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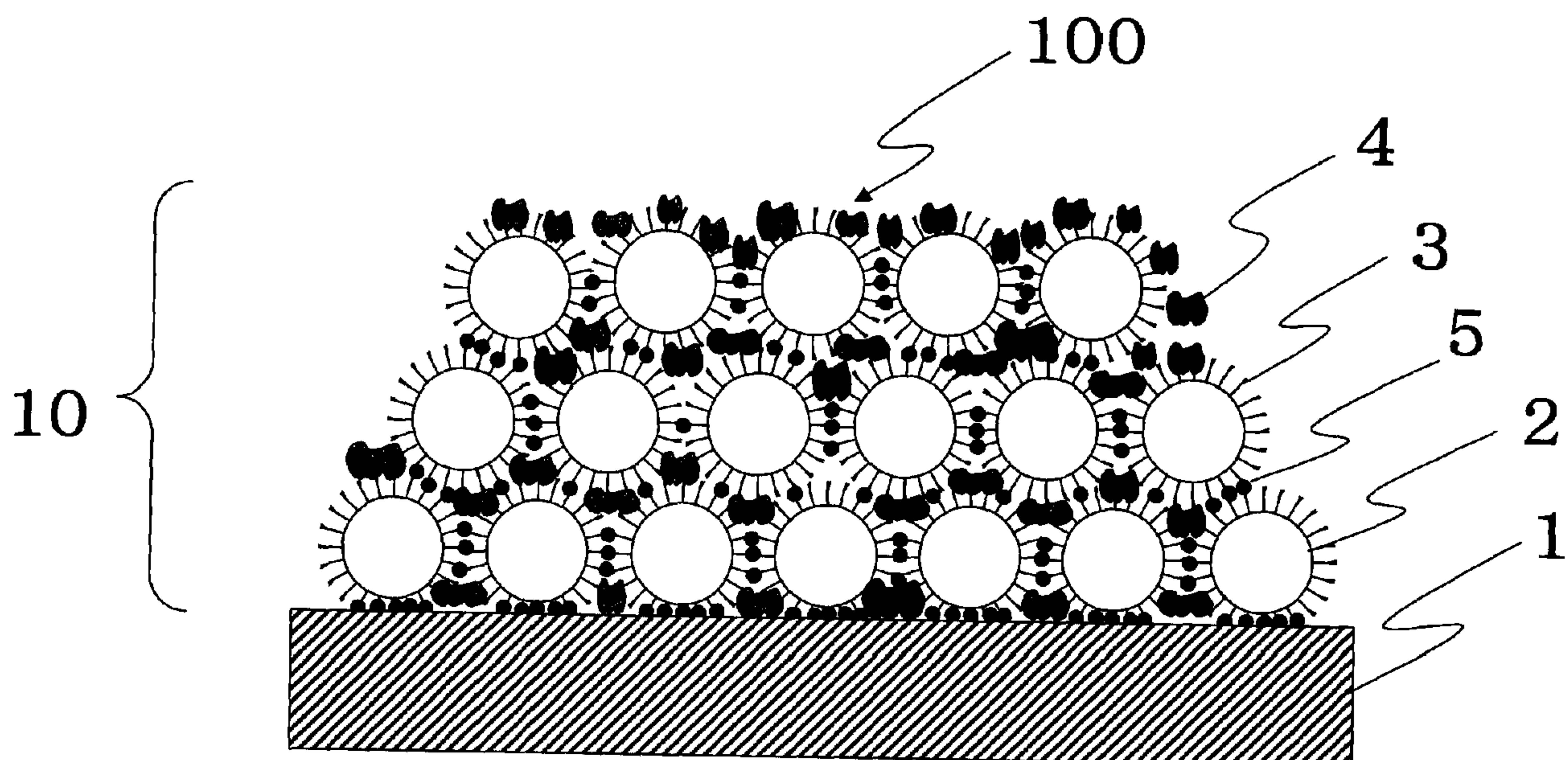
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(54) Titre : MATERIAU COMPOSITE PRESENTANT UNE PROPRIETE ANTI-SALISSURE
(54) Title: COMPOSITE MATERIAL HAVING ANTIFOULING PROPERTY



(57) Abrégé/Abstract:

Disclosed is a composite material exhibiting excellent antidust property and antifouling property, while having high durability. Specifically disclosed is a composite material wherein an inorganic fine particle layer is formed on the surface of a base through a chemical bond. The inorganic fine particle layer contains inorganic fine particles, each of which is coated with a silane monomer having an unsaturated bond, and 0.1-40% by mass of a binder component relative to the fine particles.



ABSTRACT

[Abstract]

[Object] To provide a dustproof, antifouling, and highly durable composite material.

10 [Solving Means] An inorganic fine particle layer containing inorganic fine particles and a binder component is formed on a surface of a substrate by chemical bonding. The inorganic fine particles are coated with silane monomer each having an unsaturated bond. The content of the binder
15 component is in the range of 0.1% by mass to 40% by mass to the content of the inorganic fine particles.

5

DESCRIPTION

ANTIFOULING COMPOSITE MATERIAL

Technical Field

The present invention relates to an antifouling
10 composite material on which suspended particulate matter
composed of fine particles, such as soil dust, sand dust, or
pollen, or a liquid substance, such as soy sauce, coffee, or
juice, hardly deposits or from which suspended particulate
matter or a liquid substance is easily removable even when
15 the suspended particulate matter or the liquid substance
deposits thereon.

Background Art

In recent years, allergic diseases caused by suspended
20 matter, such as cedar pollen, dead mites, fungal spores, or
house dust, have become a major social problem. The
suspended particulate matter deposits easily on clothes or
air conditioner filters. Thus, the suspended particulate
matter deposited on the clothes and the filters may, in turn,
25 detach therefrom and pollute an indoor environment.
Furthermore, the suspended particulate matter decreases the
sucking force or the ventilation capacity of filters in
cleaners or ventilating fans.

The suspended particulate matter tends to deposit on
30 fibrous structures having a complicated structure of rough
surface and voids. Furthermore, because cedar pollen has
projections, cedar pollen deposits easily on fibrous

5 structures. Thus, cedar pollen can easily enter a house.
Filters of air conditioners and their cases, ventilating
fans, or cleaners composed of molded-plastic members become
charged by friction. Thus, the suspended particulate matter
is well known to deposit on them and become a major cause of
10 contamination and deterioration in product functions.

Furthermore, the deposition of a liquid substance, such
as soy sauce, coffee, or juice, to clothes, wallpapers, or
carpets may cause stains or generate molds, which may in
turn generate fungal spores. In addition, after the liquid
15 substance dries, components contained in the liquid
substance may be suspended in the air, thereby polluting an
indoor environment.

As an antifouling (hereinafter also referred to as
dustproof) technique for preventing the deposition of "solid
20 dirt," such as motes or dust, fibers on which cedar pollen
hardly deposits or treatments that prevent the deposition of
cedar pollen have recently been proposed. Examples of the
fibers include textiles treated with a processing agent that
contains a nonionic antistatic agent, silica sol containing
25 colloidal silica modified with aluminosilicate, and an
aqueous polyethylene emulsion (see, for example, Patent
Document 1); cellulose-based fibers on which alumina fine
particles having a size of 1.0 μm or less are deposited or
cellulose-based fibers impregnated with the alumina fine
30 particles (see, for example, Patent Document 2); and fibrous
structures treated with colloidal silica and a processing
liquid containing a glyoxal-based resin or a silicone resin

5 compound (see, for example, Patent Document 3).

Treatment of clothes, wallpapers, or carpets with water-repellents is generally performed as an antifouling technique for preventing the deposition of "liquid stain" such as "soy sauce, coffee, juice, oil, dirty water, or
10 blood" as well as "solid dirt" such as motes or dust. Examples of the water-repellents include aqueous solutions that contain an acrylate or a methacrylate each having a fluoroalkyl group and an alkoxysilane coupling agent (see, for example, Patent Document 4); processing liquids that
15 contain an alkoxysilane and an alkyl-modified silicone oil dispersed in an organic solvent (see, for example, Patent Document 5); and compositions that include a phosphorus acid compound having a perfluoroalkyl group and a thermoplastic resin or a thermosetting resin (see, for example, Patent
20 Document 6). These compositions are applied to the surface of fibers, such as clothing or carpets, to provide antifouling characteristics.

