acrylate, monomethyl dipropylsilyl (meth)acrylate, and methyl ethyl propylsilyl (meth)acrylate; polymers containing a component unit of a metal compound of a polymeric unsaturated carboxylic acid, such as a component unit of a metal salt of hydroxyl (meth)acrylate; vinyl-based copolymers containing a polymeric unsaturated monomer having a polymeric unsaturated group and siloxane-bonded portions and another polymeric unsaturated monomer that can be copolymerized with the monomer in the molecules as copolymerization components, such as γ -methacryloyloxy-propylpolydimethylsiloxane; urethane resins, and the like. The pigment can be mixed in a range of 1 part by mass to 1000 parts by mass with respect to 100 parts by mass of the encapsulating polymer. In

addition, the antifouling coating material can also contain xylene, ethanol, isopropanol, or the like as an organic solvent in addition to the above components.

Examples

[0047] Hereinafter, the invention will be described in more detail using examples. However, the scope of the invention is not limited to the examples. "%" indicates "% by mass" unless otherwise stated.

[0048] [Example 1]

(1) Surface treatment process

Silica powder (mean particle diameter $D_{50} = 20 \mu\text{m}$) was dispersed as a core material in an aqueous solution of stannous fluoride (1 g/L), stirred, filtered, then washed with water, furthermore, dispersed in an aqueous solution of silver nitrate (1 g/L), stirred, filtered, then washed with water, and dried, thereby producing a surface-treated core material A1.

[0049] (2) Electrodeposition process and water washing process

Next, 10 g of the surface-treated core material A1 was added to 1 L of an aqueous electrolytic solution, electrodes were installed, and an electrical current was made to flow for 36 minutes under the following conditions while the solution was stirred using a magnetic stirrer, thereby electrodepositing cuprous oxide to the surface-

treated core material A1. The pH of the aqueous electrolytic solution was increased as the electrodeposition proceeded, but chloric acid (concentration: 2%) was appropriately added so as to maintain the pH of the aqueous solution in a range of 9 to 10. Next, the aqueous electrolytic solution was filtered, the filtered substance was washed with water, then dispersed in an aqueous solution of glycerin, then filtered, and dried, thereby producing 21 g of particles coated with cuprous oxide B1. The absolute specific gravity of the particles coated with cuprous oxide B1 was 3.1 g/cm^3 .

[0050] <Aqueous electrolytic solution>

Sodium chloride: 250 g/L (concentration of chlorine ions: 152 g/L)

Glycerin: 10 g/L

pH: 7

<Treatment conditions>

Current density: 7 A/dm^2

Temperature of the aqueous electrolytic solution:
40°C

Electrodes: copper plates for both anode and cathode

[0051] [Example 2]

(1) Surface treatment process

Fly ash (mean particle diameter $D_{50} = 41 \text{ }\mu\text{m}$) was

dispersed as a core material in an aqueous solution of silver nitrate (1 g/L), stirred, filtered, then washed with water, and dried, thereby producing a surface-treated core material A2.

[0052] (2) Electrodeposition process and water washing process

Next, 10 g of the surface-treated core material A2 was added to 1 L of an aqueous electrolytic solution, electrodes were installed, and an electrical current was made to flow for 18 minutes under the following conditions while the solution was stirred using a magnetic stirrer, thereby electrodepositing cuprous oxide to the surface-treated core material A2. The pH of the aqueous electrolytic solution was increased as the electrodeposition proceeded, but chloric acid (concentration: 2%) was appropriately added so as to maintain the pH of the aqueous solution in a range of 9 to 10. Next, the aqueous electrolytic solution was filtered, the filtered substance was washed with water, then dispersed in an aqueous solution of glycerin, then filtered, and dried, thereby producing 16 g of particles coated with cuprous oxide B2. The absolute specific gravity of the particles coated with cuprous oxide B2 was 1.2 g/cm³.

[0053] <Aqueous electrolytic solution>

Sodium chloride: 200 g/L (concentration of chlorine ions: 121 g/L)

Glycerin: 10 g/L

pH: 7

<Treatment conditions>

Current density: 7 A/dm²

Temperature of the aqueous electrolytic solution:
30°C

Electrodes: copper plates for both anode and cathode
[0054] [Example 3]

(1) Surface treatment process

Silica stone powder (mean particle diameter $D_{50} = 32$ μm) was dispersed as a core material in an aqueous solution of stannous fluoride (1 g/L), stirred, filtered, then washed with water, furthermore, dispersed in an aqueous solution of palladium chloride containing chloric acid (palladium chloride 0.2 g/L, chloric acid: 1 ml/L), stirred, filtered, then washed with water, and dried, thereby producing a surface-treated core material A3.

