A method for producing an inorganic particle composite body formed of a mixture of a plastically deformable metal, and inorganic particles that do not plastically deform under a condition under which the metal plastically deforms, wherein the method comprises: a step of preparing an inorganic particles structural body that is formed of a mixture of the metal and the inorganic particles and that contains a vacant space therein, and a step of plastically deforming the metal in the structural body.
METHOD FOR PRODUCING INORGANIC PARTICLE COMPOSITE BODY

TECHNICAL FIELD

[0001] The present invention relates to a method for producing an inorganic particle composite body made of metal and inorganic particles.

BACKGROUND ART

[0002] Front panels of flat panel displays, displays of portable instruments such as cellular phones, and the like have been provided with treatment to increase surface hardness for the purpose of prevention of scratching, more specifically, treatment to form a hardcoat layer. Conventionally known technologies to form a hardcoat layer on a substrate include a method comprising applying a mixture of inorganic particles, an ultraviolet-curable resin, and so on to a substrate and then ultraviolet curing it, and a method comprising laminating a coating material made of only a silica precursor or a mixture of a silica precursor and inorganic particles on a substrate and then curing the coating material by the sol-gel method (see JP 2008-150484 A and JP 2007-529588 T). In the above-described conventional technologies, however, since a hardcoat layer containing inorganic particles is different from a substrate in properties (e.g., modulus of elasticity and coefficient of linear expansion), the higher the surface hardness of a hardcoat layer is made, the more liable to peel off the hardcoat layer is. When a film made of only a hardcoat layer is formed by removing a substrate, the harder the film is, the more brittle it is. In addition, surface hardness decreases as the brittleness of a film is reduced.

DISCLOSURE OF THE INVENTION

[0003] An object of the present invention is to provide an inorganic particle composite body having reduced brittleness or reduced ease in peeling while having surface hardness derived from inorganic particles. The present invention provides the following [1] through [12].

[0004] [1] A method for producing an inorganic particle composite body formed of a mixture of a plastically deformable metal, and inorganic particles that do not plastically deform under a condition under which the metal plastically deforms, wherein the method comprises: a step of preparing an inorganic particle structural body that is formed of a mixture of the metal and the inorganic particles and that contains a vacant space therein, and a step of plastically deforming the metal in the structural body.

[0005] [2] The method according to [1], wherein the volume of the inorganic particles is larger than the volume of the metal in the inorganic particle structural body.

[0006] [3] The method according to [1] or [2], wherein the step of plastically deforming the metal is a step of plastically deforming the metal by pressurizing the inorganic particle structural body.

[0007] [4] The method according to [1] or [2], wherein the step of plastically deforming the metal is a step of plastically deforming the metal by applying an electromagnetic wave to the inorganic particle structural body.

[0008] [5] The method according to any one of [1] to [4], wherein the method further comprises a step of applying hydrophilization to the surface of the structural body produced by carrying out the step of plastically deforming the metal.

[0009] [6] The method according to any one of [1] to [4], wherein the method further comprises a step that is a step of applying hydrophilization to the surface of the inorganic particle structural body that is carried out before carrying out the step of plastically deforming the metal.

[0010] [7] The method according to any one of [1] to [4], wherein the method further comprises a step of applying hydrophilization to the surface of the structural body produced by carrying out the step of plastically deforming the metal.

[0011] [8] The method according to any one of [1] to [4], wherein the method further comprises a step that is a step of applying hydrophilization to the surface of the inorganic particle structural body that is carried out before carrying out the step of plastically deforming the metal.

[0012] [9] The method according to any one of [1] to [4], wherein the method further comprises a step of applying antireflecting treatment to the surface of the structural body produced by carrying out the step of plastically deforming the metal.

[0013] [10] The method according to any one of [1] to [4], wherein the method further comprises a step that is a step of applying antireflecting treatment to the surface of the inorganic particle structural body that is carried out before carrying out the step of plastically deforming the metal.

[0014] [11] The method according to any one of [1] to [4], wherein the method further comprises a step of giving a glass layer to the surface of the structural body produced by carrying out the step of plastically deforming the metal.

[0015] [12] The method according to any one of [1] to [4], wherein the method further comprises a step that is a step of giving a glass layer to the surface of the inorganic particle structural body that is carried out before carrying out the step of plastically deforming the metal.

[0016] According to the method of the present invention, it is possible to obtain an inorganic particle composite body having reduced brittleness or reduced ease in peeling while having surface hardness derived from inorganic particles.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] FIG. 1 is a schematic diagram of an inorganic particle structural body 3a.

[0018] FIG. 2 is a schematic diagram of an inorganic particle composite body 4a obtained by pressurizing the inorganic particle structural body 3a.

[0019] FIG. 3 is a schematic diagram of an inorganic particle structural body 3b.

[0020] FIG. 4 is a schematic diagram of an inorganic particle composite body 4b obtained by pressurizing the inorganic particle structural body 3a.

[0021] FIG. 5 is a schematic diagram of an inorganic particle structural body 3c.

[0022] FIG. 6 is a schematic diagram of an inorganic particle composite body 4c obtained by pressurizing the inorganic particle structural body 3c.

[0023] FIG. 7 is a schematic diagram of an inorganic particle structural body 3d.

[0024] FIG. 8 is a schematic diagram of an inorganic particle composite body 4d obtained by pressurizing the inorganic particle structural body 3d.
FIG. 9 is a schematic diagram of an inorganic particle structural body 3e.

FIG. 10 is a schematic diagram of an inorganic particle composite body 4e obtained by pressurizing the inorganic particle structural body 3e.

FIG. 11 is a schematic diagram of a hydrophilic inorganic particle composite body 5a obtained by applying hydrophilization to the surface of the composite body 4a illustrated in FIG. 2.

FIG. 12 is a schematic diagram of a hydrophilic inorganic particle composite body 5b obtained by applying hydrophilization to the surface of the composite body 4b illustrated in FIG. 4.

FIG. 13 is a schematic diagram of a hydrophobic inorganic particle composite body 7a obtained by applying hydrophobization to the surface of the composite body 4a illustrated in FIG. 2.

FIG. 14 is a schematic diagram of a hydrophobic inorganic particle composite body 7b obtained by applying hydrophobization to the surface of the composite body 4b illustrated in FIG. 4.

FIG. 15 is a schematic diagram of an antireflective inorganic particle composite body 10a obtained by applying antireflecting treatment to the surface of the composite body 4a illustrated in FIG. 2.

FIG. 16 is a schematic diagram of an antireflective inorganic particle composite body 10b obtained by applying antireflecting treatment to the surface of the composite body 4b illustrated in FIG. 4.

FIG. 17 is a schematic diagram of an inorganic particle composite body 11a obtained by giving a glass layer to the surface of the composite body 4a illustrated in FIG. 2.

FIG. 18 is a schematic diagram of an inorganic particle composite body 11b obtained by giving a glass layer to the surface of the composite body 4b illustrated in FIG. 4.

FIG. 19 is a schematic diagram of the inorganic particle structural body 3a.

FIG. 20 is schematic diagram 4a of an inorganic particle composite molded article obtained by molding the inorganic particle structural body 3a.

FIG. 21 is a schematic diagram of the inorganic particle structural body 3b.

FIG. 22 is schematic diagram 4b of an inorganic particle composite molded article obtained by molding the inorganic particle structural body 3b.

FIG. 23 is a schematic diagram of the process for molding (press molding) the composite body 4a illustrated in FIG. 2.

FIG. 24 is a schematic diagram concerning a method of determining a volume fraction V (%) of the metal with which an inorganic particle layer has been filled.

FIG. 25 is a TEM photograph of a cross section of the inorganic particle composite body produced in Example 1.

FIG. 26 is a TEM photograph of a cross section of the inorganic particle composite body produced in Comparative Example 1.

FIG. 27 is a TEM photograph of a cross section of the inorganic particle composite body produced in Example 2.

FIG. 28 is a TEM photograph of a cross section of the inorganic particle composite body produced in Example 2.

The metal contained in the inorganic particle structural body is not particularly restricted if it is a metal capable of being plastically deformed, in other words, if it has plasticity. The plasticity as referred to herein is a property to deform continuously with generation of permanent strain when a stress has exceeded the limit of elasticity. That a metal plastically deforms means that a stress exceeding the limit of elasticity is applied to a metal and, as a result, a permanent strain is produced, so that the metal is deformed and the metal is brought into a state that the deformed condition is maintained even if the stress is removed. Examples of such a metal include metals such as platinum, gold, palladium, silver, copper, nickel, zinc, aluminum, iron, cobalt, rhodium, ruthenium, tin, lead, bismuth, tungsten, and indium, alloys and solders composed of two or more metals. The metal may be in any shape, e.g., a particulate shape, a tabular shape, and a fibrous shape. As to the metal, a single kind of metal may be used, or two or more kinds of metals may be used in combination.

When the metal is in a particulate shape, the particle diameter thereof can be measured in the same way used in the particle diameter measurement of inorganic particles described later. Although the particle diameter of metal particles is not limited, the particle diameter is from 1 to 500 nm, preferably from 1 to 200 nm, and more preferably from 2 to 100 nm when the aspect ratio is 2 or less.

Examples of the inorganic particles contained in an inorganic particle structural body include: metal oxides, such as iron oxide, magnesium oxide, aluminum oxide, silicon oxide (silica), titanium oxide, cobalt oxide, copper oxide, zinc oxide, cerium oxide, yttrium oxide, indium oxide, silver oxide, tin oxide, holmium oxide, bismuth oxide, and indium tin oxide; metal complex oxides such as indium tin oxide; metal salts such as calcium carbonate and barium sulfate; and inorganic layered compounds such as clay minerals and carbon-based intercalation compounds. Inorganic particles do not include metal particles.

As an inorganic layered compound, an inorganic layered compound having a property that it is swollen and cleaved by a solvent is used preferably from a viewpoint that a large aspect ratio can be used easily. As such an inorganic layered compound having a property that it is swollen and cleaved by a solvent, a clay mineral that exhibits swellability and cleavability in a solvent is used particularly preferably. Clay minerals are generally classified into a type having a two-layer structure having, on a silica tetrahedral layer, an octahedral layer containing aluminum, magnesium or the like.
as a central metal, and a type having a three-layer structure in which an octahedral layer containing aluminum, magnesium or the like as a central metal is sandwiched on its both sides by silica tetrahedral layers. Examples of the former type include kaolinite series, antigorite series, and so on, whereas examples of the latter type include smectite series, vermiculite series, mica series, and so on depending on the number of interlayer cations. Clay minerals are minerals containing silicate minerals having a layered crystal structure as their primary ingredients. Examples thereof include kaolinite series, antigorite series, smectite series, vermiculite series, and mica series. Specific examples include kaolinite, dickite, nacrite, halloysite, antigorite, chrysotile, pyrophyllite, montmorillonite, hectorite, tetrasylic mica, sodium taeniolite, muscovite, margarite, talc, vermiculite, phlogopite, xanthophyllite, and chlorite. As to the inorganic particle, only a single kind of inorganic particles may be used, or two or more kinds of inorganic particles may be used in combination. It is also possible to form an inorganic particle structural body by combining particles differing in average particle diameter.

When inorganic particles constituting an inorganic particle layer are hydrophilic, since the inorganic particle composite body has a portion with superior hydrophilicity, it has antifouling property (self-cleaning property), by which dirt can be removed by water, and property of difficult attachment or easy detachment of snow or ice (prevention of snow/ice attachment) in addition to property to prevent surface scratching, it is suited as building components such as a roof of a dome stadium, a roof of a stadium, a roof of a carport, roofs of other types of buildings, an awning, a wall of a building, a window, a traffic display, and acoustical insulation boards for roads or buildings; agricultural components such as a film for agricultural houses, a film for tunnels, a film for curtains, a mulch film, a sprinkling hose, sprinkling materials, and a seed and seeding box; components of instruments for transportation such as skirt parts, exterior boards, and windows of trains and exterior boards, windows, bumpers, and mirrors of cars; furniture members such as mirrors, floorings, table tops, chairs, and sofas; household appliances such as television, personal computer, washing machines, and refrigerators; electric members such as electric wires, cables, antennas, steel towers for electric wires and cables, and lighting members of solar cells.