[Patent Document 1] Japanese Unexamined Patent Application Publication No. 2004-270039

25 [Patent Document 2] Japanese Unexamined Patent Application Publication No. 2005-163236

[Patent Document 3] Japanese Unexamined Patent Application Publication No. 2004-003046

[Patent Document 4] Japanese Unexamined Patent
30 Application Publication No. 9-241622

[Patent Document 5] Japanese Unexamined Patent Application Publication No. 11-092714

5 [Patent Document 6] Japanese Unexamined Patent
Application Publication No. 2003-096311

Disclosure of Invention

Problems to be Solved by the Invention

10 However, the textiles and the fibrous structures
described above have the following problems.

 For example, in textiles described in Patent Document 1,
an antideposition function is imparted by a nonionic
antistatic agent, that is, a detergent. The detergent may
15 be washed away by washing or rain. The antideposition
effect on pollen is difficult to maintain for a long period
of time. Furthermore, in fiber products described in Patent
Document 2, alumina fine particles are immobilized on
cellulose-based fibers. This disadvantageously limits the
20 type of fiber material. In fibrous structures described in
Patent Document 3, colloidal silica is immobilized on the
fibers with a glyoxal-based resin binder. The fibrous
structures may become charged easily because of some
component in the resin binder. Suspended particulate matter
25 can therefore easily deposit on the fibrous structures, and
the deposited suspended particulate matter is difficult to
remove.

 In Patent Documents 4 and 5, because a water-repellent
compound is washed away by washing or rain, the antifouling
30 property is difficult to maintain for a long period of time.
In Patent Document 6, a binder of a thermoplastic resin or a
thermosetting resin becomes charged easily. Hence, while

5 the antifouling effect is achieved, the dustproof effect is not observed. Furthermore, deposited suspended particulate matter is difficult to remove.

To solve these known problems, the present inventors perfected the present invention by discovering that silane
10 monomer-coated inorganic fine particles immobilized on a substrate to prevent triboelectrification can provide an excellent antifouling composite material. The inorganic fine particles can prevent the deposition of suspended particulate matter or liquid substances. Even when
15 suspended particulate matter or liquid substances deposit on the composite material, the suspended particulate matter or the liquid substances can easily be removed.

Means for Solving the Problems

20 A first aspect of the present invention provides an antifouling composite material that includes a substrate and an inorganic fine particle layer disposed on a surface of the substrate, the inorganic fine particle layer including inorganic fine particles and a binder component, the
25 inorganic fine particles being coated with silane monomer each having an unsaturated bond, wherein the content of the binder component in the inorganic fine particle layer is in the range of 0.1% by mass to 40% by mass to the content of the inorganic fine particles. According to the present
30 invention, a binder component enters gaps between the silane monomer-coated inorganic fine particles and combines silane monomer that do not participate in the bonding between the

5 fine particles. This increases the strength of the bonding between the fine particles, thus providing an antifouling composite material having high strength and of much practical use.

10 In the antifouling composite material according to the first aspect of the present invention, the binder component may contain a water-repellent substance or an oil-repellent substance. According to the present invention, the water-repellent substance or the oil-repellent substance is oriented in gaps between the silane monomer-coated inorganic
15 fine particles and on the surface of the inorganic fine particle layer at any intervals, thus efficiently exhibiting water repellency or oil repellency at low concentration. The presence of a very small volume of space through which electrons can pass makes triboelectrification difficult,
20 thus preventing the deposition of suspended particulate matter, such as soil dust or pollen, or a liquid substance, such as soy sauce, coffee, or juice.

Furthermore, in the antifouling composite material according to the first aspect of the present invention, the
25 binder component may contain a fluorinated compound. According to the present invention, the binder component composed of the fluorinated compound is regularly oriented on the surface of the fine particles at any intervals, thus efficiently exhibiting water repellency or oil repellency at
30 low concentration. The presence of a very small volume of space through which electrons can pass makes triboelectrification difficult, thus preventing the

5 deposition of suspended particulate matter, such as soil
dust or pollen, or a liquid substance, such as soy sauce,
coffee, or juice.

Furthermore, in the antifouling composite material
according to the first aspect of the present invention, the
10 unsaturated bonds of the silane monomer disposed on the
inorganic fine particles in the inorganic fine particle
layer may form chemical bonds, thereby forming the inorganic
fine particle layer, and the unsaturated bonds of the silane
monomer disposed on the inorganic fine particles in the
15 inorganic fine particle layer may be bound to the surface of
the substrate through the chemical bonds, thereby fixing the
inorganic fine particle layer onto the substrate.

In the antifouling composite material according to the
fourth aspect of the present invention, the chemical bonds
20 may be formed by graft polymerization.

In the antifouling composite material according to the
fifth aspect of the present invention, the graft
polymerization may be radiation graft polymerization.

In the antifouling composite material according to the
25 first aspect of the present invention, at least the surface
of the substrate may be formed of a resin.

In the antifouling composite material according to the
first aspect of the present invention, the substrate may be
formed of a resin.

30 In the antifouling composite material according to the
first aspect of the present invention, the substrate may
have a fibrous structure.

5 The present invention also provides clothing formed of
an antifouling composite material according to the eighth
aspect of the present invention.

 The present invention also provides a filter formed of
an antifouling composite material according to the eighth
10 aspect of the present invention.

 The present invention also provides a mosquito net
formed of an antifouling composite material according to the
eighth aspect of the present invention.

 The present invention also provides a building material
15 formed of an antifouling composite material according to the
seventh aspect of the present invention.

 The present invention also provides an interior
material formed of an antifouling composite material
according to the eighth aspect of the present invention.
20

Brief Description of the Drawings

 Fig. 1 is a fragmentary enlarged schematic view of an
antifouling composite material according to an embodiment of
the present invention.

25 Fig. 2A is one of comparative photographs of
antifouling clothing according to an embodiment of the
present invention and untreated clothing, and shows a
photograph of the antifouling clothing.

 Fig. 2B is one of comparative photographs of
30 antifouling clothing according to an embodiment of the
present invention and untreated clothing, and shows a
photograph of the untreated clothing.

5 Fig. 3A is one of comparative photographs of an antifouling filter according to an embodiment of the present invention and an untreated filter, and shows a photograph of the antifouling filter.

10 Fig. 3B is one of comparative photographs of an antifouling filter according to an embodiment of the present invention and an untreated filter, and shows a photograph of the untreated filter.

15 Fig. 4A is one of comparative photographs of an antifouling mosquito net according to an embodiment of the present invention and an untreated mosquito net, and shows a photograph of the antifouling mosquito net.

20 Fig. 4B is one of comparative photographs of an antifouling mosquito net according to an embodiment of the present invention and an untreated mosquito net, and shows a photograph of the untreated mosquito net.

25 Fig. 5A is one of comparative photographs of an antifouling building material according to an embodiment of the present invention and an untreated building material, and shows a photograph of the antifouling building material.

30 Fig. 5B is one of comparative photographs of an antifouling building material according to an embodiment of the present invention and an untreated building material, and shows a photograph of the untreated building material.

30 Fig. 6A is one of comparative photographs of an antifouling interior material according to an embodiment of the present invention and an untreated interior material, and shows a photograph of the antifouling interior material.

5 Fig. 6B is one of comparative photographs of an antifouling interior material according to an embodiment of the present invention and an untreated interior material, and shows a photograph of the untreated interior material.

10 Reference Numerals

- 100 antifouling composite material
- 1 substrate
- 2 inorganic fine particle
- 3 silane monomer
- 15 4 binder component
- 5 chemical bond
- 10 10 inorganic fine particle layer

Best Mode for Carrying Out the Invention

20 An antifouling composite material according to an embodiment of the present invention will now be described in detail.

 Fig. 1 is a fragmentary enlarged cross-sectional view of an antifouling composite material 100 according to an
25 embodiment of the present invention. The antifouling composite material 100 according to the present embodiment consists of an inorganic fine particle layer 10 fixed on a substrate 1. The inorganic fine particle layer 10 includes inorganic fine particles 2 and a binder component 4.

30 In Fig. 1, for the purpose of clarifying an embodiment of the present invention, while the inorganic fine particle layer 10 contains one type of fine particles, the inorganic

5 fine particle layer 10 may contain two or more types of fine particles. Furthermore, the inorganic fine particle layer 10 may include a fine particle monolayer or a fine particle multilayer.