[0055] (2) Electrodeposition process and water washing process

Next, 10 g of the surface-treated core material A3 was added to 1 L of an aqueous electrolytic solution, electrodes were installed, and an electrical current was made to flow for 25 minutes under the following conditions

while the solution was stirred using a magnetic stirrer, thereby electrodepositing cuprous oxide to the surface-treated core material A3. The pH of the aqueous electrolytic solution was increased as the electrodeposition proceeded, but chloric acid (concentration: 2%) was appropriately added so as to maintain the pH of the aqueous solution in a range of 9 to 10. Next, the aqueous electrolytic solution was filtered, the filtered substance was washed with water, then dispersed in an aqueous solution of glycerin, then filtered, and dried, thereby producing 16 g of particles coated with cuprous oxide B3. The absolute specific gravity of the particles coated with cuprous oxide B3 was 3.2 g/cm^3 .

<Aqueous electrolytic solution>

Sodium chloride: 200 g/L (concentration of chlorine ions: 121 g/L)

Glycerin: 10 g/L

pH: 7

<Treatment conditions>

Current density: 5 A/dm^2

Temperature of the aqueous electrolytic solution:
50°C

Electrodes: copper plates for both anode and cathode

[0056] [Example 4]

(1) Surface treatment process

Polyethylene powder (mean particle diameter $D_{50} = 20 \mu\text{m}$) was washed as a core material with an aqueous solution of sodium hydroxide, subsequently, roughened on the surfaces with a mixed acid of chromic acid, nitric acid, and phosphoric acid, then dispersed in an aqueous solution of stannous fluoride (1 g/L), stirred, filtered, then washed with water, furthermore, dispersed in an aqueous solution of silver nitrate (1 g/L), stirred, filtered, then washed with water, and dried, thereby producing a surface-treated core material A4.

[0057] (2) Electrodeposition process and water washing process

Next, 10 g of the surface-treated core material A4 was added to 1 L of an aqueous electrolytic solution, electrodes were installed, and an electrical current was made to flow for 15 minutes under the following conditions while the solution was stirred using a magnetic stirrer, thereby electrodepositing cuprous oxide to the surface-treated core material A4. The pH of the aqueous electrolytic solution was increased as the electrodeposition proceeded, but chloric acid (concentration: 2%) was appropriately added so as to maintain the pH of the aqueous solution in a range of 9 to 10. Next, the aqueous electrolytic solution was filtered,

the filtered substance was washed with water, then dispersed in an aqueous solution of glycerin, then filtered, and dried, thereby producing 14.6 g of particles coated with cuprous oxide B4. The absolute specific gravity of the particles coated with cuprous oxide B4 was 1.2 g/cm^3 .

<Aqueous electrolytic solution>

Sodium chloride: 250 g/L (concentration of chlorine ions: 152 g/L)

Glycerin: 10 g/L

pH: 7

<Treatment conditions>

Current density: 7 A/dm^2

Temperature of the aqueous electrolytic solution:
 30°C

Electrodes: copper plates for both anode and cathode

[0058] [Example 5]

(1) Surface treatment process

Fused silica powder (non-crystalline mean particle diameter $D_{50} = 20 \text{ }\mu\text{m}$) was alkali-washed as a core material with an aqueous solution of sodium hydroxide, roughened on the surfaces with a hydrofluoric acid, then dispersed in an aqueous solution of stannous fluoride (1 g/L), stirred, filtered, then washed with water, furthermore, dispersed in an aqueous solution of silver nitrate (1 g/L), stirred,

filtered, then washed with water, and dried, thereby producing a surface-treated core material A5.

[0059] (2) Electrodeposition process and water washing process

Next, 10 g of the surface-treated core material A5 was added to 1 L of an aqueous electrolytic solution, electrodes were installed, and an electrical current was made to flow for 15 minutes under the following conditions while the solution was stirred using a magnetic stirrer, thereby electrodepositing cuprous oxide to the surface-treated core material A5. The pH of the aqueous electrolytic solution was increased as the electrodeposition proceeded, but chloric acid (concentration: 2%) was appropriately added so as to maintain the pH of the aqueous solution in a range of 9 to 10. Next, the aqueous electrolytic solution was filtered, the filtered substance was washed with water, then dispersed in an aqueous solution of glycerin, then filtered, and dried, thereby producing 14.3 g of particles coated with cuprous oxide B5. The absolute specific gravity of the particles coated with cuprous oxide B5 was 2.8 g/cm^3 .