Moreover, taking advantage of antistatic property that a hydrophilic particle film easily emits, it is suitable also as antistatic members, such as an antistatic film, a film for packaging, a film for removing electricity, a material for packaging electronic components, and a material for food packaging. Examples of hydrophilic inorganic particles include particles of metal oxides. Inorganic particles to which hydrophilization has been applied can also be used.

The shape of inorganic particles may be any shape, such as spherical shape, needle-like shape, scaly shape, and fibrous shape. In the present invention, the particle diameter of such particles refers to an average particle diameter measured by the dynamic light scattering method, the Sear's method, or the laser diffraction scattering method or a spherical equivalent diameter calculated from a BET specific surface area. In the case of a fibrous shape, it means a diameter of a section thereof. The Sear's method, which is disclosed in Analytical Chemistry, Vol. 28, p. 1981-1983, 1956, is an analytical method to be applied to the measurement of the average particle diameter of silica particles; it is a method in which the surface area of silica particles is determined from the amount of NaOH to be consumed for making a colloidal silica dispersion liquid from pH=3 to pH=9 and then a sphere equivalent diameter is calculated from the determined surface area. When inorganic particles have an aspect ratio of up to 2, the average particle diameter thereof can be determined also from an image observed using an optical microscope, a laser microscope, a scanning electron microscope, a transmission electron microscope, an atomic force microscope, or the like. The particle diameter of inorganic particles is preferably from 1 to 10000 nm from the viewpoint of interaction force between particles, such as atomic force and van der Waals force. When the inorganic particles have an aspect ratio of 2 or less, the particle diameter is from 1 to 500 nm, preferably from 1 to 200 nm, and more preferably from 2 to 100 nm. When the inorganic particles are an inorganic layered compound, the particle diameter is from 10 to 3000 nm, preferably from 20 to 2000 nm, and more preferably from 100 to 1000 nm.

While inorganic particles that do not plastically deform under conditions under which metal plastically deforms are used in the method of the present invention, the fact that inorganic particles that do not plastically deform under conditions under which metal plastically deforms can be confirmed by heating or pressurizing the inorganic particles under operation conditions under which metal plastically deforms and checking the change in shape or property of the inorganic particles.

In the case that the inorganic particle structural body is formed from a mixture of inorganic particles and metal particles, the mixing ratio of both particles is arbitrary, but from the viewpoint of keeping surface hardness, it is preferred that the volume fraction of the inorganic particles in the inorganic particle structural body be larger than the volume fraction of the metal particles.

In the present invention, a substrate refers to a material that supports an inorganic particle structural body. The substrate is not particularly restricted if it can support metal or an inorganic particle structural body. Specifically, metal, resin, glass, ceramics, paper, cloth, and the like are used in a form (tabular form such as film form and sheet form, rod form, fibrous form, spherical form, three-dimensional structural form, etc.), if necessary.

The inorganic particle structural body to be used in the present invention is a structural body that has vacant spaces in at least a part thereof, and representative examples of the structure thereof are shown in FIG. 1 and FIG. 3. As illustrated in these drawings, the inorganic particle structural body suitable for the present invention usually has a porous structure, and it is preferred that at least some of the pores interconnect. The interconnection of pores in a structural body allows vacant spaces in the structural body to be filled easily with metal plastically deformed by pressuring the structural body.

Methods for producing an inorganic particle structural body include the following, for example.

Method 1: a method that comprises applying a coating liquid containing inorganic particles, particulate metal, and a liquid dispersion medium to a substrate, and then removing the liquid dispersion medium from the applied coating liquid (in other words, drying the coating liquid) to form an inorganic particle structural body.

Method 2: a method that comprises applying a coating liquid containing metal and an inorganic particle structural body, and then removing the liquid dispersion medium from the applied coating liquid (in other words, drying the coating liquid) to form an inorganic particle structural body.

FIG. 1 is a schematic diagram of an inorganic particle structural body 3a formed by the above-described Method 1 (a substrate is omitted). This example is a case that
the shape of inorganic particles is a sphere. An inorganic particle structural body formed of spherical inorganic particles and metal particles has vacant spaces between the particles. By pressurizing the structural body \(3a\), the metal part in the structural body \(3a\) plastically deforms and fills the vacant spaces in the structural body \(3a\) gradually. It is conceivable that an inorganic particle composite body produced by the method of the present invention is formed as a result of moving the plastically deformed metal to at least some of the vacant spaces in the structural body \(3a\) and filling them. An inorganic particle composite body in the case of having filled up all vacant spaces with metal is the composite body \(4a\) illustrated in FIG. 2.

[0060] In the method of the present invention, by plastically deforming metal existing in a structural body, the plastically deformed metal is filled into vacant spaces in the structural body. In some cases, however, some vacant spaces among many vacant spaces in the structural body are filled up with metal but the other remain unfilled with metal, or in some cases a vacant space is partially filled with metal. Of course, all vacant spaces may be completely filled up with metal. The degree of plastic deformation of metal or filling of metal into vacant spaces varies depending upon the intended function of an inorganic particle composite body.

[0061] FIG. 3 is a schematic diagram of an inorganic particle structural body \(3b\) formed by the above-described Method 1. This example is a case that the shape of inorganic particles is plate-like. The structural body formed of plate-like inorganic particles and metal particles has vacant spaces between these particles. By pressurizing the structural body \(3b\), the metal part in the structural body \(3b\) plastically deforms and fills the vacant spaces in the structural body \(3b\) gradually. It is conceivable that an inorganic particle composite body produced by the method of the present invention is formed as a result of moving the plastically deformed metal to at least some of the vacant spaces in the structural body \(3b\) and filling them. An inorganic particle composite body in the case of having filled up all vacant spaces with metal is the composite body \(4b\) illustrated in FIG. 4.

[0062] FIG. 5 is a schematic diagram of a stacked structure body \(3c\) produced by forming an inorganic particle structural body by the above-described Method 1, then plastically deforming the metal contained in the structural body to form a hybridized inorganic particle structural body, and subsequently further forming thereon a layer made of a mixture of metal and inorganic particles. This example shows the case that inorganic particles are spherical and metal is in the form of spherical particles. The stacked structural body \(3c\): formed of spherical inorganic particles and spherical metal particles has vacant spaces between these particles.

[0063] First, an inorganic particle structural body made of inorganic particles and metal particles by the above-described Method 1 using a mixture of the inorganic particles and the metal particles. This inorganic particle structural body is hereinafter referred to as an "initial inorganic particle structural body." Subsequently, the metal particles in the initial inorganic particle structural body are plastically deformed and thereby the inorganic particles in the initial structural body are rearranged to pack in a higher density, so that the volume of the vacant spaces in the structural body decreases. The resulting structural body is called a "hybridized inorganic particle structural body." Next, on the hybridized inorganic particle structural body is formed a layer made of a mixture of metal particles and inorganic particles differing in composition from the above-described mixture used for the preparation of the initial inorganic particle structural body. Consequently, a stacked structure body \(3c\) comprising the hybridized inorganic particle structural body and a newly formed layer is formed. The aforementioned layer newly formed also contains vacant spaces because it is made of particles. Next, the metal in the stacked structural body, that is, the metal particles in the aforementioned newly formed layer and the plastically deformed metal and the remaining metal particles in the hybridized inorganic particle structural body, is plastically deformed. As a consequence, the inorganic particles in the stacked structural body are rearranged and packed in a higher density. The volume of vacant spaces of the stacked structural body decreases. Thus, an inorganic particle composite body \(4c\) illustrated in FIG. 6 is formed.

[0064] FIG. 7 illustrates a stacked structural body produced using plate-like inorganic particles; the stacked structural body is basically the same of the stacked structural body illustrated in FIG. 5 except that the inorganic particles contained are not spherical but plate-like. Using the stacked structural body illustrated in FIG. 7, the metal contained therein, that is, the metal already plastically deformed and the remaining metal particles in the hybridized inorganic particle structural body and the metal particles contained in the layer formed on the hybridized inorganic particle structural body, is plastically deformed. As a result, inorganic particles in the stacked structural body are rearranged and packed in a higher density. Thus, the volume of vacant spaces in the stacked structural body \(4d\) decreases, so that an inorganic particle composite body illustrated in FIG. 8 is formed.

[0065] FIG. 9 is a schematic diagram of another stacked structural body \(3e\). This stacked structural body \(3e\) is formed by performing the operations described below: an inorganic particle structural body is formed by the above-described Method 1; subsequently, the metal contained in the inorganic particle structural body is plastically deformed to form a hybridized inorganic particle structural body; then, a layer made of a mixture of metal and inorganic particles is further formed on the hybridized inorganic particle structural body to form a first stacked structural body; next, a layer made of a mixture of metal and inorganic particles is further formed on the first stacked structural body to form a second stacked structural body; subsequently, a layer made of a mixture of metal and inorganic particles is further formed on the second stacked structural body to form a third stacked structural body; next, the metal contained in the third stacked structural body is plastically deformed and thereby the inorganic particles contained in the stacked structural body are rearranged to pack in a higher density. This example shows the case that inorganic particles are spherical and metal is in the form of spherical particles. The stacked structural body \(3e\) formed of spherical inorganic particles and spherical metal particles has vacant spaces between these particles.

[0066] First, an inorganic particle structural body made of inorganic particles and metal particles by the above-described Method 1 using a mixture of inorganic particles and metal particles. This inorganic particle structural body is hereinafter referred to as an "initial inorganic particle structural body." Subsequently, the metal particles in the initial inorganic particle structural body are plastically deformed and thereby the inorganic particles in the initial structural body are rearranged to pack in a higher density, so that the volume of the vacant spaces in the structural body decreases. The resulting structural body is called a "hybridized inorganic particle structural body." Next, on the hybridized inorganic particle structural body is formed a layer made of a mixture of metal particles and inorganic particles differing in composition from the above-described mixture used for the preparation of the initial inorganic particle structural body. Consequently, a stacked structure body \(3e\) comprising the hybridized inorganic particle structural body and a newly formed layer is formed. The aforementioned layer newly formed also contains vacant spaces because it is made of particles. Next, the metal in the stacked structural body, that is, the metal particles in the aforementioned newly formed layer and the plastically deformed metal and the remaining metal particles in the hybridized inorganic particle structural body, is plastically deformed. As a consequence, the inorganic particles in the stacked structural body are rearranged and packed in a higher density. The volume of vacant spaces of the stacked structural body decreases. Thus, an inorganic particle composite body \(4e\) illustrated in FIG. 6 is formed.
spaces in the structural body decreases. The resulting structural body is called a “hybridized inorganic particle structural body.” Next, on the hybridized inorganic particle structural body is formed a layer made of a mixture of metal particles and inorganic particles differing in composition from the above-described mixture used for the preparation of the initial inorganic particle structural body. Consequently, a stacked structure body 3e composed of the hybridized inorganic particle structural body and a newly formed layer is formed. Moreover, a layer made of a mixture of metal particles and inorganic particles is stacked in the similar way. These newly formed layers also contain vacant spaces because they are made of particles. Next, the metal in the stacked structural body, that is, the metal particles in the aforementioned newly formed layer and the plastically deformed metal and the remaining metal particles in the hybridized inorganic particle structural body, is plastically deformed. As a consequence, the inorganic particles in the stacked structural body are rearranged and packed in a higher density. The volume of vacant spaces of the stacked structural body decreases. Thus, an inorganic particle composite body 4c illustrated in FIG. 10 is formed.

The inorganic particle composite body illustrated in FIG. 10 has four inorganic particle layers and the voidages of the inorganic particle layers become smaller stepwise from the part derived from the inorganic particle structural body formed first (hereinafter referred to as “initial inorganic particle layer-derived part”) toward the part derived from the layer formed last (hereinafter referred to as “last inorganic particle layer-derived part”). The last inorganic particle layer-derived part has almost no vacant spaces. An inorganic particle composite body can be produced by stacking a plurality of inorganic particle layers so that the voidage may vary stepwise to produce a stacked inorganic particle structural body and then plastically deforming the metal contained in the stacked inorganic particle structural body. The voidage of an inorganic particle layer can be adjusted by changing the particle diameter of the inorganic particles that constitute the layer. By filling up from the initial inorganic particle layer-derived part to the last inorganic particle layer-derived part with metal, the inorganic particle composite body 4c of FIG. 10 is formed. The resulting inorganic particle composite body has a region where the property of the metal is dominant and a region where the property of the inorganic particles is dominant. If the combination of inorganic particles and metal is optimized, completely different properties can be given to one inorganic particle composite body.