10 The surface of the inorganic fine particles 2 according to the present embodiment is bound to outwardly oriented silane monomer 3 having an unsaturated bond. The unsaturated bonds face outward from the surface of the inorganic fine particles 2. The surface of the inorganic fine particles 2 is coated by the silane monomer 3. A 15 hydrophilic silanol terminal group of the silane monomer 3 at the one end is attracted to the hydrophilic surface of the inorganic fine particles 2. A hydrophobic unsaturated bond of the silane monomer 3 at the other end is located away from the surface of the inorganic fine particles 2. 20 The silanol group of the silane monomer 3 is bound to the surface of the inorganic fine particles 2 by dehydration condensation. Thus, the silane monomer 3 is oriented with the unsaturated bond facing outward.

For example, in a specific treatment, the silane 25 monomer 3 is added to a solution containing the inorganic fine particles 2 dispersed in an organic solvent and is pulverized into fine particles. The dispersion solution is subjected to solid-liquid separation to collect the inorganic fine particles 2. The inorganic fine particles 2 30 are heated at a temperature in the range of 100°C to 180°C to combine the silane monomer 3 with the inorganic fine particles 2. Alternatively, for example, the silane monomer

5 3 is added to a solution containing the inorganic fine
particles 2 dispersed in an organic solvent, and are
pulverized into fine particles. The dispersion solution is
then transferred into a flask equipped with a condenser tube
and is heated in an oil bath to combine the silane monomer 3
10 to the surface of the inorganic fine particles 2.

The amount of silane monomer 3 introduced onto the
surface of the inorganic fine particles 2 by condensation
reaction may be such that the silane monomer 3 covers 0.5%
to 100% of the surface of the inorganic fine particles 2.

15 The diameters of the inorganic fine particles and other
fine particles in the materials described above are not
limited, provided that these fine particles are formed by a
method according to the present embodiment. However, the
average particle size of the inorganic fine particles is
20 preferably 300 nm or less to appropriately perform graft
polymerization described below. Furthermore, stronger
bonding between the inorganic fine particles and the
substrate 1 can be achieved at an average particle size of
100 nm or less. Hence, this range is more preferred in
25 terms of durability.

The material of the substrate 1 for use in the
antifouling composite material 100 according to the present
embodiment may be any material that can form chemical bonds
5 with the silane monomer 3 having an unsaturated bond.
30 Examples of such a material include resins, synthetic fibers,
and natural fibers. At least a surface of the substrate 1
for use in the antifouling composite material 100 according

5 to the present embodiment is formed of a resin.

The surface of the substrate 1 or the entire substrate 1 may be formed of a synthetic resin or a natural resin. Examples of the synthetic resin and the natural resin include thermoplastic resins, such as polyethylene resins, polypropylene resins, polystyrene resins, ABS resins, AS resins, EVA resins, polymethylpentene resins, polyvinyl chloride resins, polyvinylidene chloride resins, polymethyl acrylate resins, polyvinyl acetate resins, polyamide resins, polyimide resins, polycarbonate resins, polyethylene terephthalate resins, polybutylene terephthalate resins, polyacetal resins, polyacrylate resins, polysulfone resins, polyvinylidene fluoride resins, Vectran (registered trademark), and PTFE; biodegradable resins, such as polylactic acid resins, polyhydroxybutyrate resins, modified starch resins, polycaprolactone resins, polybutylene succinate resins, polybutylene adipate terephthalate resins, polybutylene succinate terephthalate resins, and polyethylene succinate resins; thermosetting resins, such as phenolic resins, urea resins, melamine resins, unsaturated polyester resins, diallyl phthalate resins, epoxy resins, epoxy acrylate resins, silicon resins, acrylic polyurethane resins, and urethane resins; elastomers, such as silicone resins, polystyrene elastomers, polyethylene elastomers, polypropylene elastomers, and polyurethane elastomers; and natural resins such as Japanese lacquer.

The resin forming the substrate 1 according to the present embodiment may have various shapes and sizes

5 depending on the purpose of the usage and may be, but not limited to, a plate, a film, a fibrous structure formed of a fibrous material, including fabric, knit fabric, or nonwoven fabric, a roll, a web, or a honeycomb.

When the major portion of the substrate 1 is formed of
10 a metallic material, such as aluminum, magnesium, or iron, or an inorganic material, such as glass or ceramic, the resin forming the substrate 1 may be layered on the metallic material or the inorganic material. The resin forming the substrate 1 may be formed as a thin film on the metallic
15 material or the inorganic material by coating, such as spray coating, dip coating, or electrostatic coating, or printing, such as screen printing or offset printing.

Furthermore, the resin forming the substrate 1 may be colored with a pigment or a dye. The resin forming the
20 substrate 1 may contain an inorganic material, such as silica, alumina, diatomaceous earth, or mica.

The substrate 1 may be formed of synthetic resin fiber (synthetic fiber or chemical fiber). Examples of the synthetic fiber forming the substrate 1 include polyester
25 fiber, polyamide fiber, polyvinyl alcohol fiber, acrylic fiber, polyvinyl chloride fiber, polyvinylidene chloride fiber, polyolefin fiber, polycarbonate fiber, fluorocarbon fiber, polyurea fiber, elastomer fiber, Vecry (registered trademark), and composite fiber of a material constituting
30 these fibers and the resin material described above.

As described above, since at least a surface of the substrate 1 according to the present embodiment is formed of

5 a resin, when the material of the substrate 1 is fiber other than synthetic resins, the fiber may be coated with the resin by a coating method described above to form a thin film of the resin on the fiber. Thus, the material of the substrate 1 may be formed of natural fiber, such as cotton, 10 hemp, or silk, or a Japanese paper made from natural fiber.

The inorganic fine particles 2 for use in the antifouling composite material 100 according to the present embodiment may be composed of a nonmetal oxide, a metal oxide, or a complex metal oxide. The inorganic fine 15 particles 2 may be crystal or amorphous. Examples of the nonmetal oxide include silicon oxide. Examples of the metal oxide include magnesium oxide, barium oxide, barium peroxide, aluminum oxide, tin oxide, titanium oxide, zinc oxide, titanium peroxide, zirconium oxide, iron oxide, iron 20 hydroxide, tungsten oxide, bismuth oxide, and indium oxide. Examples of the complex metal oxide include barium titanium oxide, cobalt aluminum oxide, lead zirconate, lead niobate, $\text{TiO}_2\text{-WO}_3$, $\text{AlO}_3\text{-SiO}_2$, $\text{WO}_3\text{-ZrO}_2$, and $\text{WO}_3\text{-SnO}_2$.

The surface of the inorganic fine particles 2 may have 25 catalyst fine particles of a noble metal, such as Au, Pt, Pd, Rh, and/or Ru, or catalyst fine particles of oxide fine particles composed of Ni, Co, Mo, W, Mn, Cu, V, and/or Se.

A fine particle layer formed of one type of inorganic fine particles 2 may be overlaid with another fine particle 30 layer formed of one or more types of inorganic fine particles. The inorganic fine particles 2 may form a fine particle layer in combination with a photocatalytic material,

5 an antimicrobial material, a negative ion-releasing material,
a material emitting far-infrared rays, an antireflective
material, or a material absorbing near-infrared rays.

When photocatalyst fine particles are used as the
inorganic fine particles 2 or when the fine particle layer
10 contains photocatalyst fine particles, the hydrophilicity of
the photocatalyst fine particles provides another effect of
allowing deposited contaminants to be washed away easily,
and photolysis of an organic substance by the photocatalyst
fine particles provides still another effect of decomposing
15 and eliminating deposited contaminants. Excellent dustproof
and antifouling effects can therefore be achieved on not
only suspended particulate matter, but also liquid, tarry,
misty, fummy, or gaseous pollutants or adsorption substances.

The term "photocatalyst particle" used herein means a
20 particle that exhibits a photocatalytic function when
irradiated with light having a wavelength corresponding to
the energy of at least its band gap. The photocatalyst
particle may be composed of a known metallic compound
semiconductor, such as titanium oxide, zinc oxide, tungsten
25 oxide, iron oxide, strontium titanate, cadmium sulfide, or
cadmium selenide, alone or in combination. Preferably, the
photocatalyst particle is composed of titanium oxide because
of its high transparency, high durability, and harmlessness.