[0060] <Aqueous electrolytic solution>

Sodium chloride: 250 g/L (concentration of chlorine ions: 152 g/L)

Glycerin: 10 g/L

pH: 7

<Treatment conditions>

Current density: 7 A/dm²

Temperature of the aqueous electrolytic solution:
30°C

Electrodes: copper plates for both anode and cathode
[0061] [Comparative Example 1]

Particles coated with cuprous oxide b1 were obtained by the same method as in Example 1 except that the pH of the aqueous electrolytic solution was not adjusted in the electrodeposition process. The pH of the aqueous electrolytic solution was increased as the electrodeposition proceeded, and exceeded 13. The absolute specific gravity of the obtained particles coated with cuprous oxide b1 was 2.6 g/cm³.

[0062] [Comparative Example 2]

Particles coated with cuprous oxide b2 were obtained by the same method as in Example 2 except that the pH of the aqueous electrolytic solution was not adjusted in the electrodeposition process. The pH of the aqueous electrolytic solution was increased as the electrodeposition proceeded, and exceeded 13. The absolute specific gravity of the obtained particles coated with cuprous oxide b2 was 1.1 g/cm³.

[0063] [Comparative Example 3]

Particles coated with cuprous oxide b3 were obtained by the same method as in Example 3 except that the pH of the aqueous electrolytic solution was not adjusted in the electrodeposition process. The pH of the aqueous electrolytic solution was increased as the electrodeposition proceeded, and exceeded 13. The absolute specific gravity of the obtained particles coated with cuprous oxide b3 was 3.1 g/cm^3 .

[0064] [Comparative Example 4]

Particles coated with cuprous oxide b4 were obtained by the same method as in Example 4 except that the pH of the aqueous electrolytic solution was not adjusted in the electrodeposition process. The pH of the aqueous electrolytic solution was increased as the electrodeposition proceeded, and exceeded 13. The absolute specific gravity of the obtained particles coated with cuprous oxide b4 was 1.1 g/cm^3 .

[0065] [Comparative Example 5]

Particles coated with cuprous oxide b5 were obtained by the same method as in Example 5 except that the pH of the aqueous electrolytic solution was not adjusted in the electrodeposition process. The pH of the aqueous electrolytic solution was increased as the electrodeposition proceeded, and exceeded 13. The

absolute specific gravity of the obtained particles coated with cuprous oxide b5 was 2.7 g/cm^3 .

[0066] [Evaluation]

A scanning electron microscope image of the particles coated with cuprous oxide, which were obtained in Example 1, is shown in Fig. 1, and a scanning electron microscope image of the particles coated with cuprous oxide, which were obtained in Comparative Example 1, is shown in Fig. 2. As is clear from Fig. 1, it is found that a dense layer configured with an assembly of octahedral cuprous oxide particles completely coats the surface of the core material in the particles coated with cuprous oxide which were obtained in Example 1. 90 or more out of 100 cuprous oxide particles, which were observation targets, had an octahedral shape. In contrast to the above, as is clear from Fig. 2, a layer configured with an assembly of amorphous cuprous oxide particles coats the surface of the core material in the particles coated with cuprous oxide which were obtained in Comparative Example 1. In addition, although not shown, it was confirmed that, similarly to the particles coated with cuprous oxide of Example 1, a dense layer configured with an assembly of octahedral cuprous oxide particles completely coats the surface of the core material in the particles coated with cuprous oxide which were obtained in

Examples 2 to 5. In these examples, 90 or more out of 100 cuprous oxide particles, which were observation targets, had an octahedral shape. The cuprous oxide particles, which were obtained in Comparative Examples 2 to 5, had an amorphous shape.

[0067] The mass ratio of the core material to the cuprous oxide (core material/cuprous oxide) was 50/50 in Example 1, but 76/24 in Comparative Example 1, which shows that a small amount of the cuprous oxide was attached in Comparative Example 1. The above fact is considered to cause the absolute specific gravity of the particles coated with cuprous oxide in Comparative Example 1 to be lower than that of the particles coated with cuprous oxide in Example 1. The same measurements were carried out on the particles coated with cuprous oxide of Examples 2 to 5 and Comparative Examples 2 to 5. The results are shown in the following Table 1.

[0068] In addition, as a result of a measurement by the above method, the particle diameter of the octahedral particles in the cuprous oxide particle layer in Example 1 was 0.7 μm . The particle diameter of the cuprous oxide particles in Comparative Example 1 could not be measured since the particles had an amorphous shape. The same measurements were carried out on the particles coated with cuprous oxide of Examples 2 to 5 and Comparative Examples

2 to 5. The results are shown in the following Table 1.

[0069] Furthermore, the adhesion of the cuprous oxide layers in the particles coated with cuprous oxide, which were obtained in Examples 1 to 5 and Comparative Examples 1 to 5, was evaluated by the following method.

(1) 2.2 g of the particles coated with cuprous oxide, 90 g of 1 mmφ zirconia beads, and 10 ml of toluene were fed into a vessel.