Now, consideration is made to the initial inorganic particle layer-derived part, which has the highest voidage, and the last inorganic particle layer-derived part, which has the lowest voidage. When all the vacant spaces of a portion derived from the initial inorganic particle layer, which is the highest in voidage, have been filled up with metal, the presence ratio of the metal to the inorganic particles in this layer is high, so that this layer has a property that is a combination of the property of the inorganic particles and the property of the metal.

On the other hand, when the metal has been filled in the vacant spaces of a portion derived from the last inorganic particle layer, which is lowest in voidage, this layer has a property the same as that of the inorganic particles because the presence ratio of the metal to the inorganic particles in this layer is very low and therefore this layer is hardly influenced by the property of the metal.

Usually, if substances differing in property have been united, adhesiveness will become poor because of the difference in properties between the substances. For example, a laminate of glass and a resin film easily delaminates because the coefficient of linear expansion of an interface between glass and resin is different. However, as illustrated in FIG. 10, in an inorganic particle composite body in which the voidage is varied stepwise and thereby properties of respective layers are varied stepwise, adhesiveness between layers is high since a property varies gradually within the composite body. As a result, completely different properties can be imparted to an inorganic particle composite body while keeping the adhesiveness between layers good. It is preferred to fill at least some of the vacant spaces of the stacked inorganic particle layer by plastically deforming the metal.

FIG. 11 is a schematic diagram of a hydrophilic inorganic particle composite body 5a obtained by applying hydrophilization to the surface of a structural body obtained by performing a step of plastically deforming metal (this corresponds to the inorganic particle composite body 4a illustrated in FIG. 2). Preferred methods of hydrophilization include a method comprising stacking a layer containing a hydrophilizing agent onto at least a part of the surface of a structural body and/or a method comprising reacting a hydrophilizing agent to at least a part of the surface of a structural body.

FIG. 12 is a schematic diagram of a hydrophilic inorganic particle composite body 5b obtained by applying hydrophilization to the surface of a structural body obtained by performing a step of plastically deforming metal (this corresponds to the inorganic particle composite body 4b illustrated in FIG. 4). Preferred methods of hydrophilization include a method comprising stacking a layer containing a hydrophilizing agent onto at least a part of the surface of a structural body and/or a method comprising reacting a hydrophilizing agent to at least a part of the surface of a structural body.

FIG. 13 is a schematic diagram of a hydrophobic inorganic particle composite body 7a obtained by applying hydrophobization to the surface of a structural body obtained by performing a step of plastically deforming metal (this corresponds to the inorganic particle composite body 4a illustrated in FIG. 2). Preferred methods of hydrophobization include a method comprising stacking a layer containing a hydrophobizing agent onto at least a part of the surface of a structural body and/or a method comprising reacting a hydrophobizing agent to at least a part of the surface of a structural body.

FIG. 14 is a schematic diagram of a hydrophobic inorganic particle composite body 7b obtained by applying hydrophobization to the surface of a structural body obtained by performing a step of plastically deforming metal (this corresponds to the inorganic particle composite body 4b illustrated in FIG. 4). Preferred methods of hydrophobization include a method comprising stacking a layer containing a hydrophobizing agent onto at least a part of the surface of a structural body and/or a method comprising reacting a hydrophobizing agent to at least a part of the surface of a structural body.

FIG. 15 is a schematic diagram of an antireflective inorganic particle composite body 9a obtained by applying antireflecting treatment to the surface of a structural body obtained by performing a step of plastically deforming metal (this corresponds to the inorganic particle composite body 4a ...
illustrated in FIG. 2). A preferred method of antireflection treatment is a method comprising providing an antireflecting agent to the surface of a structural body by wet coating and/or dry coating (i.e., vapor deposition).

FIG. 16 is a schematic diagram of an antireflective inorganic particle composite body 9b obtained by applying antireflecting treatment to the surface of a structural body obtained by performing a step of plastically deforming metal (this corresponds to the inorganic particle composite body 4b illustrated in FIG. 4). A preferred method of antireflection treatment is a method comprising providing an antireflecting agent to the surface of a structural body by wet coating and/or dry coating (i.e., vapor deposition).

FIG. 17 is a schematic diagram of a glass-coated inorganic particle composite body 11a obtained by giving a glass layer to the surface of a structural body obtained by performing a step of plastically deforming metal (this corresponds to the inorganic particle composite body 4a illustrated in FIG. 2). Preferred methods of giving a glass layer include a method comprising bonding a glass sheet and a structural body together via an adhesive, a method comprising coating the surface of a structural body with a glass precursor and then converting the glass precursor into glass, and a method comprising extrusion-laminating molten glass to a structural body.

FIG. 18 is a schematic diagram of a glass-coated inorganic particle composite body 11b obtained by giving a glass layer to the surface of a structural body obtained by performing a step of plastically deforming metal (this corresponds to the inorganic particle composite body 4b illustrated in FIG. 4). Preferred methods of providing a glass layer include a method comprising bonding a glass sheet and a structural body together via an adhesive, a method comprising coating the surface of a structural body with a glass precursor and then converting the glass precursor into glass, and a method comprising extrusion-laminating molten glass to a structural body.

FIG. 19 is a schematic diagram of an inorganic particle structural body 3a formed by the above-described Method 1. By forming the structural body 3a, a metal portion in the structural body 3a deforms plastically and this gradually fills vacant spaces in the structural body 3a and, simultaneously, the three-dimensional shape of the surface of a molding machine in contact with the structural body is transferred to the surface of the structural body, so that the three-dimensional shape is given to the surface of the structural body. When all vacant spaces have been filled up, an inorganic particle composite molded article 4a of FIG. 20 is formed. To leave some vacant spaces unfilled is preferred because it is easy to perform painting treatment or the like later.

FIG. 21 is a schematic diagram of an inorganic particle structural body 3b formed by the above-described Method 1. By forming the structural body 3b, a metal portion in the structural body 3b deforms plastically and this gradually fills vacant spaces in the structural body 3b and, simultaneously, the three-dimensional shape of the surface of a molding machine in contact with the structural body is transferred to the surface of the structural body, so that the three-dimensional shape is given to the surface of the structural body. When all vacant spaces have been filled up, an inorganic particle composite molded article 4b of FIG. 22 is formed. To leave some vacant spaces unfilled is preferred because it is easy to perform painting treatment or the like later.

FIG. 23 is a schematic diagram of the process (press molding) for producing the composite body 4a illustrated in FIG. 2. It is also permitted to preheat the inorganic particle structural body before press molding or to heat or cool it in a mold during press molding.

In the practice of the above-described Method 1, a coating liquid containing inorganic particles, a particular metal, and a liquid dispersion medium is prepared. Although the liquid dispersion medium may be any one having a function to disperse particles and water and volatile organic solvents can be used, water is preferred because it is easy to handle. In order to improve the dispersibility to the solvent, it is permitted to apply surface treatment to particles and also permitted to add a dispersion medium electrolyte, a dispersing aid, and the like. When dispersing particles colloidal in a coating liquid, it is permitted to perform pH adjustment or add an electrolyte or a dispersing agent, if necessary. In order to disperse particles uniformly, it is permitted to use techniques, such as stirring with a stirrer, ultrasonic dispersion, and super high pressure dispersion (super high pressure homogenizer), if necessary. Although the particle concentration of a coating liquid is not particularly limited, it is preferably from 1 to 50% by weight for maintaining the stability of the particles in the solution. When the inorganic particles are made of aluminum and the coating liquid is in a colloidal state, it is preferred to add an anion, such as chloride ion, sulfate ion, and acetate ion, to the coating liquid. When the inorganic particles are made of silica and the coating liquid is in a colloidal state, it is preferred to add a cation, such as ammonium ion, alkali metal ion, and alkaline earth metal ion, to the coating liquid. To the coating liquid may be added additives, such as surfactant, polyhydric alcohols, soluble resins, dispersibility resins, and organic electrolytes, for the purpose of stabilizing the dispersion of particles.

When the coating liquid contains a surfactant, the content thereof is usually 0.1 parts by weight or less based on 100 parts by weight of the liquid dispersion medium. The surfactant to be used is not particularly restricted and examples thereof include anionic surfactants, cationic surfactants, nonionic surfactants, and ampholytic surfactants. Examples of the anionic surfactants include alkali metal salts of carboxylic acids and specifically include sodium caprylate, potassium caprylate, sodium decanoate, sodium caprate, sodium myristate, potassium oleate, tetramethylammonium stearate, and sodium steartate. Especially, alkali metal salts of carboxylic acids with alkyl chains having from 6 to 24 carbon atoms are preferred. Examples of the cationic surfactants include cetyltrimethylammonium chloride, dioctadecyl dimethylammonium chloride, N-octadecylpyridinium bromide, and cetyltriethylphosphonium bromide. Examples of the nonionic surfactants include sorbitan esters of fatty acids and glycerol esters of fatty acids. Examples of the ampholytic surfactants include 2-alkyl-N-carboxymethyl-N-hydroxyethylimidazolinium betaine, lauric acid amidopropyl betaine, and the like.

When the coating liquid contains a polyhydric alcohol, the content thereof is preferably 10 parts by weight or less, more preferably 5 parts by weight or less based on 100 parts by weight of the liquid dispersion medium. Addition of a small amount of a polyhydric alcohol can improve the antistatic property of an inorganic particle composite body. The polyhydric alcohol to be used is not particularly restricted, and examples thereof include glycol type polyhydric alcohols, such as ethylene glycol, diethylene glycol,
polyethylene glycol, propylene glycol, dipropylene glycol, and polypropylene glycol, glycerol type polyhydric alcohols, such as glycerol, diglycerol, and polyglycerol, and methylol type polyhydric alcohols, such as pentaerythritol, dipentaerythritol, and tetramethylolethane.

[0085] When the coating liquid contains a soluble resin, the content thereof is preferably 1 part by weight or less, more preferably 0.1 parts by weight or less based on 100 parts by weight of the liquid dispersion medium. Addition of a small amount of a soluble resin can make the formation of an inorganic particle structural body easier and can impart a function of the soluble resin. The soluble resin to be used here is not particularly restricted if it is soluble in the liquid dispersion medium, and example thereof include polyvinyl alcohol type resins, such as polyvinyl alcohol, ethylene-vinyl alcohol copolymers, and copolymers containing vinyl alcohol units, and polysaccharides, such as cellulose, methylcellulose, hydroxymethylcellulose, and carboxymethylcellulose.

[0086] When the coating liquid contains a resin dispersible in a solution, the content thereof is usually 10 parts by weight or less, preferably 5 parts by weight or less based on 100 parts by weight of the liquid dispersion medium. Addition of a small amount of a dispersible resin can make the formation of an inorganic particle structural body easier and can impart a function of the dispersible resin. The weight ratio of the inorganic particles to the dispersible resin, which is not particularly limited, is preferably 50/50<weight fraction of inorganic particles>/weight fraction of dispersible resin<99/9/0.1, more preferably 90/10<weight fraction of inorganic particles>/weight fraction of dispersible resin<95/5/0.5, and even more preferably 95/5<weight fraction of inorganic particles>/weight fraction of dispersible resin<99/1. The dispersible resin to be used here is not particularly restricted with respect to the type of resin as far as it can be dispersed, and a wide variety of resins can be used. As to the existence form of a resin in a solution, a dispersible resin in the form of particles called suspension or emulsion in a medium is preferably used. Examples thereof include a fluororesin-based particle dispersion liquid, a silicone resin-based particle dispersion liquid, an ethylene-vinyl acetate copolymer resin-based particle dispersion liquid, and a polyvinylidene chloride resin-based particle dispersion liquid. Specific examples of the fluororesin-based particle dispersion liquid include PTFE dispersion 31-JR, 34-JR produced by Du Pont-Mitsui Fluorchemistry Co., Ltd. and FluonPTFE dispersion AD911L, AD912L, and AD938L produced by Asahi Glass Co., Ltd.

