

[TITLE OF THE INVENTION]

Coating containing high-purity graphene and production method for said coating

[BACKGROUND OF THE INVENTION]

[Field of the Invention]

[0001]

The present invention relates to a coating containing high-purity graphene and a production method for the coating. An object thereof is to provide a coating having a fluororesin coating layer containing fluororesin and high-purity graphene, that has a very small amount of metal seepage and has antistatic property, and a production method for the aforementioned coating.

[Description of Related Art]

[0002]

Fluororesin is excellent in corrosion resistance, chemical resistance, permeation resistance, heat resistance, durability, and the like, and is used as a coating film on a substrate consisting of metal and the like.

[0003]

A process for manufacturing electronic components and precision instruments represented by semiconductors includes steps of polishing, washing, and heating materials, and the like. Therefore, devices for manufacturing electronic components and precision instruments that are coated with fluororesin coatings excellent in corrosion resistance and the like, have been known (Patent Document 1).

[0004]

Mixing therewith fillers (filler materials) for the purpose of improving corrosion resistance and the like of fluororesin films has also been known.

[0005]

Metals are often used for such fillers. For example, Patent Document 2 discloses that an alkali metal is contained as a filler for the purpose of improving durability.

[0006]

And, since fluororesin coatings are generally insulative substances, when they are in contact with liquids or powders, which are fluids, and friction occurs, static electricity may be generated and static breakdown may occur in the coatings. Furthermore, when the generated static electricity is accumulated, there exists a risk that organic solvents or the like may be ignited or exploded thereby. In order to solve this problem, the coatings may be mixed with fillers (filler materials) to provide antistatic property.

[0007]

[Patent Document 1] Japanese Unexamined Patent Application Publication No. 2013-071341

[Patent Document 2] Japanese Unexamined Patent Application Publication No. 2000-297231

[BRIEF SUMMARY OF THE INVENTION]

[Problem to be Solved by the Invention]

[0008]

Corrosion resistance, chemical resistance, permeation resistance, heat resistance as well as durability, antistatic property, and the like are improved when fluororesin contains a filler. In contrast, in devices for manufacturing electronic components and precision instruments (e.g., tanks for semiconductor manufacturing devices, etc.) coated with such fluororesin, there arises a problem that metallic components of the filler seep out as metal ions to treatment liquids used in the process for manufacturing electronic components and precision instruments and remain as impurities in the electronic components and precision instruments, which results in degrading cleanliness of the electronic components and precision instruments. Or, when chemical reaction tanks (reactors), filtration tanks, mixing tanks comprising impellers, reservoirs, distillation tanks, or the like are coated with such fluororesin, there arises a problem that metallic components seep out as metal ions to chemicals in the tanks.

[0009]

The present invention, made in view of the above problems, is to provide a coating having a small amount of metal seepage while having excellent antistatic property, corrosion resistance, chemical resistance, permeation resistance, heat resistance, durability, and the like, and a production method for the aforementioned coating.

[Means for Solving the Problem]

[0010]

The coating of the present invention relates to a coating comprising: a substrate; a primer layer formed on the surface of the substrate; and one or more fluororesin coating layers formed on the primer layer, wherein the one or more fluororesin coating layers contain fluororesin and high-purity graphene.

[0011]

According to the related coating, it is possible to provide a coating having a small amount of metal seepage while having excellent antistatic property, corrosion resistance, chemical resistance, permeation resistance, heat resistance, and durability.

[0012]

The above-mentioned high-purity graphene used in the coating is 1 or 2 nm thick or less than or equal to 5 nm thick in the thickness direction, and it may be from 10 nm to 20 nm thick. Furthermore, the particles thereof have an average particle diameter of from 1 μm to 100 μm .

[0013]

The above-mentioned high-purity graphene used in the coating has a relatively small oxygen content, and it preferably has an oxygen content of less than 5% by mass and it may have an oxygen content of less than 1% by mass.

[0014]

The above-mentioned high-purity graphene used in the coating has a surface area of at least from 30 to 60 m^2/g or it may have a surface area of 80 m^2/g and it could even have a surface area of from 100 or 120 m^2/g to 150 m^2/g when the specific surface area is measured based on the Brunauer-Emmett-Teller method (hereinafter, referred to as BET specific surface area). For example, the BET specific surface area may be from 300 m^2/g to 750 m^2/g .