(2) The mixture is stirred for 10 minutes in a stirring apparatus.

(3) After stirring, the particles coated with cuprous oxide and the zirconia beads were classified using a sieve.

(4) The classified particles coated with cuprous oxide were filtered using a funnel.

(5) The particles coated with cuprous oxide were naturally dried.

(6) The separation state of the cuprous oxide particles from the core material was observed using a scanning electron microscope (with a magnification of 500 times, the magnification was selected so that about 50 particles were present in a single view).

(7) 10 random views were observed, the number of separated particles in each view was counted, and the average value was observed.

The numbers of separated particles, which were measured by the above method, are shown in the following Table 1. A smaller number of the separated particles means a better adhesion of the cuprous oxide layer.

[0070] Furthermore, antifouling coating materials of the following formulation were produced using the particles coated with cuprous oxide which were obtained in Examples 1 to 5 and Comparative Examples 1 to 5 as a pigment. The viscosities of the antifouling coating materials were measured using a Stormer viscometer immediately after the production and after 36 days of storage at 50°C. The results are shown in the following Table 1.

[0071] [Formulation of the antifouling coating material]

- Powder coated with cuprous oxide 10%
- Xylene 25%
- Methanol 5%
- Xylene solution of a 40% urethane resin 60%

[0072]

[Table 1]

	Particle type	Mass ratio of core material/cuprous oxide	Particle diameter of cuprous oxide particles (μm)	Adhesion (number of separated particles/particles)	Coating material stability (viscosity Ku)	
					Immediately after production	After 36 days of storage
Example 1	B1	50/50	0.7	1	79	81
Example 2	B2	62/38	0.7	1	78	80
Example 3	B3	62/38	0.9	1	77	80
Example 4	B4	68/32	0.7	1	77	79
Example 5	B5	70/30	0.6	1	79	80
Comparative Example 1	b1	76/24	Not measurable	20	77	101
Comparative Example 2	b2	71/29	Not measurable	22	78	102
Comparative Example 3	b3	54/46	Not measurable	22	79	100
Comparative Example 4	b4	78/22	Not measurable	24	80	103
Comparative Example 5	b5	71/29	Not measurable	21	79	101

[0073] As a result, it was found that, in the particles coated with cuprous oxide which were obtained in Examples 1 to 5, the number of separated particles was 1 or less, and the adhesion of the cuprous oxide layer is excellent since the number of separated particles was small compared with the particles coated with cuprous oxide which were obtained in Comparative Examples 1 to 5. In addition, it was found that an increase in the viscosities of the antifouling coating materials including the particles coated with cuprous oxide, which were obtained in Examples 1 to 5, was suppressed from immediately after the production to 36 days of storage, and the coating material stability is excellent compared with the antifouling materials including the particles coated with cuprous oxide, which were obtained in Comparative Examples 1 to 5.

Claims

[Claim 1]

Particles coated with cuprous oxide having a surface of a core material coated with a cuprous oxide layer,

wherein the cuprous oxide layer completely coats the surface of the core material, and is configured with an assembly of octahedral cuprous oxide particles.

[Claim 2]

The particles coated with cuprous oxide according to Claim 1, wherein D_{50} of the core material is 0.5 μm to 100 μm .

[Claim 3]

The particles coated with cuprous oxide according to Claim 1 or 2, wherein the core material is a silicic acid-containing inorganic compound.

[Claim 4]

The particles coated with cuprous oxide according to Claim 1 or 2, wherein the core material is an alkali earth metal compound.

[Claim 5]

The particles coated with cuprous oxide according to Claim 1 or 2, wherein the core material is an organic compound.

[Claim 6]

The particles coated with cuprous oxide according to any one of Claims 1 to 5, which are used as a pigment for an antifouling coating material.

[Claim 7]

An antifouling coating material, comprising:
the particles coated with cuprous oxide according to any one of Claims 1 to 6; and
an encapsulating polymer.

[Claim 8]

A method for producing the particles coated with cuprous oxide according to Claim 1, comprising:

a surface treatment process in which a core material is brought into contact with one or two or more surface treatment aqueous solutions of an aqueous solution of stannous salt, an aqueous solution of silver salt, and an aqueous solution of palladium salt, thereby producing a surface-treated core material; and

an electrodeposition process in which the surface-treated core material is dispersed in an aqueous electrolytic solution containing an electrolyte and an antioxidant, and electrolysis is carried out using metallic copper as the anode so that the cuprous oxide is electrodeposited on the surface of the surface-treated core material, thereby producing the particles coated with cuprous oxide,

wherein electrodeposition of cuprous oxide is carried out while maintaining the pH of the aqueous electrolytic solution at between 7 to 13 in the electrodeposition process.