[0087] When the coating liquid contains an organic electrolyte, the content thereof is usually 10 parts by weight or less, preferably 1 part by weight or less based on 100 parts by weight of the liquid dispersion medium. Addition of a small amount of an organic electrolyte can make the formation of an inorganic particle structural body easier and can impart a function of the organic electrolyte. The organic electrolyte to be used here is not particularly restricted if it is soluble in a liquid dispersion medium, and examples thereof include combinations of inorganic anions, such as BO$_3^{3-}$, F$, PF_6^-$, BF$_4^-$, AsF$_6^-$, SBF$_4^-$, ClO$_4^-$, AlF$_6^-$, AlCl$_4^-$, TaF$_6^-$, NbF$_6^-$, SiF$_6^-$, CN$, and F (HF)$^-$, wherein n represents a number of from 1 to 4, with organic cations described below, combinations of organic anions with organic cations described below, and combinations of organic anions with inorganic anions, such as lithium ion, sodium ion, potassium ion, and hydrogen ion. Organic cations are cationic organic compounds, examples of which include organic quaternary ammonium cations and organic quaternary phosphonium cations. Organic quaternary ammonium cations are quaternary ammonium cations having hydrocarbon groups selected from the group consisting of alkyl groups (having 1 to 20 of carbon atoms) cycloalkyl groups (having 6 to 20 of carbon atoms), aryle groups (having 6 to 20 of carbon atoms), and aralkyl groups (having 7 to 20 of carbon atoms), and organic quaternary phosphonium cations are quaternary phosphonium cations having hydrocarbon groups like those described above. The aforementioned hydrocarbon groups may have a hydroxyl group, an amino group, a nitro group, a cyano group, a carboxyl group, an ether group, an aldehyde group, and so on. Organic anions are anions containing hydrocarbon groups that may have a substituent, and examples thereof include anions selected from the group consisting of N(SO$_2$R)$^-$, C(SO$_2$R)$^-$, RICO$, and RISO$^-$ (R$^-$ represents a perfluoralkyl group having 1 to 12 carbon atoms), and anions resulting from removal of active hydrogen atoms from organic acids, such as carboxylic acids, organic sulfonic acids, and organic phosphorus acids, or phenol.

[0088] A coagulant may be added, if necessary, when obtaining a coating liquid. By the addition of a coagulant, an inorganic particle structural body with controlled structure can be obtained. Examples of such a coagulant include an acidic substance such as hydrochloric acid or its aqueous solution, an alkaline substance such as sodium hydroxide or its aqueous solution, isopropyl alcohol, and ionic liquids.

[0089] The coating liquid can be applied by wet coating methods such as gravure coating, reverse coating, brush roll coating, spray coating, kiss coating, die coating, dipping, and bar coating. By using such methods as ink jet printing, screen printing, flexographic printing, and gravure printing, arbitrary patterns can be given to an inorganic particle layer. Although the number of times of applying a coating liquid and the amount of the coating liquid to be applied in one application are arbitrary, the amount to be applied in one application is preferably from 0.5 g/m$^2$ to 40 g/m$^2$ for applying in a uniform thickness. In the method of removing the liquid dispersion medium from the applied coating liquid, that is, the drying method, the pressure and the temperature of an atmosphere may be chosen appropriately depending upon the inorganic particles, the metal, and the liquid dispersion medium to be used. For example, when the liquid dispersion medium is water, the liquid dispersion medium can be removed at 25$^\circ$C to 60$^\circ$C under ordinary pressure.

[0090] In one embodiment of the method of the present invention, an inorganic particle composite body can be obtained through the following steps (1) to (3) using an inorganic particle structural body:

(1) a step of plastically deforming the metal contained in the structural body,

(2) a step of stacking a layer made of inorganic particles differing in composition from the inorganic particles contained in the structural body,

(3) a step of plastically deforming the metal contained in the inorganic particle structural body on which the inorganic particle layer has been stacked.

[0091] By practicing the step (1), the plastically deformed metal is filled into vacant spaces in the structural body. In some cases, however, some vacant spaces among many vacant spaces in the structural body are filled up with metal but the other remain unfilled with metal, or in some cases a
vacant space is partially filled with metal. Of course, all vacant spaces may be completely filled up with metal. The degree of plastic deformation of metal or filling of metal into vacant spaces varies depending upon the intended function of an inorganic particle composite body.

[0092] There is no limitation on the means for plastically deforming the metal. Examples thereof include a method comprising pressurizing an inorganic particle structural body, a method comprising heating the structural body, a method comprising irradiating the structural body with an electromagnetic wave, and methods using these. It is preferred to adopt a method comprising at least pressurizing as means for plastically deforming metal.

[0093] The aforementioned step (2) is a step of stacking a layer made of metal and/or inorganic particles differing in composition from the metal and/or inorganic particles contained in the inorganic particle structural body. Now, the “metal and/or inorganic particles differing in composition from the metal and/or inorganic particles contained in the inorganic particle structural body” is described.

[0094] First, as to the metal and the inorganic particles contained in an inorganic particle structural body, the kind and the proportion thereof are specified. For example, suppose that there is a structural body including 10% by weight of silver having an average particle diameter of 5 nm, 60% by weight of silica having an average particle diameter of 70 nm, 20% by weight of silica having an average particle diameter of 5 nm, and 10% by weight of fluororesin having an average particle diameter of 10 nm as an inorganic particle structural body. In this case, the metal contains silver having an average particle diameter of 5 nm and the proportion thereof is 12.5% by weight. Two kinds of silica, i.e., the silica having an average particle diameter of 70 nm and the silica having an average particle diameter of 5 nm are contained as inorganic particles; as to the proportions thereof, the former is 75% by weight and the latter is 12.5% by weight. The metal and/or inorganic particles differing in composition from the metal and/or inorganic particles contained in the structural body include the following:

(i) mixed particles failing to contain at least one of silica having an average particle diameter of 70 nm and silica having an average particle diameter of 5 nm,

(ii) mixed inorganic particles, a mixture of silica having an average particle diameter of 70 nm that is the same as the silica having an average particle diameter of 70 nm contained in the inorganic particle structural body and silica that is the same as the silica having an average particle diameter of 5 nm contained in the structural body, wherein the mixed proportion of the former is not 75% by weight and the mixed proportion of the latter is not 12.5% by weight,

(iii) mixed particles containing 75% by weight of inorganic particles having an average particle diameter of 70 nm and 12.5% by weight of inorganic particles having an average particle diameter of 5 nm, wherein at least one of them is not silica.

[0095] Examples of the method of stacking, to an inorganic particle structural body, a layer made of metal and/or inorganic particles differing in composition from the metal and/or inorganic particles contained in the structural body include the following methods:

Method 1: a method comprising applying a coating liquid containing metal and/or inorganic particles and a liquid dispersion medium to the surface of the inorganic particle structural body and removing the liquid dispersion medium from the applied coating liquid,

Method 2: a method comprising stacking a plate-shaped material containing metal and/or inorganic particles to the surface of an inorganic particle structural body.

[0096] Specifically, wet coating methods, such as a reverse coating method, a dip coating method, a gravure coating method, a flexographic coating method, an ink jet coating method, and a screen printing method, and dry coating methods, such as a sputtering method, a CVD method, a plasma CVD method, a plasma polymerization method, and a vacuum deposition method, are preferably used. These may be used singly or two or more of them may be used in combination. Step (2) and step (3) each may be performed two or more times.

[0097] According to the method including the above-described steps (1) to (3), an inorganic particle composite body can be obtained in which interlayer adhesion force has been improved while the property derived from each layer is exerted. Moreover, the inorganic particle composite body of the present invention can develop various properties depending upon the kind of inorganic particles or a metal. In particular, when the same metal has been filled throughout a plurality of layers as illustrated in FIGS. 5 through 10, the interface between the metal and an inorganic particle portion of each functional layer is a continuous phase of the metal, and this probably reduces brittleness or susceptibility of delamination. When metal fills vacant spaces of an inorganic particle structural body in a very high filling ratio as illustrated in FIG. 6, FIG. 8, and FIG. 10, it becomes possible to form an inorganic particle composite body superior also in substance barrier property.

[0098] In the step of plastically deforming metal in the method of the present invention, the inorganic particle structural body is irradiated with an electromagnetic wave and the metal contained in the structural body is plastically deformed. An electromagnetic wave is preferred as means for plastically deforming the metal because it can be applied selectively to the metal in the structural body. By applying an electromagnetic wave to an inorganic particle structural body, it is possible to plastically deform metal selectively and fill it into at least some of the vacant spaces contained in the structural body without softening or melting inorganic particles contained in the structural body. The electromagnetic wave is preferably at least one selected from the group consisting of proton beam, electron beam, neutron beam, gamma rays, X-rays, ultraviolet rays, visible rays, infrared rays, microwaves, low frequency waves, high frequency waves, and laser beams thereof. The optimal values of application conditions, such as the wavelength, output, and application time of an electromagnetic wave, to be used when an electromagnetic wave is applied to an inorganic particle structural body vary depending upon the electromagnetic wave absorbing characteristics of the inorganic particle structural body, the inorganic particles, and the metal. By applying an electromagnetic wave within a wavelength range in which there is a small absorption due to inorganic particles and there is a large absorption due to metal, it is possible to plastically deform the metal efficiently without damaging inorganic particles, an inorganic particle structural body, or an inorganic particle composite body to be formed.

[0099] In addition to electromagnetic wave irradiation, an auxiliary method may be used in order to make plastic defor-
of the metal easier. Examples of such an auxiliary method include a method comprising adding heat to soften metal, a method comprising applying a chemical to soften metal, and a method comprising increasing the affinity or slipping property at the interface of metal and a vacant space; among these the method comprising adding heat to soften metal is preferably used. Examples of the method of heating the whole of an inorganic particle structural body to soften metal include a method comprising feeding the structural body into a heating atmosphere using an oven, a heater, or the like and a method comprising bringing the structural body into contact with a heat medium, such as a heated metal plate or roll.

[0100] In one preferred embodiment of the method of the present invention, the surface of the structural body obtained by practicing the step of plasticly deforming metal is hydrophilized, and in another preferred embodiment of the method of the present invention, a step of hydrophilizing the surface of the inorganic particle structural body is carried out prior to the execution of the step of plasticly deforming metal. The hydrophilization may be performed to either a part of the surface of an inorganic particle structural body or the whole of the surface. The hydrophilization in the present invention is not particularly restricted if it is a treatment to improve the hydrophilicity of the surface of an inorganic particle structural body. Preferable examples include a method comprising coating the surface of an inorganic particle structural body with a hydrophilizing agent, and cleaning of the surface of a structural body with a solvent, or the like. Hydrophilic inorganic particles may be used as the hydrophilizing agent for coating the surface of an inorganic particle structural body. A hydrophilic inorganic particle is a particle that has a hydrophilic group and is high in affinity to water and examples thereof include calcium carbonate, titanium dioxide, talc, aluminum silicate, calcium silicate, alumina silicate trihydrate, alumina, zirconia, ceria, silica, calcium sulfate, and glass microspheres.

[0101] The mechanism of coating the surface of an inorganic particle structural body with a hydrophilizing agent is not particularly restricted; it is permitted to make the surface of the inorganic particle structural body adsorb the hydrophilizing agent physically and also permitted to react the surface of the inorganic particle structural body with the hydrophilizing agent (chemical adsorption). The method of coating the surface of an inorganic particle structural body with a hydrophilizing agent is not particularly restricted, and wet coating methods, such as a reverse coating method, a die coating method, a dip coating method, a gravure coating method, a flexographic coating method, an ink jet coating method, and a screen printing method, and dry coating methods (i.e., vapor deposition methods), such as a sputtering method, a CVD method, a plasma CVD method, a plasma polymerization method, and a vacuum deposition method, are preferably used. The thickness of the hydrophilizing agent layer to be formed on the surface of an inorganic particle structural body, which is not particularly limited, is preferably from 1 to about 50 nm; if it is excessively thick, surface hardness becomes difficult to develop, whereas if it is less than 1 nm, hydrophobicity is poor. The thickness is more preferably from 2 to 30 nm, particularly preferably from 3 to about 10 nm.

[0102] As such a hydrophilizing agent, compounds that contain a fluorine atom and that have low surface energy and low interfacial energy are preferred, examples of which compounds include silicone compounds having a fluorinated hydrocarbon group and polymers containing a fluorinated hydrocarbon group. A fluorine-containing surface-antifouling agent, OPTOOL DSX produced by Daikin Industries, Ltd., and so on can be obtained as commercially available products.