The crystal structure of titanium oxide may be rutile,
30 anatase, brookite, or even amorphous. The photocatalyst
particle may be composed of $\text{TiO}_2\text{-XNX}$, in which part of
oxygen atoms of titanium oxide is replaced with anionic

5 nitrogen atoms, or $\text{TiO}_2\text{-X}$, which lacks an oxygen atom and is significantly out of the stoichiometric ratio (X is 1.0 or less).

The photocatalyst particle may contain a metal, such as vanadium, copper, nickel, cobalt, chromium, palladium,
10 silver, platinum, or gold, or a metallic compound therein or thereon to enhance the photocatalytic function.

Antimicrobial inorganic fine particles 2 can reduce contaminants particularly resulting from the propagation of mold, bacteria, or microorganisms. Typical examples of
15 inorganic antimicrobial material include silver, copper, zinc, tin, lead, and compounds thereof. In particular, at least one antimicrobial material selected from the group consisting of silver, copper, zinc, and compounds thereof is utilized in various applications because of its
20 antimicrobial properties or no harmful effect on human body.

These metals and compounds thereof may be used alone. However, because some of them change color or cause discoloration of antimicrobial products, they are used in a supported form in which they are loaded on fine particles of
25 an inorganic material. Examples of the inorganic material include zeolite, such as high-silica zeolite, sodalite, mordenite, analcite, and erinite, and apatite such as hydroxyapatite. These inorganic materials have ion exchange properties. Other typical examples of the inorganic
30 material include titanium dioxide, silicon dioxide, alumina oxide, magnesium oxide, calcium oxide, calcium carbonate, barium sulfate, zirconium oxide, barium titanate, and

5 zirconium phosphate.

Commercially available antimicrobial fine particles, for example, "Novaron" from Toagosei Co., Ltd., "Zeomic" from Sinanen Zeomic Co., Ltd., "Apatizer A" from Sangi Co., Ltd., "Daikiller" from Dainichiseika Color & Chemicals Mfg. Co., Ltd., "Amenitop" from Matsushita Electric Industrial Co., Ltd., "Atomy Ball" from Catalysts & Chemicals Industries Co., Ltd., and "Bactekiller" from Kanebo Chemical Industries LTD., may be used alone or in combination.

In the antifouling composite material according to the present embodiment, the inorganic fine particle layer 10 containing the inorganic fine particles 2 is fixed on the substrate 1 with the silane monomer 3 having an unsaturated bond through the chemical bonds 5 (filled circles in Fig. 1).

Specific examples of the unsaturated bond of the silane monomer 3 include a vinyl group, an epoxy group, a styryl group, a methacryl group, an acryloxy group, and an isocyanate group.

In the antifouling composite material according to the present embodiment, the reactive silane monomer 3 combines the inorganic fine particles 2 together through chemical bonds generated by the dehydration condensation reaction of silanol groups of the silane monomer 3, and also combines the inorganic fine particles 2 with the substrate 1 through the chemical bonds 5 generated by the graft polymerization of the functional group of the silane monomer 3 to the resin surface of the substrate 1, as described below.

Examples of the silane monomer 3 for use in an

5 antifouling composite material 100 according to the present
embodiment include vinyltrimethoxysilane,
vinyltriethoxysilane, vinyltriacetoxysilane, N- β -(N-
vinylbenzylaminoethyl)- γ -aminopropyltrimethoxysilane, N-
(vinylbenzyl)-2-aminoethyl-3-aminopropyltrimethoxysilane
10 hydrochloride, 2-(3,4epoxycyclohexyl)ethyltrimethoxysilane,
3-glycidoxypropyltrimethoxysilane, 3-
glycidoxypropylmethyldiethoxysilane, 3-
glycidoxypropyltriethoxysilane, p-styryltrimethoxysilane, 3-
methacryloxypropylmethyldimethoxysilane, 3-
15 methacryloxypropyltrimethoxysilane, 3-
methacryloxypropylmethyldiethoxysilane, 3-
methacryloxypropyltriethoxysilane, 3-
acryloxypropyltrimethoxysilane, and 3-
isocyanatepropyltriethoxysilane.

20 These silane monomers 3 may be used alone or in
combination. The silane monomer 3 is used as a solution
containing a required amount of silane monomer 3 in an
organic solvent, such as methanol, ethanol, acetone, toluene,
or xylene. A mineral acid, such as hydrochloric acid or
25 nitric acid, may be added to the solution to improve the
dispersibility.

Examples of the solvent include lower alcohols, such as
ethanol, methanol, propanol, and butanol; lower alkyl
carboxylic acids, such as formic acid and propionic acid;
30 aromatic compounds, such as toluene and xylene; esters, such
as ethyl acetate and butyl acetate; and cellosolves, such as
methyl cellosolve and ethyl cellosolve. These solvents may

5 be used alone or in combination.

The inorganic fine particles 2 for use in the antifouling composite material 100 according to the present embodiment are used for manufacture as a dispersion in the solution of the silane monomer 3. The inorganic fine
10 particles 2 may be dispersed by agitation using a homomixer or a magnetic stirrer, by pulverization using a ball mill, a sand mill, a tumbling mill, or a jet mill, or by using an ultrasonic wave.

In the production of the antifouling composite material
15 100, the inorganic fine particles 2 may be used as a colloidal dispersion or as a dispersion liquid prepared by pulverizing the inorganic fine particles 2 into fine particles. The dispersion liquid of the inorganic fine particles 2 may be used as follows: the silane monomer 3 is
20 added to a colloidal dispersion or to a dispersion liquid prepared by pulverization, and is heated under reflux to combine the silane monomer 3 with the inorganic fine particles 2 by a dehydration condensation reaction, thus coating the inorganic fine particles 2 with the silane
25 monomer 3. Alternatively, after the silane monomer 3 is added to a dispersion liquid prepared by pulverizing the inorganic fine particles 2 into fine particles, or after the silane monomer 3 is added to a dispersion liquid and is pulverized into fine particles, the dispersion solution is
30 subjected to solid-liquid separation, is heated at a temperature in the range of 100°C to 180°C to combine the silane monomer 3 with the inorganic fine particles 2 by a

5 dehydration condensation reaction, and is redispersed by pulverization.

In a case where after the silane monomer 3 is added to a dispersion liquid prepared by pulverizing the inorganic fine particles 2 into fine particles, or after the silane
10 monomer 3 is added to a dispersion liquid and is pulverized into fine particles, the dispersion solution is subjected to solid-liquid separation, is heated at a temperature in the range of 100°C to 180°C to chemically combine the silane monomer 3 with the inorganic fine particles 2, when the
15 coverage of the surface of the inorganic fine particles 2 with the silane monomer is in the range of 0.5% to 100%, the bond strength between the inorganic fine particles 2 and the substrate 1 having a resin surface is sufficient for practical applications.

20 When the inorganic fine particle layer 10 including the inorganic fine particles 2 has an increased thickness, the inorganic fine particle layer 10 may become deteriorated by cohesive failure depending on the stress of the inorganic fine particle layer 10 and the operating environment. Thus,
25 after the inorganic fine particles 2 are coated with the silane monomer 3, the addition of the binder component 4 follows. The binder component 4 combines the inorganic fine particles 2 coated with the silane monomer 3 together and also combines the inorganic fine particles 2 with the
30 substrate 1, thus preventing the detachment of the inorganic fine particle layer 10 caused by deterioration including cohesive failure. The binder component 4 preferably has an

5 unsaturated group, such as a vinyl group, an epoxy group, a styryl group, a methacryl group, an acryloxy group, or an isocyanate group, or an alkoxy group as a reactive site that can be chemically bound to the reactive group of the silane monomer 3 disposed on the inorganic fine particles 2.

10 Specific examples of the binder component 4 include monofunctional, bifunctional, and polyfunctional vinyl monomers having an unsaturated bond, such as acrylic acid, methylmethacrylate, ethyl acrylate, n-butyl acrylate, 2-hydroxyethyl acrylate, methyl methacrylate, 2-hydroxyethyl
15 acrylate, acrylamide, methacrylamide, acrylonitrile, vinyl acetate, styrene, itaconic acid, trimethylolpropane triacrylate, and pentaerythritol triacrylate.

Further examples of the binder component 4 include silane monomers having an unsaturated bond, such as
20 vinyltrimethoxysilane, vinyltriethoxysilane, vinyltriacetoxysilane, and N- β -(N-vinylbenzylaminoethyl)- γ -aminopropyltrimethoxysilane.

