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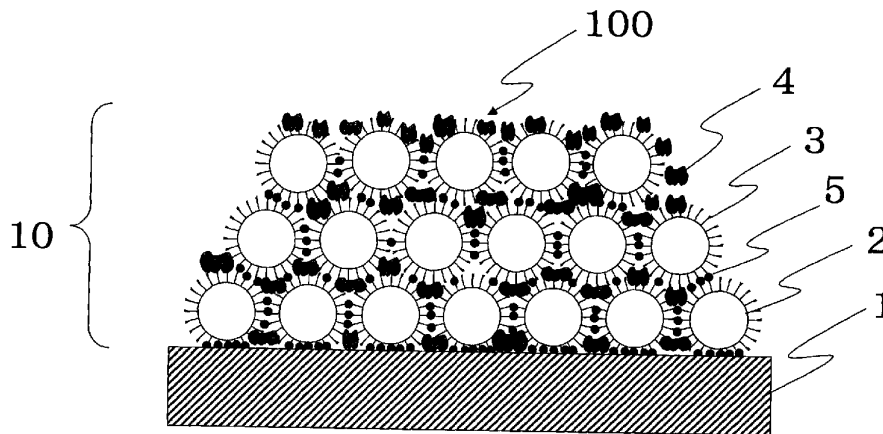
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(54) Title: COMPOSITE MATERIAL HAVING ANTIFOULING PROPERTY

(54) 発明の名称: 防汚性を有する複合部材



(57) 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.

(57) 要約: 【課題】防塵性と防汚性に優れ、且つ耐久性の高い複合部材を提供する。【解決手段】不飽和結合を有するシランモノマーで被膜された無機微粒子と、この微粒子に対し0.1質量%以上40質量%以下のバインダー成分を含む無機微粒子層を、基体表面に化学結合により形成する。

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## 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  $\mu\text{m}$  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

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

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

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

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  
5 perfected the present invention by discovering that silane 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  
10 particulate matter or liquid substances. Even when suspended particulate matter or liquid substances deposit on the composite material, the suspended particulate matter or the liquid substances can easily be removed.

#### 15 Means for Solving the Problems

A first aspect of the present invention provides an antifouling composite material comprising a substrate and an inorganic fine particle layer disposed on a surface of the substrate, the inorganic fine particle layer including  
20 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 inorganic fine particle layer is in the range of 0.1% by mass to 40% by mass to the content of  
25 the inorganic fine particles. According to the present 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  
15 oriented in gaps between the silane monomer-coated inorganic  
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.

            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.

25           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 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.

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 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. 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 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 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, 10 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 15 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 20 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 25 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 30 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  $TiO_2$ -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- $\beta$ -(N-  
vinylbenzylaminoethyl)- $\gamma$ -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- $\beta$ -(N-vinylbenzylaminoethyl)- $\gamma$ -aminopropyltrimethoxysilane.

Still further examples of the binder component 4 include alkoxy silane compounds represented by  $\text{Si}(\text{OR}_1)_4$   
25 (wherein  $\text{R}_1$  denotes an alkyl group having one to four carbon atoms), such as tetramethoxysilane and tetraethoxysilane, and alkoxy silane compounds represented by  $\text{R}_2\text{nSi}(\text{OR}_3)_{4\text{n}}$  (wherein  $\text{R}_2$  denotes a hydrocarbon group having one to six carbon atoms,  $\text{R}_3$  denotes an alkyl group having one to four  
30 carbon atoms, and  $\text{n}$  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 motes, 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,  
antivirus, antiallergenic, and/or antithrombotic properties,  
10 the antifouling composite material can easily have these  
functions without impairing the dustproof property, the  
detachability of motes, 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, an 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  $\mu\text{m}$  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/m<sup>2</sup>  
(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 particles with the polyester film by graft polymerization of  
10 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 (Kyoisha 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/m<sup>2</sup>  
(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 <sup>2</sup> )	Contact angle (°)	Electrostatic potential generated by friction (kV)	Durability (mg/dm <sup>2</sup> )
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 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 moles, 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  $\mu\text{m}$  nylon 66 warp yarn and 80  $\mu\text{m}$  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  $\mu\text{m}$  polyester  
25 fibers was treated as in Example 4 (4). Cotton lintens were sprinkled over the mosquito net, as illustrated in Fig. 4A. After cotton lintens were sprinkled over the horizontally placed mosquito net, the mosquito net was stood vertically and was tapped to remove cotton lintens (Fig. 4A). For the  
30 untreated mosquito net, cotton lintens 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  $\mu\text{m}$  (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.

Comprises/comprising and grammatical variations thereof  
when used in this specification are to be taken to specify the  
presence of stated features, integers, steps or components or  
groups thereof, but do not preclude the presence or addition  
5 of one or more other features, integers, steps, components or  
groups thereof.

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.

20          7. The antifouling composite material according to Claim  
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.