[0103] In an embodiment of the present invention where hydrophilization is applied, it is preferred to use an inorganic particle structural body, at least a part of the surface of which is constituted of an inorganic particle layer. This is because inorganic particle layers are easy to apply hydrophilization thereto since inorganic particles have been exposed. The hydrophilic inorganic particle composite body of the present invention is an object in a state that some of inorganic particles have been bonded together chemically and/or physically via metal.

[0104] In one preferred embodiment of the method of the present invention, the surface of the structural body obtained by practicing the step of plasticly deforming metal is hydrophobized, and, in another preferred embodiment of the method of the present invention, a step of hydrophobizing the surface of the inorganic particle structural body is carried out prior to the execution of the step of plasticly deforming metal.

[0105] The method of hydrophobizing the surface of an inorganic particle structural body is not particularly restricted.

[0106] Preferred is a method comprising stacking a layer containing a hydrophobizing agent to the surface of a structural body and a method comprising reacting a hydrophobizing agent. The hydrophobization may be performed to either a part of the surface of an inorganic particle structural body or the whole of the surface.

[0107] As a method for stacking a layer containing a hydrophobizing agent, wet coating methods, such as a reverse coating method, a die coating method, a dip coating method, a gravure coating method, a flexographic coating method, an ink jet coating method, and a screen printing method, and dry coating methods (i.e., vapor deposition methods), such as a sputtering method, a CVD method, a plasma CVD method, a plasma polymerization method, and a vacuum deposition method, are preferably used. The thickness of the hydrophobizing agent layer to be formed on the surface of an inorganic particle structural body, which is not particularly limited, is preferably from 1 to about 50 nm; if it is excessively thick, surface hardness becomes difficult to develop, whereas if it is less than 1 nm, hydrophobicity is poor. The thickness is more preferably from 2 to 30 nm, particularly preferably from 3 to about 10 nm.

[0108] As such a hydrophobizing agent, compounds that contain a fluorine atom and that have low surface energy and low interfacial energy are preferred, examples of which compounds include silicone compounds having a fluorinated hydrocarbon group and polymers containing a fluorinated hydrocarbon group. A fluorine-containing surface-antifouling agent, OPTOOL DSX produced by Daikin Industries, Ltd., and so on can be obtained as commercially available products.

[0109] Examples of other preferred hydrophobizing agent include fluorine-containing silicon compounds having two or more silicon atoms such as those disclosed in JP 2009-53591 A. In the case that an inorganic particle structural body is coated with this type of compound, the chemical adsorption to the inorganic particle structural body does not differ from the case that only one silicon atom is contained because silicon atoms bond each other to form a long chain. Even if,
however, the inorganic particle structural body forms almost no bond with silicon atoms, the silicon atoms bond together to form a long chain to adsorb to the structural body physically, so that a film that is relatively highly resistant to wiping can be formed. For this reason, fluorine-containing silicon compounds having two or more silicon atoms bonded to reactive functional groups are suitable.

[00110] Specific examples of the fluorine-containing silicon compound having two or more silicon atoms bonded to a reactive functional group include:

- (CH₂O)₂SiCH₂CH₃O(SiOCH₃)₂CF₂CF₂O

[00111] (CH₂O)₃SiCH₂CH₃O(SiOCH₃)₂CF₂CF₂O

- (CH₂O)₄SiCH₂CH₃O(SiOCH₃)₂CF₂CF₂O

[00112] (CH₂O)₅SiCH₂CH₃O(SiOCH₃)₂CF₂CF₂O

- (CH₂O)₆SiCH₂CH₃O(SiOCH₃)₂CF₂CF₂O

[00113] (CH₂O)₇SiCH₂CH₃O(SiOCH₃)₂CF₂CF₂O

- (CH₂O)₈SiCH₂CH₃O(SiOCH₃)₂CF₂CF₂O

[00114] (CH₂O)₉SiCH₂CH₃O(SiOCH₃)₂CF₂CF₂O

- (CH₂O)₁₀SiCH₂CH₃O(SiOCH₃)₂CF₂CF₂O

[00115] (CH₂O)₁₁SiCH₂CH₃O(SiOCH₃)₂CF₂CF₂O

- (CH₂O)₁₂SiCH₂CH₃O(SiOCH₃)₂CF₂CF₂O

[00116] (CH₂O)₁₃SiCH₂CH₃O(SiOCH₃)₂CF₂CF₂O

[00117] (CH₂O)₁₄SiCH₂CH₃O(SiOCH₃)₂CF₂CF₂O

[00118] (CH₂O)₁₅SiCH₂CH₃O(SiOCH₃)₂CF₂CF₂O

[00119] (CH₂O)₁₆SiCH₂CH₃O(SiOCH₃)₂CF₂CF₂O

[00120] (CH₂O)₁₇SiCH₂CH₃O(SiOCH₃)₂CF₂CF₂O

[00121] According to the method of the present invention, it is possible to obtain a hydrophobic inorganic particle composite body having reduced brittleness or reduced ease in peeling while having surface hardness derived from inorganic particles. Moreover, a hydrophobic inorganic particle composite body to be produced by the method of the present invention can develop various properties depending upon the kind of hydrophobization, inorganic particles or metal. When metal fills vacant spaces of an inorganic particle structural body in a very high filling ratio as illustrated in FIG. 2 and FIG. 4, it becomes possible to form a hydrophobic inorganic particle composite body superior also in substance barrier property.

[00122] In one preferred embodiment of the method of the present invention, the surface of the structural body obtained by practicing the step of plastically deforming metal is subjected to an antireflecting treatment, and in another preferred embodiment of the method of the present invention, a step of applying an antireflecting treatment to the surface of the inorganic particle structural body is carried out prior to the execution of the step of plastically deforming metal.

[00123] Representative schematic diagrams of an antireflective inorganic particle composite body are shown in FIGS. 15 and 16, but the present invention is not restricted to these. Moreover, a product in which some of the composite bodies illustrated in these representative schematic diagrams have been combined can also be used.

[00124] The inorganic particle composite body obtained through the steps of the present invention may be an inorganic particle composite body obtained by using an inorganic particle structural body having an inorganic particle layer in at least part of the surface thereof among the above-described inorganic particle structural bodies, plastically deforming the metal contained in the inorganic particle structural body, thereby filling the metal into at least some of the vacant spaces contained in the inorganic particle structural body and oozing the metal to the surface of the inorganic particle structural body. That is, the inorganic particle composite body has been covered on at least part of its surface with the metal contained in the inorganic particle structural body used. It is preferred in the present invention to obtain an inorganic particle composite body having, in at least part of its surface, a layer where inorganic particles derived from an inorganic particle structural body has been exposed. Such an inorganic particle composite body is easy to apply antireflecting treatment. The method of stacking an antireflecting agent on the surface of an inorganic particle composite body is not particularly restricted. Preferably used are a method comprising applying a coating liquid containing an antireflecting agent to the surface of an inorganic particle composite body and then drying it, wet coating methods, such as a reverse coating method, a die coating method, a dip coating method, a gravure coating method, a flexographic coating method, an ink jet coating method, and a screen printing method, and dry coating methods (i.e., vapor deposition), such as a sputtering method, a CVD method, a plasma CVD method, a plasma polymeriza-
A layer to be stacked and made of an antireflecting agent is designed in consideration of various factors, such as the wavelength of the light to be antireflected, the index of refraction of the inorganic particle composite body to be used, and the index of refraction of the atmosphere in which an antireflective inorganic particle composite body is used. The antireflective layer to be stacked may have either a single layer or multiple layers. In the case of a single layer, a composition that affords a low refractive index is used. In the case of multiple layers, the refractive index and the thickness of each layer are determined depending upon optical design. A multilayer is better in antireflecting property, whereas a single layer is better in cost. For example, in the case of preventing the reflection of a visible radiation by a single-layer antireflective layer, it is preferred to adjust the thickness of the antireflective layer to from 50 to 150 nm, more preferably from 80 to 130 nm. As to an optical design method, “Characteristics and optimum design of antireflection film/film formation technology” (2001, Technical Information Institute Co., Ltd.), “Optical practical materials - with an eye to various application development -” (2006, Johokaku Co., Ltd.), and “Characteristics and optimum design of antireflection film/film formation technology” (2001, edited by Technical Information Institute Co., Ltd.) can be referred to.

Although the method disclosed in JP 2006-327187 A is described in detail below as one example of antireflecting treatment, the antireflecting treatment in the present invention is not limited thereto.

The mixed inorganic particle dispersion liquid to be used as an antireflecting agent is prepared using inorganic particle chains (A) each composed of three or more particles with a particle diameter of 10 to 60 nm connected in a chain form, inorganic particles (B) with an average particle diameter of 1 to 20 nm, and a liquid dispersion medium and satisfies the following formula (1) and (2).

\[
0.55 \leq \text{RVA} \leq 0.90 \tag{1}
\]

\[
0.10 \leq \text{RVB} \leq 0.45 \tag{2}
\]

wherein RVA is the ratio of the volume of the inorganic particle chains (A) to the total volume of the inorganic particle chains (A) and the inorganic particles (B) in the dispersion liquid, and RVB is the ratio of the volume of the inorganic particles (B) to the total volume of the inorganic particle chains (A) and the inorganic particles (B) in the dispersion liquid.

The chemical composition of the inorganic particle chains (A) may be either the same as or different from the chemical composition of the inorganic particles (B). Examples of inorganic particles which are used as the inorganic particle chains (A) or the inorganic particles (B) include silicon oxide (i.e., silica), titanium oxide, aluminum oxide, zinc oxide, tin oxide, calcium carbonate, barium sulfate, talc, and kaolin. The inorganic particle chains (A) and the inorganic particles (B) are preferably made of silica because particles thereof are high in dispersibility in a solvent, low in refractive index, and easy to obtain a powder being small in particle size distribution. An inorganic particle chain (A) is a chain in which three or more inorganic particles with a particle diameter of 10 to 60 nm are connected in a chain form. As such inorganic particle chains can be used commercially available products, examples of which include SNOWTEX (registered trademark) PS-S, PS-SO, PS-M, and PS-MO produced by Nissan Chemical Industries, Ltd., which are silica sols containing water as a dispersion medium, and IPA-SE-UP produced by Nissan Chemical Industries, Ltd., which is silica sol containing isopropanol as a dispersion medium. The particle diameter of the particles forming inorganic particle chains and the shape of the inorganic particle chain can be determined through observation using a transmission electron microscope. The expression “connected in a chain form” as used herein is an expression opposite to “connected in a circular form” and encompasses not only particles connected in a straight form but also particles connected in a bent form.

The average particle diameter of the inorganic particles (B) is from 1 to 20 nm. The average particle diameter of the inorganic particles (B) is determined by the dynamic light scattering method or the Siers method. Measurement of the average particle diameter by the dynamic light scattering method can be performed by using a commercially available particle size distribution analyzer. The Siers method, which is disclosed in Analytical Chemistry, Vol. 28, p. 1981-1983, 1956, is an analytical method to be applied to the measurement of the average particle diameter of silica particles; it is a method in which the surface area of particles is determined from the amount of NaOH to be consumed for adjusting a colloidal silica dispersion liquid from pH = 3 to pH = 9 and then a sphere equivalent diameter is calculated from the determined surface area. A spherical equivalent diameter determined in the above way is defined an average particle diameter.

Typically, the mixed inorganic particle dispersion liquid can be prepared by, for example, any of the following methods [1] through [5], but the preparation is not limited to these methods.

[1] A method comprising adding a powder of inorganic particle chains (A) and a powder of inorganic particles (B) simultaneously to a common liquid dispersion medium and then dispersing them.

[2] A method comprising dispersing inorganic particle chains (A) in a first liquid dispersion medium to prepare a first dispersion liquid, separately dispersing inorganic particles (B) in a second liquid dispersion medium to prepare a second dispersion liquid, and then mixing the first and the second dispersion liquids.

[3] A method comprising dispersing inorganic particle chains (A) in a liquid dispersion medium to prepare a dispersion liquid, and then adding a powder of inorganic particles (B) to the dispersion liquid to disperse.