Still further examples of the binder component 4 include alkoxysilane compounds represented by $\text{Si}(\text{OR}_1)_4$
25 (wherein R_1 denotes an alkyl group having one to four carbon atoms), such as tetramethoxysilane and tetraethoxysilane, and alkoxysilane compounds represented by $\text{R}_2\text{nSi}(\text{OR}_3)_{4\text{n}}$ (wherein R_2 denotes a hydrocarbon group having one to six carbon atoms, R_3 denotes an alkyl group having one to four
30 carbon atoms, and n is an integer of 1, 2, or 3), such as methyltolylmethoxysilane, methyltriethoxysilane, dimethyldiethoxysilane, phenyltriethoxysilane,

5 hexamethyldisilazane, and hexyltrimethoxysilane.

Still further examples of the binder component 4 include water-repellent substances and oil-repellent substances, such as stearic acid acrylate and reactive silicone oils.

10 Still further examples of the binder component 4 include water-repellent substances and oil-repellent substances, such as reactive silicone oligomers, for example, Brucella D from Matsushita Electric Industrial Co., Ltd.

Still further examples of the binder component 4
15 include water-repellent substances and oil-repellent substances, such as acryl monomers having a perfluoroalkyl group, for example, 2-(perfluoropropyl)ethyl acrylate, 2-(perfluorobutyl)ethyl acrylate, 2-(perfluoropentyl)ethyl acrylate, 2-(perfluorohexyl)ethyl acrylate, 2-
20 (perfluoroheptyl)ethyl acrylate, 2-(perfluorooctyl)ethyl acrylate, 2-(perfluorononyl)ethyl acrylate, 2-(perfluorodecyl)ethyl acrylate, 3-perfluorohexyl-2-hydroxypropyl acrylate, perfluorooctylethyl methacrylate, 3-perfluorooctyl-2-hydroxypropyl acrylate, and 3-
25 perfluorodecyl-2-hydroxypropyl acrylate.

Still further examples of the binder component 4 include water-repellent substances and oil-repellent substances, such as other fluorine compounds, for example, 2-perfluorooctyl ethanol, 2-perfluorodecyl ethanol, 2-
30 perfluoroalkyl ethanol, perfluoro(propyl vinyl ether), perfluoroalkyl iodide, perfluorooctyl ethylene, and 2-perfluorooctyl ethyl phosphonic acid.

5 Still further examples of the binder component 4
include water-repellent substances and oil-repellent
substances, such as silane coupling agents having a
perfluoroalkyl group, for example, $\text{CF}_3(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$,
 $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$, $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$,
10 $\text{CF}_3(\text{CF}_2)_{11}(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$, $\text{CF}_3(\text{CF}_2)_{15}(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$,
 $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{Si}(\text{OC}_2\text{H}_5)_3$, $\text{CF}_3(\text{CH}_2)_2\text{SiCH}_3(\text{OCH}_3)_2$,
 $\text{CF}_3(\text{CF}_2)_2(\text{CH}_2)_2\text{SiCH}_3(\text{OCH}_3)_2$, $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{SiCH}_3(\text{OCH}_3)_2$,
 $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SiCH}_3(\text{OCH}_3)_2$, $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SiCH}_3(\text{OC}_2\text{H}_5)_2$,
 $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$, $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{Si}(\text{OC}_2\text{H}_5)_3$,
15 $\text{CH}_3(\text{CF}_2)_9(\text{CH}_2)_8\text{Si}(\text{OC}_2\text{H}_5)_3$, $\text{CF}_3(\text{CF}_2)_7\text{CONH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, and
 $\text{CF}_3(\text{CF}_2)_7\text{CONH}(\text{CH}_2)_2\text{SiCH}_3(\text{OCH}_3)_2$, and oligomers having a
perfluoroalkyl group and a silanol group, for example, KP-
801M (Shin-Etsu Chemical Co., Ltd.) and X-24-7890 (Shin-Etsu
Chemical Co., Ltd.).

20 Still further examples of the binder component 4
include unsaturated polyesters, unsaturated acryls, epoxy
acrylates, urethane acrylates, polyester acrylates,
polyether acrylates, polybutadiene acrylates, silicone
acrylates, maleimide, oligomers and prepolymers, such as
25 polyene/polythiol, and alkoxy oligomers. The binder
component 4 may be used alone or in combination.

In particular, when an acryl monomer having a
perfluoroalkyl group or a silane coupling agent is used as
the binder component 4, the surface of the antifouling
30 composite material 100 becomes water-repellent or oil-
repellent and is resistant to triboelectrification. This
prevents suspended particulate matter, such as soil dust or

5 pollen, or a liquid substance, such as soy sauce, coffee, or
juice, from depositing on the antifouling composite material
100. Hence, an antifouling composite material of much
practical use can be provided.

The binder component 4 may be added such that the
10 content of the binder component 4 in the inorganic fine
particle layer 10 is at least 0.1% by mass to the content of
the inorganic fine particles 2. An increase in the content
of the binder component 4 may result in higher strength and
higher durability of the inorganic fine particle layer 10.
15 However, when the content of the binder component 4, such as
a vinyl monomer having an unsaturated bond, a silane monomer
having an unsaturated bond, an acryl monomer having a
perfluoroalkyl group, a silane coupling agent having a
perfluoroalkyl group, an unsaturated polyester, an
20 unsaturated acryl, an epoxy acrylate, an urethane acrylate,
a polyester acrylate, a polyether acrylate, a polybutadiene
acrylate, a silicone acrylate, maleimide, or an oligomer
such as polyene/polythiol is more than 40% by mass to the
content of the inorganic fine particles 2, an increase in
25 the coverage of the inorganic fine particles 2 promotes the
electrification of the surface.

The electrification impairs the dustproof property and
the detachability of deposited suspended particulate matter,
and coagulates the inorganic fine particles 2. The
30 coagulation of the inorganic fine particles 2 causes many
defects such as pinholes in the inorganic fine particle
layer 10. When the content of the binder component 4 is

5 less than 0.1% by mass to the content of the inorganic fine particles 2, the inorganic fine particle layer cannot be fixed firmly onto the substrate 1, resulting in insufficient durability. Thus, the content of the binder component 4 is preferably in the range of 0.1% by mass to 40% by mass to
10 the content of the inorganic fine particles 2 to improve the durability while the dustproof property and the detachability of motes are maintained.

The present embodiment provides an antifouling composite material containing a water-repellent substance or
15 an oil-repellent substance, such as a fluorinated compound, as at least part of the binder component. The binder component composed of a fluorinated compound is randomly oriented on the surface of the fine particles, thus efficiently exhibiting water repellency or oil repellency at
20 low concentration. Furthermore, the presence of a very small volume of space through which electrons can pass makes triboelectrification difficult, thus preventing the deposition of suspended particulate matter, such as soil dust or pollen, or a liquid substance, such as soy sauce,
25 coffee, or juice. Hence, an antifouling composite material of much practical use can be provided.

According to the present embodiment, the binder component 4 is oriented at any intervals in a self-organized manner on the surface of the inorganic fine particles 2
30 coated with the silane monomer 3. Thus, the amount of binder component 4 can be reduced. Furthermore, the binder component 4 can efficiently exhibit water repellency or oil

5 repellency. By replacing part of the binder component 4
with a substance having antimicrobial, antiviral,
antiallergenic, and/or antithrombotic properties, an
antifouling composite material having various functions can
be provided without impairing the dustproof property, the
10 detachability of moths, and the antifouling properties, such
as water repellency and oil repellency.

A method for chemically combining the substrate 1 with
a solution that contains the inorganic fine particles 2
having the silane monomer thereon and the binder component 4
15 is described below. In the present embodiment, the chemical
bond is preferably formed by graft polymerization.

Examples of the graft polymerization in the antifouling
composite material 100 according to the present embodiment
include graft polymerization in the presence of a peroxide
20 catalyst, graft polymerization utilizing thermal or light
energy, and graft polymerization utilizing radiation
(radiation graft polymerization).

Among them, radiation graft polymerization is
particularly suitable in terms of the simplicity of the
25 polymerization process and the production rate. Examples of
radiant rays for use in graft polymerization include alpha
rays, beta rays, gamma rays, an electron beam, and
ultraviolet rays. Gamma rays, an electron beam, and
ultraviolet rays are particularly suitable in the present
30 embodiment.

The antifouling composite material 100 according to the
present embodiment is appropriately produced by graft

5 polymerization in the following way.