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

11. A filter formed of an antifouling composite material

according to Claim 8.

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

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.

15. An antifouling composite material substantially as hereinbefore described with reference to the inventive examples.

**NBC INC**

WATERMARK PATENT & TRADEMARK ATTORNEYS

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FIG.1

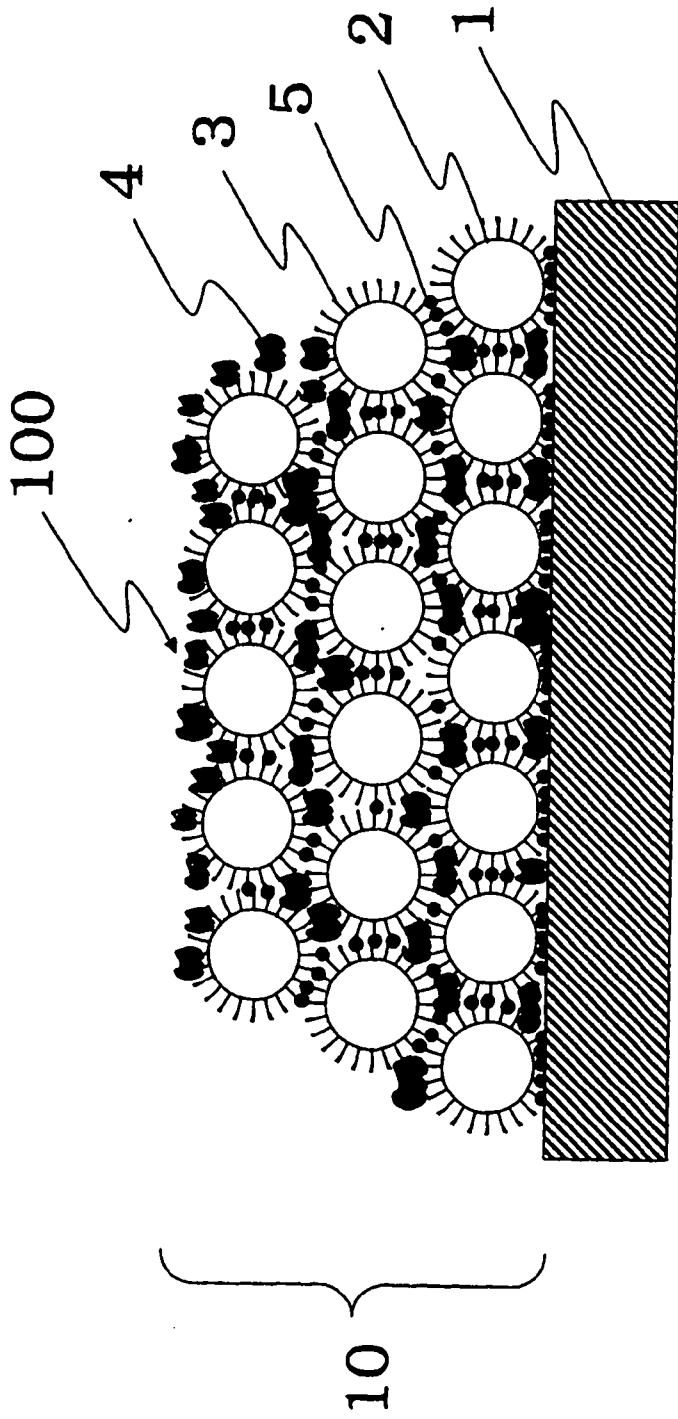


FIG.2A



FIG.2B



FIG.3A

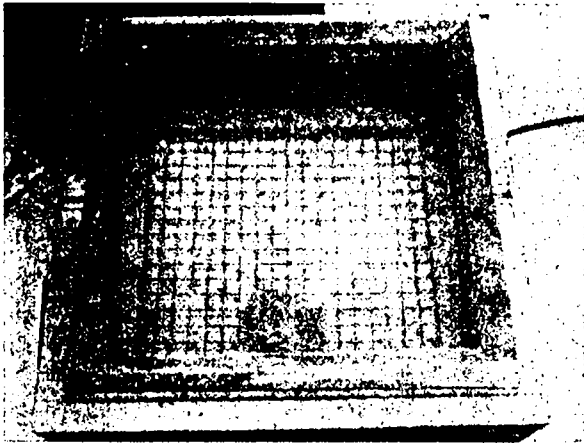


FIG.3B

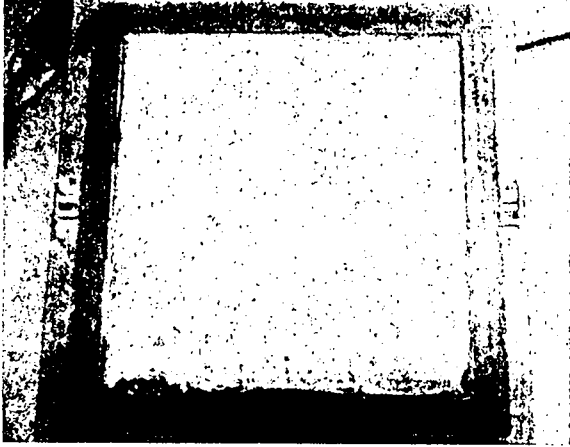


FIG.4A

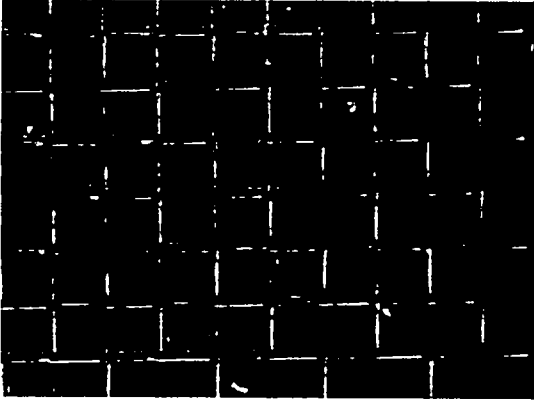


FIG.4B

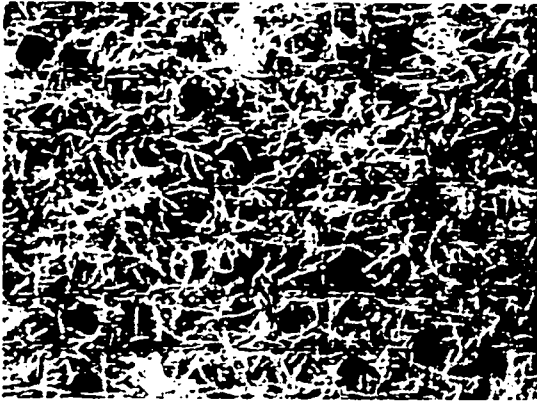


FIG.5A

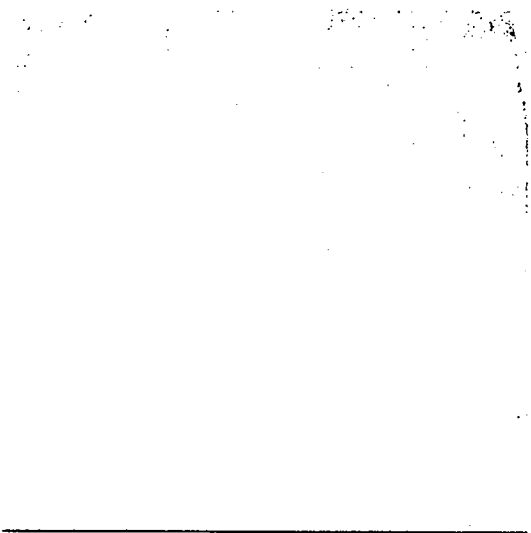


FIG.5B

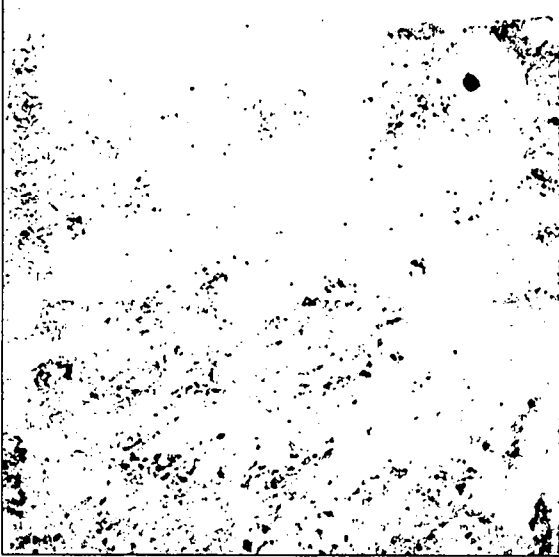


FIG.6A

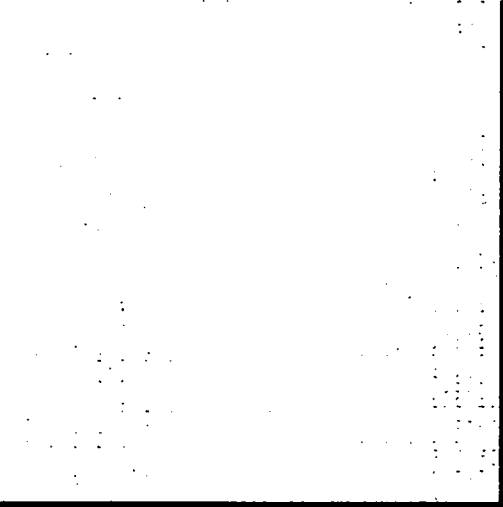


FIG.6B