[4] A method comprising dispersing inorganic particles (B) in a liquid dispersion medium to prepare a dispersion liquid, then adding a powder of inorganic particle chains (A) to the dispersion liquid to dispersed.

[5] A method comprising performing grain growth in a dispersion medium to prepare a first dispersion liquid containing inorganic particle chains (A), separately performing grain growth in a dispersion medium to prepare a second dispersion liquid containing an inorganic particles (B), and then mixing the first and second dispersion liquids.

By applying strong dispersion means, such as ultrasonic dispersion and ultrahigh pressure dispersion, it is possible to disperse inorganic particles particularly uniformly in a mixed inorganic particle dispersion liquid. In order to achieve dispersion with higher uniformity, it is preferred that inorganic particles in the dispersion liquid of inorganic par-
ticle chains (A) and the dispersion liquid of inorganic particles (B) to be used for the preparation of a mixed inorganic particle dispersion liquid and in a mixed inorganic particle dispersion liquid to be obtained finally be in a colloidal state. Water and a volatile organic solvent can be used as a dispersion medium.

[0133] In the aforementioned method [2], [3], [4], or [5], when the dispersion liquid of the inorganic particle chains (A) and the dispersion liquid of the inorganic particles (B), or both the dispersion liquid of the inorganic particle chains (A) and the dispersion liquid of the inorganic particles (B) are colloidal alunina, it is preferred to add an anion, such as chloride ion, sulfate ion, and acetate ion, as a counter anion, to the colloidal alunina in order to stabilize alunina particles to be positively charged. Although the colloidal alunina is not particularly limited with respect to pHi, it preferably has a pH of 2 to 6 from the viewpoint of the stability of a dispersion liquid. Moreover, also in the aforementioned method [1], when at least one of the inorganic particle chains (A) and the inorganic particles (B) is alunina and the mixed inorganic particle dispersion liquid is in a colloidal state, it is preferred to add an anion, such as chloride ion, sulfate ion, and acetate ion, to the mixed inorganic particle dispersion liquid.

[0134] In the aforementioned method [2], [3], [4], or [5], when the dispersion liquid of the inorganic particle chains (A) and the dispersion liquid of the inorganic particles (B) are colloidal silica, it is preferred to add a cation, such as ammonium ion, alkali metal ion, and alkaline earth metal ion, as a counter cation, to the colloidal silica in order to stabilize silica particles to be negatively charged. Although the colloidal silica is not particularly limited with respect to pH, it preferably has a pH of 8 to 11 from the viewpoint of the stability of a dispersion liquid. Moreover, also in the aforementioned method [1], when at least one of the inorganic particle chains (A) and the inorganic particles (B) is silica and the mixed inorganic particle dispersion liquid is in a colloidal state, it is preferred to add a cation, such as ammonium ion, alkali metal ion, and alkaline earth metal ion, to the mixed inorganic particle dispersion liquid.

[0135] The mixed inorganic particle dispersion liquid satisfies the following formulae (1) and (2):

\[
0.55 \leq \text{RVa} \leq 0.00
\]

\[
0.10 \leq \text{RVb} \leq 0.45
\]

wherein RVa is the ratio of the volume of the inorganic particle chains (A) to the total volume of the inorganic particle chains (A) and the inorganic particles (B) in the dispersion liquid, and RVb is the ratio of the volume of the inorganic particle chains (A) to the total volume of the inorganic particle chains (A) and the inorganic particles (B) in the dispersion liquid. In other words, RVa and RVb in the above formulae are equivalent to the volume fractions of the inorganic particle chains (A) and the volume fraction of the inorganic particles (B), respectively. If the inorganic particle chains (A) and the inorganic particles (B) are of the same chemical species, the volume fractions (RVa and RVb) of the inorganic particle chains (A) and the inorganic particles (B) are generally equal to the weight fractions of the inorganic particle chains (A) and the inorganic particles (B). Although the amount of the inorganic particle chains (A) and the inorganic particles (B) contained in the mixed inorganic particle dispersion liquid is not particularly limited, it is preferably from 1 to 20% by weight and more preferably from 3 to 10% by weight from the viewpoint of application property and dispersibility.

[0136] Additives, such as a surfactant and an organic electrolyte, may be added to the mixed inorganic particle dispersion liquid for the purpose of stabilization of the dispersion of inorganic particles, and so on. When the mixed inorganic particle dispersion liquid contains a surfactant, the content thereof is usually 0.1 parts by weight or less than 100 parts by weight of the dispersion medium. The surfactant to be used is not particularly restricted and examples thereof include anionic surfactants, cationic surfactants, nonionic surfactants, and amphoteric surfactants. The compounds provided below as examples can be used as the surfactant.

[0137] Surfactants include cationic surfactants, anionic surfactants, amphoteric surfactants, and nonionic surfactants, and there are no particular limitations. From the viewpoint of compatibility with resin and thermal stability, nonionic surfactants are preferably used.

[0138] Specific examples include: sorbitan based surfactants such as sorbitan fatty acid esters, e.g., sorbitan monopalmitate, sorbitan monostearate, sorbitan monopalmitate, sorbitan monostearate, sorbitan monooleate, and sorbitan dioleate, and alkylene oxide adducts thereof; glycerol-based surfactants such as glycerol fatty acid esters, e.g., glycerol monopalmitate, glycerol monostearate, diglycerol distearate, triglycerol monostearate, tetruglycerol dimonostearate, glycol monooleate, diglycerol monooleate, diglycerol sesquioleate, tetruglycerol monooleate, hexaglycerol monoleate, hexaglycerol trioleate, tetruglycerol triolette, tetruglycerol monooleate, and hexaglycerol monooleate, and their alkylene oxide adducts; polyethylene glycol-based surfactants such as polyethylene glycol monopalmitate and polyethylene glycol monostearate; alkylene oxide adducts of alkylphenols; esters of sorbitan/glycerol condensates with organic acids; polyoxyethylene alkylamines, such as polyoxyethylene (2 mol) stearylamine, polyoxyethylene (4 mol) stearylamine, polyoxyethylene (2 mol) stearylamine monostearate, polyoxyethylene (4 mol) laurylamine monostearate, and their fatty acid esters. Other examples include fluorine compounds having a perfluoroalkyl group, an α-hydrofluoroalkyl group, or the like (especially fluorine-containing surfactants), and silicone type compounds having an alkylsiloxane group (especially, silicone type surfactants). Specific examples of fluorine-containing surfactants include UNIYNE DS-403, DS-406, DS-401 (trade names) produced by Daikin Industries, Ltd., and SURFILON KC-40 (trade name) produced by SEI MI CHEMICAL Co., Ltd. Examples of silicone type surfactants include SH-3746 (trade name) produced by Toray Dow Corn ing Silicone Co.

[0139] When the mixed inorganic particle dispersion liquid contains an organic electrolyte, the content thereof is usually 0.01 parts by weight or less based on 100 parts by weight of the liquid dispersion medium. The compounds provided below as examples can be used as the organic electrolyte. The organic electrolyte to be used here is not particularly restricted if it has been dissolved in a liquid, and examples thereof include combinations of inorganic ions, such as $\text{BO}_3^{3-}, \text{F}^-, \text{PF}_6^-, \text{BF}_4^-, \text{AsF}_6^-, \text{SbF}_6^-, \text{ClO}_4^-, \text{AlF}_6^-, \text{AlCl}_4^-, \text{TaF}_6^-, \text{NbF}_6^-, \text{SiF}_6^{2-}, \text{CN}^-$, and $\text{F}^-(\text{HF})^n$, wherein n represents a number of from 1 to 4, with organic cations described below, combinations of organic anions with organic cations described below, and combinations of organic anions with inorganic cations, such as lithium ion, sodium ion, potassium ion, and hydrogen ion.
Organic cations are cationic organic compounds, examples of which include organic quaternary ammonium cations and organic quaternary phosphonium cations. Organic quaternary ammonium cations are quaternary ammonium cations having hydrocarbon groups selected from the group consisting of alkyl groups (having 1 to 20 of carbon atoms), cycloalkyl groups (having 6 to 20 of carbon atoms), aryl groups (having 6 to 20 of carbon atoms), and aralkyl groups (having 7 to 20 of carbon atoms), and organic quaternary phosphonium cations are quaternary phosphonium cations having hydrocarbon groups like those described above. The aforementioned hydrocarbon groups may have a hydroxyl group, an amino group, a nitrile group, a cyano group, a carboxyl group, an ether group, an aldehyde group, and so on.

Organic anions are anions containing hydrocarbon groups that may have a substituent, and examples thereof include anions selected from the group consisting of $\text{N}($SO$_2$)RF$\text{)}^\text{–}$, $\text{C}($SO$_2$)RF$\text{)}^\text{–}$, $\text{RCOO}^\text{–}$, and $\text{RISO}_3^\text{–}$ (RF represents a perfluoroalkyl group having 1 to 12 carbon atoms), and anions resulting from removal of active hydrogen atoms from organic acids, such as carboxylic acids, organic sulfonic acids, and organic phosphorus acids, or phenol.

An inorganic particle layer is formed on an inorganic particle composite body by applying a mixed inorganic particle dispersion liquid prepared using the aforementioned inorganic particle chains (A), inorganic particles (B), and dispersion liquid medium onto the inorganic particle composite body, and subsequently removing the liquid dispersion medium by suitable means from the applied mixed inorganic particle dispersion liquid. An antireflective inorganic particle composite body is thereby formed because that inorganic particle layer has an antireflecting function. The thickness of the inorganic particle layer with such an antireflecting function is not particularly limited. In the production of an antireflective inorganic particle composite body suitable for use as a surface layer of a display in order to effectively prevent the reflection of extraneous light inside the display, the thickness of the inorganic particle layer in the antireflective inorganic particle composite body is adjusted preferably to 50 to 150 nm and more preferably to 80 to 130 nm. The thickness of the inorganic particle layer can be adjusted by changing the amounts of the inorganic particle chains (A) and the inorganic particles (B) in the mixed inorganic particle dispersion liquid and the applied amount of the mixed inorganic particle dispersion liquid.

The method of applying the mixed inorganic particle dispersion liquid to the surface of the inorganic particle composite body is not particularly restricted, and the liquid can be applied by a wet coating method, such as gravure coating, reverse coating, brush roll coating, spray coating, kiss coating, die coating, dipping, and bar coating.

It is preferred to apply pretreatment, such as corona treatment, ozonization, plasma treatment, flame treatment, electron beam treatment, anchor coat treatment, and rinsing, to the surface of the inorganic particle composite body prior to the application of the mixed inorganic particle dispersion liquid to the inorganic particle composite body.

By removing the liquid dispersion medium from the mixed inorganic particle dispersion liquid applied to the inorganic particle composite body, an inorganic particle layer is formed on the inorganic particle composite body. The removal of the liquid dispersion medium can be executed, for example, by heating performed under normal pressure or reduced pressure. The pressure and the heating temperature to be used in the removal of the liquid dispersion medium may be chosen appropriately according to the materials to be used (that is, the inorganic particle chains (A), the inorganic particles (B), and the liquid dispersion medium). For example, when the dispersion medium is water, drying may be done at 50 to 80°C, preferably at about 60°C. By using the method of JP 2006-327187 A, it is possible to form an inorganic particle layer having an antireflection function and being superior in hardness on an inorganic particle composite body without performing treatment at high temperature higher than 200°C. This probably is because the formed inorganic particle layer has a structure in which the inorganic particles (B) are located in the gaps of the inorganic particle chains (A) and the inorganic particle chains (A) are bound via the inorganic particles (B).

To an antireflective inorganic particle composite body to be produced by the method of the present invention may be applied antifouling treatment, antistatic treatment, etc., if necessary. Antifouling treatment is a treatment for preventing fingerprint attachment or the like or making it easy to wipe away fingerprint soil and it can be done by coating the surface of an antireflective inorganic particle composite body with a hydrophobizing agent or the like or reacting a hydrophobizing agent to the surface of the composite body. By doing antistatic treatment, it is possible to prevent dusts from attaching for securing visibility and to prevent optical elements from being broken by discharge caused by electrification. Addition and lamination of the aforementioned surfactant or a conducting material is often done as antistatic treatment.