A first preferred method in the present embodiment is described below. Firstly, the binder component 4 is added to a dispersion solution of the inorganic fine particles 2 chemically bound to the silane monomer 3. After the
10 solution is stirred sufficiently, the solution is applied to an intended surface of the substrate 1 (resin surface). If necessary, a solvent is removed, for example, by heating. The surface of the substrate 1 to which the inorganic fine particles 2 chemically bound to the silane monomer 3 is
15 applied is then irradiated with radiant rays, such as gamma rays, an electron beam, or ultraviolet rays, thus performing both graft polymerization of the silane monomer 3 to the surface of the substrate 1 and bonding between the inorganic fine particles 2, that is, simultaneous radiation graft
20 polymerization.

A second preferred method in the present embodiment is described below. The surface of the substrate 1 is previously irradiated with radiant rays, such as gamma rays, an electron beam, or ultraviolet rays. The binder component
25 4 is added to a dispersion solution of the inorganic fine particles 2 chemically bound to the silane monomer 3. The sufficiently mixed solution is applied to the surface of the substrate 1 to perform both the reaction between the silane monomer 3 and the substrate 1 and bonding between the
30 inorganic fine particles 2, that is, simultaneous preirradiation graft polymerization.

In the present embodiment, as described above, an

5 antifouling composite material is produced by adding the
binder component 4 to a dispersion solution of the inorganic
fine particles 2 and then applying the sufficiently mixed
solution to the surface of the substrate 1.

The dispersion liquid of the inorganic fine particles 2
10 may be applied by common spin coating, dip coating, spray
coating, cast coating, bar coating, microgravure coating, or
gravure coating. The dispersion liquid of the inorganic
fine particles 2 may partly be applied by screen printing,
pad printing, offset printing, dry offset printing,
15 flexography, ink-jet printing, or any appropriate method.

For efficient and uniform graft polymerization of the
silane monomer 3, the surface of the substrate 1 may
previously be subjected to hydrophilic treatment, such as
corona discharge treatment, plasma discharge treatment,
20 flame treatment, or chemical treatment with an aqueous
solution of an oxidizing acid, such as chromic acid or
perchloric acid, or an aqueous alkaline solution containing
sodium hydroxide.

As described above, the antifouling composite material
25 100 according to the present embodiment includes the
substrate 1 having a resin surface and the inorganic fine
particle layer 10 fixed on the substrate 1. The inorganic
fine particle layer 10 includes the binder component 4 and
the inorganic fine particles 2 coated with the silane
30 monomer 3 having an unsaturated bond. The content of the
binder component 4 is in the range of 0.1% by mass to 40% by
mass to the content of the inorganic fine particles 2. The

5 binder component 4 is regularly oriented at any intervals on
the surface of the fine particles 2 coated with the silane
monomer 3. Thus, the antifouling composite material 100
according to the present embodiment can prevent suspended
particulate matter, such as soil dust, sand dust, or pollen,
10 or a liquid substance, such as soy sauce, coffee, juice, or
salad oil, from depositing thereon. Even when the suspended
particulate matter deposits thereon, the antifouling
composite material 100 according to the present embodiment
exhibits excellent detachability allowing the suspended
15 particulate matter to be removed easily therefrom.

Furthermore, the silane monomer 3 having an unsaturated
bond reactive to the substrate 1 is chemically bound to the
surface of the inorganic fine particles 2 by a dehydration
condensation reaction. The inorganic fine particles 2 are
20 fixed on the substrate 1 by combining unsaturated bonds
bound to the surface of the inorganic fine particles 2
together or reacting unsaturated bonds bound to the surface
of the inorganic fine particles 2 with the resin surface of
the substrate 1. The binder component is also included.
25 Thus, in the antifouling composite material 100 according to
the present embodiment, the inorganic fine particles 2
coated with the silane monomer 3 are firmly bound together,
and the inorganic fine particles 2 and the substrate 1 are
also firmly bound together. The antifouling composite
30 material 100 can therefore exhibit an excellent dustproof
effect and an excellent antifouling effect for a long period
of time.

5 Furthermore, according to the present embodiment, by replacing part of the binder component 4, which is oriented on the surface of the inorganic fine particles 2 coated with the silane monomer 3, with a substance having antimicrobial, antiviral, antiallergenic, and/or antithrombotic properties, 10 the antifouling composite material can easily have these functions without impairing the dustproof property, the detachability of moths, and the antifouling properties, such as water repellency and oil repellency.

 Furthermore, according to the present embodiment, the 15 inorganic fine particles 2 can firmly be fixed onto the substrate 1 through the chemical bonds 5. Thus, the inorganic fine particles 2 can be fixed onto the substrate 1 after the product form is given by spinning or in the process of production. Hence, the presence of the inorganic 20 fine particles 2 having various functions does not impair the spinning.

 Furthermore, the inorganic fine particles 2 can be formed as a particle monolayer or a particle multilayer on a substrate formed of a film, a resin plate, fiber, or cloth. 25 Thus, the inorganic fine particles 2 do not impair the texture of the substrate. Hence, the antifouling composite material according to the present embodiment can find use in a variety of applications.

 In the present embodiment, the substrate may have an 30 appropriate form (shape, size, etc.), such as a film, fiber, cloth, mesh, or honeycomb. Thus, these substrates having various forms can have a dustproof function.

5 The present embodiment can be applied to various
products: for example, agricultural materials, such as
greenhouse films and tunnel greenhouse films; building
materials, such as external wall materials, window frames,
doors, and shades; interior materials, such as wallpapers,
10 carpeting, and plastic tiles; footwear, such as clothing,
innerwear, hosiery, gloves, and shoes; bedding, such as
pajamas, sleeping mats, sheets, pillows, pillowcases,
blankets, towel blankets, quilts, and quilt covers; caps and
hats; handkerchiefs; towels; carpets; curtains; filters for
15 air cleaners, air conditioners, ventilating fans, vacuum
cleaners, and fans; electrodes and separators for fuel-
cells; mosquito nets; screen printing meshes; and components
in which biological fouling tends to occur, such as ships,
coastal structures, fish preserves, fishnets, buoys, water
20 intake openings, and water treatment filters. The dustproof
and antifouling composite material according to the present
embodiment is useful in providing various excellent products
in a variety of applications.

EXAMPLES

25 The present invention will specifically be described
with reference to the following Examples. However, the
present invention is not limited to these Examples.

Fine particle composite materials according to Examples
1 to 8 were produced by electron beam graft polymerization
30 with an electrocurtain electron beam irradiation apparatus
CB250/15/180L manufactured by Iwasaki Electric Co., Ltd.

EXAMPLE 1

5 Ten percent by mass of inorganic fine particles,
commercially available titanium dioxide particles (Ishihara
Sangyo Kaisha, Ltd., TTO-S-1), were dispersed in methanol.
The pH of the dispersion solution was adjusted to 4.0 with
hydrochloric acid. The titanium dioxide particles were
10 pulverized in a bead mill. The pulverized particles had an
average particle size of 15 nm. A silane monomer having an
unsaturated bond, 3-methacryloxypropyltrimethoxysilane
(Shin-Etsu Chemical Co., Ltd., KBM-503), in amounts of 3.0%
by mass to the inorganic fine particles was added to the
15 resulting dispersion solution.

The dispersion solution was transferred into a flask
equipped with a condenser tube and was heated under reflux
in an oil bath for four hours. The silane monomer was
chemically bound to the titanium dioxide fine particles by a
20 dehydration condensation reaction. A binder component 4,
(1) tetramethoxysilane (Shin-Etsu Chemical Co., Ltd., KBM-
04), (2) hydroxyethyl acrylate (Kyoisha Chemical Co., Ltd.),
(3) pentaerythritol triacrylate (Kyoisha Chemical Co.,
Ltd.), or (4) a binder containing silicone acrylate (GE
25 Toshiba Silicones Co., Ltd., UVHC8558), in amounts of 15% by
mass to the silane monomer-coated inorganic fine particles
was added to the dispersion solution. The titanium dioxide
particles was redispersed in a bead mill. The average
particle size of the titanium dioxide fine particles in the
30 dispersion solution was 14 nm. The term "average particle
size" used herein refers to a volume-average particle size.

The dispersion solution further containing a binder

5 component was applied to 125 μm polyester film (Toray Industries, Inc., Lumirror) with a bar coater and was dried at 110°C for one minute. The polyester film to which the dispersion liquid containing the titanium dioxide fine particles was applied was irradiated with 5 Mrad of electron
10 beam at an accelerating voltage of 200 kV. The titanium dioxide fine particles were bound to the polyester film by the graft polymerization of the silane monomer, thus producing a dustproof composite material.