Although the contact angle with pure water of the surface of the antireflective inorganic particle composite body to be produced by the method of the present invention is not particularly limited, it is preferred, from the viewpoint of water proofing property and antifouling property, to be 10° or more and the contact angle with oleic acid is preferably 70° or more.

In one preferred embodiment of the method of the present invention, a glass layer is given to the surface of the structural body obtained by practicing the step of plastically deforming metal, and in another preferred embodiment of the method of the present invention, a step of giving a glass layer to the surface of the inorganic particle structural body is carried out prior to the execution of plastically deforming metal. Schematic diagrams of representative embodiments of an inorganic particle composite body with glass stacked are shown in FIGS. 17 and 18, but the present invention is not restricted to these. Moreover, a product in which some of the composite bodies illustrated in these representative schematic diagrams have been combined may also be used.

The inorganic particle composite body to be produced by the method of the present invention may be an inorganic particle composite body obtained by using an inorganic particle structural body having an inorganic particle layer in at least part of the surface thereof, plastically deforming the metal contained in the inorganic particle structural body, thereby filling the metal into at least some of the vacant spaces contained in the inorganic particle structural body without allowing the metal to ooze out to the surface of the inorganic particle structural body. That is, the inorganic particle composite body has, in at least part of the surface thereof, an inorganic particle layer derived from an inorganic particle structural body.
The inorganic particle composite body to be produced by the method of the present invention may be an inorganic particle composite body obtained by using an inorganic particle structural body having an inorganic particle layer in at least part of the surface thereof, plastically deforming the metal contained in the inorganic particle structural body, thereby filling the metal into at least some of the vacant spaces contained in the inorganic particle structural body and oozing the metal to the surface of the inorganic particle structural body. That is, the inorganic particle composite body has been covered on at least part of its surface with the metal contained in the inorganic particle structural body used.

It is preferred in the present invention to obtain an inorganic particle composite body having, in at least part of its surface, an inorganic particle layer derived from an inorganic particle structural body. Such an inorganic particle composite body is easy to stack with a glass layer. Although the method of stacking an inorganic particle composite body with glass is not particularly restricted, a method comprising bonding an inorganic particle composite body to glass via an adhesive, a method comprising coating an inorganic particle composite body with a glass precursor and then converting the glass precursor into glass, and a method comprising extrusion-laminating molten glass to an inorganic particle composite body are preferred as described below.

Examples of the method comprising bonding an inorganic particle composite body to glass via an adhesive include a method comprising applying an adhesive to a surface of the inorganic particle composite body, and then curing the adhesive with the applied portion stacked on glass, a method comprising applying an adhesive to glass, and then curing the adhesive with the applied portion stacked on the surface of an inorganic particle composite body, and a method comprising applying an adhesive to both glass and an inorganic particle composite body, and then curing the adhesive with their applied portions kept in contact with each other. The kind of the adhesive is not particularly restricted. Ceramics, water glass, rubber-based adhesives, epoxy type adhesives, acrylic adhesives, urethane type adhesives, and the like can be used. Use of a water-soluble adhesive is preferred in order to handle. Examples of the water-soluble adhesive include glue, starch, polyvinyl alcohol, polyvinylpyrrolidone, polyacrylamide, and acrylamide-diacetaion acrylamide copolymers. Moreover, the adhesive can contain additives such as a tackifier, a plasticizer, a filler, an antioxidant, a stabilizer, a pigment, a diffusion particles, a curing agent, and a solvent. The thickness of the adhesive layer, which is not particularly limited, is preferably up to 100 nm.

The composition, the production method and so on of glass that can be used are not particularly restricted. Soda glass, crystal glass, borosilicate glass, quartz glass, aluminosilicate glass, borate glass, phosphate glass, alkali-free glass, composite glass with ceramics, and the like can be used.

The method comprising coating an inorganic particle composite body with a glass precursor and then converting the glass precursor into glass is not particularly restricted. Examples thereof include heating by an oven or the like and local heating of the glass precursor by electromagnetic wave radiation or the like. Silane compounds, metal alkoxides, water glass, glass paste, and so on can be used as the glass precursor. Examples of the silane compounds include tetraethoxysilane, tetraethoxysilane, methyltrimethoxysilane, phenyltrimethoxysilane, vinyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane, p-styryltrimethoxysilane, 3-(meth)acryloxypropyltrimethoxysilane, 3-aminopropyltrimethoxysilane, 3-ureidopropyltrimethoxysilane, 3-chloropropyltrimethoxysilane, 3-mercaptopropyltrimethoxysilane, and 3-isocyanatopropyltrimethoxysilane.

Examples of the metal alkoxides include alkoxides of titanium (e.g., tetraisopropoxidef), alkoxides of zirconium (e.g., tetra-n-butoxyxirconium), alkoxides of aluminum (e.g., tri-is-butoxyaluminum), and condensates thereof. Such a condensate may be either a condensate of a single kind of compound or a complex condensate of two or more compounds. Silane compounds and metal alkoxides may be used in the form of a solution. The method of coating an inorganic particle composite body with a glass precursor is not particularly restricted. Wet coating methods, such as a reverse coating method, a die coating method, a dip coating method, a gravure coating method, a flexographic coating method, an ink jet coating method, and a screen printing method, are preferably used.

The method of extrusion-laminating molten glass to an inorganic particle composite body is not particularly restricted.

While the inorganic particle composite body to be produced by the method of the present invention is not particularly limited with respect to its voidage, the voidage is preferably 90% by volume or less, more preferably 50% by volume or less, even more preferably 30% by volume or less, particularly 10% by volume or less, and most preferably 5% by volume or less. When the voidage is higher than 90% by volume, strength as an inorganic particle composite body tends to be short. An inorganic particle composite body increases in strength as it decreases in voidage, and ideally, it preferably has no vacant spaces. When the shape of the inorganic particles of the inorganic particle composite body of the present invention is spherical, the voidage is 30% by volume or less, preferably 10% by volume or less, more preferably 5% by volume or less, and particularly preferably 1% by volume or less. When the shape of the inorganic particles of the inorganic particle composite body of the present invention is layer-form, the voidage is 50% by volume or less, preferably 30% by volume or less, more preferably 10% by volume or less, particularly preferably 5% by volume or less, and most preferably 1% by volume or less.

In place of the voidage, a volume fraction of a part in which vacant spaces have been filled with metal, calculated when the volume of a region where there are inorganic particles is defined as 100%, is represented by V (%), which is used as a measure of voidage. The larger the V, the less the vacant spaces in an inorganic particle layer, whereas the smaller the V, the more the vacant spaces. The range of V is 0<V<100, preferably 1<V<90, more preferably 10<V<95, and particularly preferably 50<V<90. Although there is no limitation on the method of determining V, V can be calculated by the following method when an inorganic particle structural body composed of a plate-shaped metal with plasticity and an inorganic particle layer stacked together has been hybridized to form an inorganic particle composite body as illustrated in FIG. 24.

While a region 14 (having a thickness D) of an inorganic particle composite body, in which inorganic particles are present, is etched gradually from a surface ds in which inorganic particles are present to a part de in which there is only metal,
the amount A (d) of element A derived from the inorganic particles and the amount B (d) of element B derived from the metal are measured at several points (for example, five points of ds, d1, d2, d3, and de in the depth direction). Taking d1, d2, and d3 on an abscissa and B (d)/A (d) on an ordinate, the depth d0 at which B (d)/A (d) becomes zero is determined by extrapolation.

V can be expressed by Formula (1) using d0 and D.

\[ V = \frac{100(\text{d}_0 - \text{d})}{\text{D}} \]  

**Formula (1)**

**[0161]** There is no limitation on the means for plastically deforming the metal. Examples thereof include a method of pressurizing an inorganic particle structural body and a method of heating an inorganic particle structural body; these may be used together. For example, there can be mentioned a method that comprises heating an inorganic particle structural body to plastically deform metal and then pressurizing the metal to further plastically deform, a method that comprises pressurizing an inorganic particle structural body to plastically deform metal and then heating the metal to further plastically deform, a method that comprises performing heating and pressurizing simultaneously to plastically deform metal in an inorganic particle structural body. As a method of plastically deforming metal, a method of at least pressurizing an inorganic particle structural body is preferred. Examples of the pressurizing method include a pressing method comprising pressurizing an inorganic particle structural body while sandwiching it between plates, a roll pressing method by which it can be pressurized continuously while nipping it between rolls, and a method comprising applying a static pressure while placing it in a liquid. The pressure is not limited as far as it is higher than the atmospheric pressure, and it depends on the degree of the plasticity of the metal. That is, a low pressure can be used when softening progresses and a large permanent strain is produced by a low stress, whereas a high pressure is needed when a high stress is needed. The pressure is for example 0.1 kgf/cm² or more, preferably 1 kgf/cm² or more, more preferably 10 kgf/cm² or more, and particularly preferably 100 kgf/cm² or more. The number of times of pressurization is arbitrary and pressurizing operations under two or more conditions may be combined.

**[0162]** Examples of the method of heating an inorganic particle structural body to plastically deform metal include a method comprising heating the whole of the inorganic particle structural body, and a method comprising locally heating the metal in the inorganic particle structural body. Examples of the method of heating the whole include a method comprising heating a structural body in a heating atmosphere using an oven, a heater, or the like, a method comprising bringing a structural body into contact with a heat medium, such as a heated metal plate, a method comprising bringing a structural body into contact with a hot roll and then pressurizing it, and a method comprising bringing it into contact with a hot roll, and examples of the method of locally heating include a method comprising heating it by irradiation with an electromagnetic wave, such as an infrared radiation, a laser, a microwave, irradiation in a high quantity of light in a very short time (the flash-annealing method), and radiation, such as an electron beam, and a method comprising keeping only an arbitrary portion of an inorganic particle structural body in contact with a heat medium and simultaneously cooling other portion. For metal, induction heating using a magnetic force line and the aforementioned irradiation with an electromagnetic wave are preferably used. The temperature, pressure, and time of pressing are not particularly limited because they vary depending upon the property of metal, and conditions suitable for the metal to be filled into vacant space portions are used. There is no limitation also on a pressurizing condition and it is determined according to the property of metal. That is, it is preferred to take conditions of pressurizing time, pressurizing temperature, pressure and means of pressurization under and by which inorganic particles substantially fail to plastically deform and metal plastically deforms and can fill vacant spaces of an inorganic particle structural body or an inorganic particle structural body with an inorganic particle layer stacked. The temperature of heating an inorganic particle structural body is not particularly limited because it varies depending upon the property of metal, and conditions suitable for the metal to be filled into vacant space portions are used.

**[0163]** In order to plastically deform metal more easily, auxiliary means may be added. The auxiliary means referred to herein means a method of increasing the plasticity of the metal having plasticity. Examples of the method of increasing the plasticity of metal having plasticity include a method comprising softening the metal using a chemical substance and a method comprising increasing the affinity or the slip coefficient at the interface of metal and a vacant space.

**[0164]** There is no particular limitation on the shape of inorganic particle composite bodies to be produced by the method of the present invention and a shape according to a required function and an intended application is used. Examples thereof include a tubular shape such as film and sheet, a rod-like shape, a fibrous shape, a spherical shape, and a three-dimensional structure shape. In the case that the intended application is a flat-panel display, a flexible display, or the like, it is preferred that the shape of the inorganic particle composite body of the present invention also be a film-like shape. In this case, the thickness of the inorganic particle composite body, which is not particularly limited, is 100 µm or less, preferably 10 µm or less, more preferably 5 µm or less, and particularly preferably 1 µm or less. In the case that flexibility or the like is further required, the thickness of the inorganic particle composite body is 5 µm or less, preferably 1 µm or less, more preferably 0.5 µm or less, and particularly preferably 0.2 µm or less. When the thickness of an inorganic particle composite body is greater than 100 µm, the composite body tends to become brittle, whereas when it is 0.01 µm or less, hardness tends to be difficult to develop. It is also permitted to further stack a resin layer or a metal thin film on the inorganic particle composite body to be produced by the method of the present invention. The inorganic particle composite body of the present invention can develop various properties depending upon the kind of inorganic particles or metal. When metal fills vacant spaces of an inorganic particle structural body in a very high filling ratio, it becomes possible to form an inorganic particle composite body superior in substance barrier property.

**EXAMPLES**

**[0165]** The present invention will be described in detail below with reference to Examples, to which the present invention is not limited.

**[0166]** Main materials used are as follows.

*Inorganic Particle*

**[0167]** SNOWTEX (registered trademark) ST-XS (colloidal silica produced by Nissan Chemical Industries, Ltd.; aver-
average particle diameter: 4 to 6 mm; solid concentration: 20% by weight), which is hereinafter referred to as “ST-XS.”

Kunipia G (registered trademark) (inorganic layered compound produced by KUNIMINE INDUSTRIES CO., LTD.; average particle diameter: 300 nm)

SNOWTEX (registered trademark) 20 (colloidal silica produced by Nissan Chemical Industries, Ltd.; average particle diameter: 20 nm; solid concentration: 20% by weight)

ALUMINASOL. (registered trademark) 520 (colloidal alumina produced by Nissan Chemical Industries, Ltd.; average particle diameter: 20 nm; solid concentration: 20% by weight)

Sumecet SA (registered trademark) (inorganic layered compound produced by KUNIMINE INDUSTRIES CO., LTD.; average particle diameter: 20 nm)

Silver particles (silver colloid “MG-101” produced by Ishihara Sangyo Kaisha, Ltd.; average particle diameter: 10 nm; solid concentration: 50 wt %)

Teonex (registered trademark) (polyethylene naphthalate film produced by Teijin DuPont Limited; thickness: 125 μm)

Coating Liquid A

A coating liquid prepared by mixing and stirring MG-101 (3.6 g) in a 3 wt % aqueous solution (12 g) of Kunipia G.

Coating Liquid B

A coating liquid prepared by mixing and stirring MG-101 (0.6 g) in a 3 wt % aqueous solution (4 g) of Kunipia G.

Coating Liquid C

A coating liquid prepared by mixing and stirring ion exchange water (79.584 g), a 1 wt % Smeecton SA solution (9.0 g), ALUMINASOL 520 (9,000 g) and SNOWTEX 20 (2.4 g), sodium caprylate (0.014 g), and sodium p-toluene sulfonate (0.002 g).

Coating Liquid D

A coating liquid prepared by mixing and stirring MG101 (4.0 g), ST-XS (4.0 g), and pure water (2.0 g).

Coating Liquid E

A coating liquid prepared by mixing and stirring pure water (15 g) and glycerol (5.0 g).

Coating Liquid F

A coating liquid prepared by mixing and stirring an antifouling coating (OPTOOL (registered trademark) DSX; produced by Daikin Industries, Ltd.) (1.0 g), and fluorine oil (DEMNAM (registered trademark) SOLVENT; produced by Daikin Industries, Ltd.) (199.0 g).

The methods of evaluating properties are as follows.

Degree of Scratch Resistance

Using steel wool (#0000, produced by Nippon Steel Wool Co., Ltd.), the surface of an inorganic particle composite body was rubbed ten strokes under a load of 125 to 500 gf/cm² and then the presence of scratches was checked visually. The case that there were 10 or less scratches was judged as Level 1, the case that there were more than 10 but not more than 20 scratches was judged as Level 2, and the case that there were more than 20 scratches was judged as Level 3.

Electron Microscopic Observation

Samples were subjected to FIB cutting, and then observation by a transmission electron microscope (manufactured by Hitachi, Ltd., model: H900) was carried out for Examples 1, 2, and Comparative Example 1.

Oxygen Permeability

Oxygen permeability was measured by using an oxygen permeability analyzer OX-TRAN manufactured by MOCON (measurement conditions: 23°C, 0%RH).

Example 1

Coating liquid A was applied to a substrate by using a bar coater (manufactured by Dai-ichi Rika Co., Ltd., wire gauge: #8) and was dried at 23°C, so that inorganic particle structural body (1) was obtained. The structural body was sandwiched between a dielectric heat processor and an iron plate and a weight of 1 kg was placed thereon. Then, pressurizing treatment was applied with the portion of MG101 locally heated (dielectric heating conditions: 1000 W, 15 minutes), so that inorganic particle composite body (1) was obtained. The oxygen permeability of the inorganic particle structural body (1) was 4 cc/m²/Da and the oxygen permeability of the inorganic particle composite body was 0.5 cc/m²/Da; therefore oxygen barrier property was developed with a particle film by hybridization. Observation by TEM of a section of the film confirmed that there was a structure such that there were inorganic particle portions and metal particles in the inorganic particle structural body and vacant spaces had been filled up with metal portions melted and plastically deformed through local heating and pressurization. When the inorganic particle composite body (1) was rubbed ten strokes with a wiping cloth (commercial name: KIMTOWEL, produced by NIPPON PAPER CRECIA Co., LTD.). There was no collapsed composite body. A section of the inorganic particle composite body (1) is shown in FIG. 25.

Comparative Example 1

When the inorganic particle structural body (1) was rubbed ten strokes with KIMTOWEL, part of the structural body collapsed and the substrate surface was exposed. A sectional TEM photograph of the inorganic particle structural body (1) is shown in FIG. 26.

Example 2

Coating liquid B was applied to a substrate by using a bar coater (manufactured by Dai-ichi Rika Co., Ltd., wire
gage: #4) and was dried at 23°C, so that inorganic particle structural body (2) was obtained. The thickness of the inorganic particle structural body is 0.2 μm. The inorganic particle structural body (2) was preheated at 160°C for 3 minutes by using a compression molding machine and then pressed under a certain condition, i.e., primary compression: at 160°C, 370 kgf/cm², for 3 minutes, secondary compression: at 30°C, 370 kgf/cm² for 3 minutes, so that inorganic particle composite body (2) was obtained. The oxygen permeability of the inorganic particle structural body (2) was 0.3 cc/m²·Day and the oxygen permeability of the inorganic particle composite body (2) was 0.9 cc/m²·Day; therefore oxygen barrier property was developed with a film by hybridization. Observation by TEM of a section of the film confirmed that there was a structure such that there were inorganic particle portions and metal particles in the inorganic layered compound and vacant spaces had been filled up with metal portions melted and plastically deformed. A sectional TEM photograph of the inorganic particle composite body (2) of Example 2 is shown in FIG. 27.

Example 3

[0188] The inorganic particle structural body (1) was subjected to pressurizing treatment while applying local heating treatment (dielectric heating conditions: 1400 W, 9 minutes) to silver portions in the same manner as in Example 1, so that inorganic particle composite body (3) was obtained. The oxygen permeability of the inorganic particle composite body (3) was 0.3 cc/m²·Day and therefore oxygen barrier property was developed with a film by hybridization. When the inorganic particle composite body (3) was rubbed ten strokes with KIMTOWEL, no collapse of the composite body was observed.

Example 4

[0189] Coating liquid C was applied to a support by using a bar coater (manufactured by Dai-ichi Rika Co., Ltd., wire gage: #4) and was dried at 23°C, so that inorganic particle structural body (3) was obtained. Coating liquid D was applied to the inorganic particle structural body (3) by using a bar coater (manufactured by Dai-ichi Rika Co., Ltd., wire gage: #1) and was dried at 23°C, so that inorganic particle structural body (4) was obtained. The inorganic particle structural body (4) obtained above was pressed by using a compression molding machine (manufactured by SHINTO Metal Industries Corporation) under a certain condition, i.e., primary compression: at 200°C, 70 kgf/cm², for 5 minutes, secondary compression: at 30°C, 70 kgf/cm² for 5 minutes, so that inorganic particle composite body (4) was obtained. The inorganic particle composite body (4) had a degree of scratch resistance under a 30 g load of Level 1 and a water contact angle of 29°.

Comparative Example 2

[0190] The inorganic particle structural body (4) had a degree of scratch resistance under a 30 g load of Level 3 and a water contact angle of 20°.

Example 5

[0191] After applying corona treatment to the inorganic particle composite body (4), coating liquid E was applied by using a bar coater (manufactured by Dai-ichi Rika Co., Ltd., wire gage: #1), so that inorganic particle composite body (5) was obtained. The inorganic particle composite body (5) had a degree of scratch resistance under a 30 g load of Level 1 and a water contact angle of 4°.

Example 6

[0192] The inorganic particle composite body (4) was immersed in coating liquid F and was dried at 23°C, so that inorganic particle composite body (6) was obtained. The inorganic particle composite body (6) obtained above had a degree of scratch resistance under a 30 g load of Level 1 and a water contact angle of 103°.

INDUSTRIAL APPLICABILITY

[0193] The method of the present invention is superior as a method for producing a metal-inorganic particle composite body superior in strength and hardness in which metal having plasticity has been filled in vacant space portions. It can exhibit various characteristics depending upon the kinds of the inorganic particles and the metal. For example, when the metal having plasticity is metal, such effects as electrical conductivity, paramagnetism, ferromagnetism, light reflectibility, light absorptivity by plasmon resonance, rigidity, low linear expansion, ductility, heat resistance, thermal conductivity, chemistry activity, and/or catalytic activity are exhibited. Because of this, when an inorganic particle composite body is formed on a film-shaped substrate or into a film, it is possible to be applied to antistatic films, electric conduction films, transparent electric conduction films, electromagnetic wave shielding films, magnetic films, reflection films, ultraviolet shielding films, light diffusing films, antireflection films, antiglare films, hardcoat films, polarizing films, retardation films, light diffusing films, front plates of flat panel displays, windows of portable displays (e.g., cellular phones), films for flexible transparent substrates, gas barrier films, heat conduction films, heat radiation films, antibacterial films, catalyst support films, capacitor electrode films, electrode films of secondary batteries, electrode films of fuel cells, and so on. Moreover, when the inorganic particles are made of a clay mineral, the composite body is extremely superior in substance barrier property due to a maze effect caused by a high aspect ratio of the clay mineral. For this reason, the inorganic particle composite body is expected to have properties like those of transparent metal foil when it has been formed on a film-shaped substrate or into a film and, therefore, it is particularly useful for films for flexible transparent substrates, gas barrier films, transparent electric conduction films, and the like. Because of superior in hardness, an inorganic particle composite body that is produced by the method of the present invention is used for optical information media such as a read only optical disk, an optical recording disk, and a magnetooptical recording disk, and display medium members and optical members such as a display screen of a personal computer, a flexible display, an electronic paper, and a contact lens for the purpose of preventing a surface from scratching.

1. A method for producing an inorganic particle composite body formed of a mixture of a plastically deformable metal, and inorganic particles that do not plastically deform under a condition under which the metal plastically deforms, wherein the method comprises:

step of preparing an inorganic particles structural body that is formed of a mixture of the metal and the inorganic particles and that contains a vacant space therein, and
a step of plastically deforming the metal in the structural body.

2. The method according to claim 1, wherein the volume of the inorganic particles is larger than the volume of the metal in the inorganic particle structural body.

3. The method according to claim 1, wherein the step of plastically deforming the metal is a step of plastically deforming the metal by pressurizing the inorganic particle structural body.

4. The method according to claim 1, wherein the step of plastically deforming the metal is a step of plastically deforming the metal by applying an electromagnetic wave to the inorganic particle structural body.

5. The method according to claim 1, wherein the method further comprises a step of applying hydrophilization to the surface of the structural body produced by carrying out the step of plastically deforming the metal.

6. The method according to claim 1, wherein the method further comprises a step that is a step of applying hydrophilization to the surface of the inorganic particle structural body and that is carried out before carrying out the step of plastically deforming the metal.

7. The method according to claim 1, wherein the method further comprises a step of applying hydrophilization to the surface of the structural body produced by carrying out the step of plastically deforming the metal.

8. The method according to claim 1, wherein the method further comprises a step that is a step of applying hydrophobization to the surface of the inorganic particle structural body and that is carried out before carrying out the step of plastically deforming the metal.

9. The method according to claim 1, wherein the method further comprises a step of applying antireflecting treatment to the surface of the structural body produced by carrying out the step of plastically deforming the metal.

10. The method according to claim 1, wherein the method further comprises a step that is a step of applying antireflecting treatment to the surface of the inorganic particle structural body and that is carried out before carrying out the step of plastically deforming the metal.

11. The method according to claim 1, wherein the method further comprises a step of giving a glass layer to the surface of the structural body produced by carrying out the step of plastically deforming the metal.

12. The method according to claim 1, wherein the method further comprises a step that is a step of giving a glass layer to the surface of the inorganic particle structural body and that is carried out before carrying out the step of plastically deforming the metal.

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