EXAMPLE 2

15 Example 2 is the same as Example 1 except that a water repellent substance, (1) stearyl acrylate (Kyoisha Chemical Co., Ltd.) as an acryl monomer or (2) silicone oligomer (Matsushita Electric Industrial Co., Ltd., Frescera D), in amounts of 15% by mass to the silane monomer-coated
20 inorganic fine particles was added as the binder component in the dispersion solution.

EXAMPLE 3

Inorganic fine particles, commercially available titanium dioxide fine particles (Tayca Corporation, MT-
25 100HD), in amounts of 10.0% by mass of methanol and a silane monomer, 3-methacryloxypropyltrimethoxysilane (Shin-Etsu Chemical Co., Ltd., KBM-503), in amounts of 3.0% by mass to the fine particles was added. The pH of the resulting mixture was adjusted to 3.0 with hydrochloric acid. The
30 titanium dioxide fine particles were pulverized in a bead mill. The pulverized particles had an average particle size of 18 nm. The dispersion solution was subjected to solid-

5 liquid separation in a lyophilizer and was heated at 120°C
to chemically combine the silane monomer with the titanium
dioxide fine particles by a dehydration condensation
reaction. Ten percent by mass of the resulting surface-
treated titanium dioxide fine particles were added to
10 methanol. A binder component, an oligomer having a
perfluoroalkyl group and a silanol group (Shin-Etsu Chemical
Co., Ltd., KP-801M), in amounts of (1) 1% by mass, (2) 5% by
mass, or (3) 10% by mass to the silane monomer-coated
inorganic fine particles was added to the methanol. Other
15 procedures were the same as in Example 1.

EXAMPLE 4

Example 4 is the same as Example 1 except that an
inorganic fine particle layer was formed on an 80-mesh
polyester used in place of the polyester film substrate.

20 EXAMPLE 5

Example 5 is the same as Example 3 except that an
inorganic fine particle layer was formed on an 80-mesh
polyester used in place of the polyester film substrate.

EXAMPLE 6

25 Example 6 is the same as Example 3 except that an
inorganic fine particle layer was formed on a polyester
nonwoven fabric having a mass per unit area of 70 g/m²
(Asahi Kasei Corporation, Eltas E01070) used in place of the
polyester film substrate.

30 EXAMPLE 7

Example 6 is the same as Example 3 except that (1) 0.1%
by mass or (2) 40% by mass of binder component is added to

5 the dispersion solution.

EXAMPLE 8

Example 8 is the same as Example 7 except that the polyester film was not irradiated with an electron beam, that is, a process of combining the titanium dioxide fine
10 particles with the polyester film by graft polymerization of the silane monomer was omitted.

COMPARATIVE EXAMPLE 1

Comparative Example 1 is the same as Example 3 except that (1) no or (2) 0.05% by mass of binder component was
15 added to the dispersion solution.

COMPARATIVE EXAMPLE 2

Comparative Example 2 is the same as Example 3 except that 50% by mass of binder component, pentaerythritol triacrylate (Kyoeisha Chemical Co., Ltd.), was added to the
20 dispersion solution and that an 80-mesh polyester was used in place of the polyester film substrate.

COMPARATIVE EXAMPLE 3

The properties of an untreated 80-mesh polyester were evaluated.

25 COMPARATIVE EXAMPLE 4

A commercially available water and oil repellent (Sumitomo 3M Ltd., SCOTCHGARD) was sprayed onto the 80-mesh polyester used in Example 5. After the 80-mesh polyester was placed at room temperature for two hours, the properties
30 of the polyester were evaluated.

COMPARATIVE EXAMPLE 5

The properties of a commercially available fluorinated

5 nonwoven fabric having a mass per unit area of 70 g/m²
(Nitto Denko Corporation, NTF9307) were evaluated without
any treatment.

Table 1 summarizes the conditions of Examples 1 to 8
and Comparative Examples 1 to 3. The binder content is
10 expressed in % by mass.

Table 1

	Substrate	Inorganic fine particle layer			Chemical bond
		Inorganic fineparticle e	Binder	Binder content	
Example 1 (1)	PET film	Titanium dioxide	Tetramethoxysilane	15	Graft polymerization
(2)	"	"	Hydroxyethyl acrylate	"	"
(3)	"	"	Pentaerythritol triacrylate	"	"
(4)	"	"	Silicone acrylate	"	"
Example 2 (1)	"	"	Stearyl acrylate	"	"
(2)	"	"	Silicone oligomer	"	"
Example 3 (1)	"	"	Oligomer having perfluoroalkyl and silanol groups	1	"
(2)	"	"	"	5	"
(3)	"	"	"	10	"
Example 4 (1)	PET mesh	"	Tetramethoxysilane	15	"
(2)	"	"	Hydroxyethyl acrylate	"	"
(3)	"	"	Pentaerythritol triacrylate	"	"
(4)	"	"	Silicone acrylate	15	"
Example 5 (1)	"	"	Oligomer having perfluoroalkyl and silanol groups	1	"
(2)	"	"	"	5	"
(3)	"	"	"	10	"
Example 6 (1)	Nonwoven fabric	"	"	1	"
(2)	"	"	"	5	"
(3)	"	"	"	10	"
Example 7 (1)	PET film	"	"	0.1	"
(2)	"	"	"	40	"
Example 8 (1)	"	"	"	0.1	None
(2)	"	"	"	40	None
Comparative Example 1 (1)	"	"	None	None	Graft polymerization
(2)	"	"	Oligomer having perfluoroalkyl and silanol groups	0.05	"
Comparative Example 2	PET mesh	"	"	50	"
Comparative Example 3	"	None	None	None	None
Comparative Example 4	"	None	None	None	None
Comparative Example 5	Nonwoven fabric	None	None	None	None

5 (Evaluation of properties)

Dustproof property: A sample was cut into a 10 cm x 10 cm test piece. KANTO loam, quartz sand, or mixed dust each in conformity with JIS Z 8901 was evenly sprinkled over the piece. The mass of the test piece was measured before and
10 after the deposition of dust.

Wettability: Surface wettability is a measure of an antifouling property. Two microliters of distilled water was dropped onto a composite material. The contact angle of the droplet was measured with a solid-liquid interface
15 analyzer DropMaster 300 manufactured by Kyowa Interface Science Co., Ltd. In general, a larger contact angle is indicative of a higher "antifouling property" against the liquid (repel the liquid or resist liquid stain).

Electrostatic potential generated by friction: A test
20 piece (10 cm x 10 cm) was electrically charged by the friction with a feather duster. The electrostatic potential was measured with a static electricity meter (SV-73A) manufactured by Nippon Static Co., Ltd.

Durability of dustproof property: A test piece was
25 washed by moving a commercial sponge back and forth 10 times under a load of 100 g. A change in dustproof property was determined as a measure of durability. For Comparative Examples 2, 3, 4, and 5, the durability test was not performed, because their initial dustproof properties were
30 poor.

5 **Table 2**

		Dustproof property (mg/dm ²)	Contact angle (°)	Electrostatic potential generated by friction (kV)	Durability (mg/dm ²)
Example 1	(1)	0	17.9	-0.4	0
	(2)	0	16.3	-0.1	0
	(3)	1	36.2	-0.6	0
	(4)	0	37.6	-0.7	1
Example 2	(1)	1	106.8	-0.6	0
	(2)	0	100.9	-0.8	0
Example 3	(1)	0	95.1	-0.1	0
	(2)	0	126.4	-0.3	1
	(3)	0	132.1	-1.0	0
Example 4	(1)	0	80 >	-0.1	0
	(2)	1	80 >	-0.1	0
	(3)	1	80 >	-0.5	1
	(4)	1	80 >	-0.5	1
Example 5	(1)	0	105.3	-0.1	0
	(2)	0	123.8	-0.4	1
	(3)	1	132.2	-0.8	0
Example 6	(1)	2	129.0	-0.1	1
	(2)	4	136.3	-0.1	3
	(3)	3	141.7	-0.3	3
Example 7	(1)	0	78.3	-0.1	1
	(2)	0	138.6	-1.5	0
Example 8	(1)	0	75.4	-0.2	4
	(2)	0	133.5	-1.7	5
Comparative Example 1	(1)	0	17.7	-0.2	4
	(2)	0	36.7	-0.3	2
Comparative Example 2		18	80 >	-6.0	—
Comparative Example 3		58	80 >	-6.0	—
Comparative Example 4		38	130.4	-4.0	—
Comparative Example 5		113	131.2	-5.0	—

"80 >" in Table 2 means the contact angle is approximately less than 80°.

Table 2 shows that in Example 1, which contained the
10 binder component 4, the mass of mixed dust deposited on the
test piece was almost unchanged in the durability test,
indicating that the dustproof property was maintained. In
Comparative Example 1, a large difference in the mass of
mixed dust deposited on the test piece was observed,

5 indicating deterioration in dustproof property. The results demonstrated that the durability was improved by the addition of the binder component 4.

10 In Comparative Example 2, in which 50% by mass of binder component 4 was included, neither the dustproof property nor the detachability of motes was exhibited because of triboelectrification. Examples 1 to 8, in which the content of the binder component 4 was in the range of 0.1% by mass to 40% by mass, had the dustproof property. The results show that when the content of the binder
15 component 4 is in the range of 0.1% by mass to 40% by mass to the inorganic fine particles 2, the antifouling composite material 100 can have an excellent dustproof property, excellent detachability of motes, and sufficient durability for practical applications.

20 Examples 2, 3, 5, 6, 7, and 8 include a water-repellent substance or an oil-repellent substance as the binder component 4. These Examples show that even when the content of the binder component 4 is as low as about 15%, the test piece has a water contact angle of 100° or more and thus
25 exhibit high water repellency, suggesting that the test piece has an antifouling property preventing a liquid substance, such as juice or soy sauce, from depositing thereon. Furthermore, friction did not cause charges, indicating that the test piece had a dustproof property.

30 In contrast, PET nonwoven fabric of Comparative Example 4 and PTFE nonwoven fabric of Comparative Example 5 were water-repellent, but were electrically charged by friction.

5 Furthermore, they did not have the dustproof property.

Furthermore, in Examples 2, 3, 5, 6, and 7, a change in the mass of mixed dust deposited on the test piece, which was a measure of durability, differed little from the initial property (dustproof property). Thus, use of a
10 water-repellent substance or an oil-repellent substance in the binder component 4 can provide a highly durable antifouling composite material. Even when suspended particulate matter or a liquid substance deposits on the antifouling composite material, the suspended particulate
15 matter or the liquid substance is easily removable therefrom.

Furthermore, difference in durability between Example 7 and Example 8 demonstrated that fixation of inorganic fine particles by graft polymerization improves the durability.

As shown by the results on durability in Examples,
20 because the binder component 4 has an unsaturated group, such as a vinyl group, an epoxy group, a styryl group, a methacryl group, an acryloxy group, or an isocyanate group, or an alkoxy group as a reactive site that can be chemically bound to the reactive group of the silane monomer 3 disposed
25 on the inorganic fine particles 2, the composite material has an excellent dustproof property, excellent detachability of moths, and sufficient durability for practical applications.

A cloth of 65% polyester and 35% cotton blend, which is
30 generally used in clothing or aprons, was used as an example of a commercial product. Soy sauce was dropped on a cloth treated as in Example 3 (2), as illustrated in Fig. 2A. The

5 droplet spread immediately on an untreated cloth (Fig. 2B) and left a stain. In contrast, the droplet maintained its shape on the treated cloth (Fig. 2A) and left almost no stain when the droplet was removed immediately.

As one of commercial filter products, a sieve for use
10 in flour milling was treated according to the present invention. Wheat flour was sifted through the sieve, as illustrated in Fig. 3A. A mesh woven from 62 μm nylon 66 warp yarn and 80 μm nylon 66 weft yarn (NBC Inc., NXX7) was treated as in Example 4 (1). The mesh was attached to a
15 square frame having inside dimensions of 200 mm x 200 mm to make a sieve. The sieve was mounted in a vibrating screen machine. After 600 g of wheat flour was sifted, the sieve was removed and was tapped to remove wheat flour left on the sieve (Fig. 3A). For a sieve including an untreated mesh,
20 after 500 g of wheat flour was sifted, little wheat flour could pass the sieve. After the sieve was tapped, almost the front of the openings were blocked by wheat flour (Fig. 3B).

A 50 mesh mosquito net weaved from 100 μm polyester
25 fibers was treated as in Example 4 (4). Cotton linters were sprinkled over the mosquito net, as illustrated in Fig. 4A. After cotton linters were sprinkled over the horizontally placed mosquito net, the mosquito net was stood vertically and was tapped to remove cotton linters (Fig. 4A). For the
30 untreated mosquito net, cotton linters were difficult to remove and remained caught in the net (Fig. 4B).

Building materials, such as metals, wood, ceramics, and

5 resins, can be used as a single item. The surfaces of
building materials are often painted, coated with a resin,
or overlaid with a laminate such as a resin film. As an
example of a building material, a fluorocarbon resin film
having a thickness of 50 μm (Asahi Glass Co., Ltd., ETFE
10 film, Aflex 50N) was treated as in Example 1 (3). Mixed
dust was sprinkled over the film, as illustrated in Fig. 5A.
After mixed dust conforming to JIS Z 8901 was sprinkled over
the horizontally placed ETFE film, the ETFE film was stood
vertically and was tapped to remove mixed dust (Fig. 5A).
15 For an untreated ETFE film, mixed dust was difficult to
remove and was left on the ETFE film (Fig. 5B).

As an example of an interior material, a commercial
polyester curtain fabric was treated as in Example 1 (3).
Mixed dust was sprinkled over the curtain fabric, as
20 illustrated in Fig. 6A. After mixed dust conforming to JIS
Z 8901 was sprinkled over the horizontally placed curtain
fabric, the curtain fabric was picked up and was tapped to
remove mixed dust (Fig. 6A). For an untreated curtain
fabric, mixed dust was difficult to remove and was left on
25 the curtain fabric (Fig. 6B).

Embodiments of the present invention are not limited to
the product examples described above. For example, the
substrate may have an appropriate form (shape, size, etc.),
such as a film, fiber, cloth, mesh, or honeycomb. Products
30 that include these substrates of various forms having a
dustproof function are contemplated.

5

CLAIMS

1. An antifouling composite material comprising:

a substrate; and

an inorganic fine particle layer disposed on a surface
10 of the substrate, the inorganic fine particle layer
including inorganic fine particles and a binder component,
the inorganic fine particles being coated with silane
monomer each having an unsaturated bond,

wherein the content of the binder component in the
15 inorganic fine particle layer is in the range of 0.1% by
mass to 40% by mass to the content of the inorganic fine
particles.

2. The antifouling composite material according to Claim
20 1, wherein the binder component comprises a water-repellent
compound or an oil-repellent compound.

3. The antifouling composite material according to Claim
1, wherein the binder component comprises a fluorinated
25 compound.

4. The antifouling composite material according to Claim
1, wherein

the unsaturated bonds of the silane monomer disposed on
30 the inorganic fine particles in the inorganic fine particle
layer form chemical bonds, thereby forming the inorganic
fine particle layer, and

5 the unsaturated bonds of the silane monomer disposed on
the inorganic fine particles in the inorganic fine particle
layer are bound to the surface of the substrate through the
chemical bonds, thereby fixing the inorganic fine particle
layer onto the substrate.

10

5. The antifouling composite material according to Claim
4, wherein the chemical bonds are formed by graft
polymerization.

15 6. The antifouling composite material according to Claim
5, wherein the graft polymerization is radiation graft
polymerization.

7. The antifouling composite material according to Claim
20 1, wherein at least the surface of the substrate is formed
of a resin.

8. The antifouling composite material according to Claim
1, wherein the substrate is formed of a resin.

25

9. The antifouling composite material according to Claim
1, wherein the substrate has a fibrous structure.

10. Clothing formed of an antifouling composite material
30 according to Claim 8.

11. A filter formed of an antifouling composite material

5 according to Claim 8.

12. A mosquito net formed of an antifouling composite material according to Claim 8.

10 13. A building material formed of an antifouling composite material according to Claim 7.

14. An interior material formed of an antifouling composite material according to Claim 8.

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Figures: 2A, 2B, 3A, 3B, 4A, 4B, 5A, 5B, 6A, 6B

Pages: 2/5, 3/5, 4/5, 5/5

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FIG.1