[0015]

The above-mentioned high-purity graphene contained in the fluororesin coating layers has an amorphous carbon content of less than or equal to 5.0% by mass. The content is preferably less than or equal to 5.0% by mass, and more preferably less than or equal to 3.0% by mass.

[0016]

Amorphous carbon is an incomplete component of graphite without a crystal structure, and is in a form in which carbon atoms are connected to each other randomly. Amorphous carbon is also a component to become a precursor of graphite as it burns at more than or equal to 600°C and tends to form a crystal structure at a higher temperature; and amorphous carbon, the incomplete component of graphite, burns and volatilizes at less than 600°C, from around 300°C to around 530°C.

[0017]

Theoretically, graphite having a crystal structure burns only at a high temperature; however, often each particle does not have a complete crystal structure at the edges, and in particular, when each particle has a small particle diameter, it may burn from these edges. Since there exist many end groups other than carbon in these parts, if graphite comprises a large amount of this amorphous carbon component, graphite also comprises a large amount of end groups, so that the content other than carbon also increases.

[0018]

The above-mentioned high-purity graphene contained in the fluororesin coating layer has an amorphous carbon content of less than or equal to 5.0% by mass, and when suitable high-purity graphene is used, it becomes possible to achieve a reduction in the amount of metal seepage while providing antistatic property.

[0019]

The above-mentioned high-purity graphene contained in the fluororesin coating layer is mixed with PET resin and solvent at a ratio of high-purity graphene: PET resin: solvent = 1:2:40 and stirred with a stirrer, which then is applied as a coating such that the thickness will be 15 μm and preferably, the surface resistivity measured by the 4-Probe

method after being dried will be from $1.0 \times 10^2 \text{ } \Omega/\text{sq}$ to $4.0 \times 10^2 \text{ } \Omega/\text{sq}$. And, the surface resistivity could even be less than or equal to $1.0 \times 10^2 \text{ } \Omega/\text{sq}$.

[0020]

It is possible to improve antistatic property of the coating and further prevent breakage due to static electricity by using high-purity graphene that satisfies the above-mentioned conditions.

[0021]

The coating has a volume resistivity of less than $10^8 \text{ } \Omega$, and has antistatic property.

[0022]

The coating may further be provided with a top layer formed on the above-mentioned fluororesin coating layer.

[0023]

It becomes possible to further reduce the amount of metal seepage by forming a suitable top layer. The top layer can also prevent separation of high-purity graphene from the fluororesin coating layer.

[0024]

The above-mentioned top layer preferably contains one or more types of fluororesin selected from the group consisting of PTFE, PFA, FEP, ethylene tetrafluoroethylene copolymer (ETFE), polychlorotrifluoroethylene (PCTFE), and polyvinylidene fluoride (PVDF). Without limitation, more preferably the above-mentioned top layer has a thickness of from $10 \text{ } \mu\text{m}$ to $300 \text{ } \mu\text{m}$.

[0025]

It is possible to achieve further improvements in corrosion resistance, chemical resistance, permeation resistance, heat resistance, durability, and the like as well as a further reduction in the amount of metal seepage by having a suitable top layer containing one or more types of fluororesin selected from the group consisting of PTFE, PFA, FEP, ethylene tetrafluoroethylene copolymer (ETFE), polychlorotrifluoroethylene (PCTFE), and polyvinylidene fluoride (PVDF).

[0026]

The top layer should be selected carefully, since if an unsuitable top layer is selected, it cannot prevent a reduction in the amount of metal seepage and it could become a contamination factor. Also, the top layer affects the performance such as corrosion resistance, chemical resistance, permeation resistance, heat resistance, durability and the like. Furthermore, if the thickness is not sufficient, the top layer cannot sufficiently prevent separation of high-purity graphene from the fluororesin coating layer. If the thickness is excessive, potential metal seepage due to the top layer increases.

[0027]

The above-mentioned fluororesin coating layer preferably contains from 80% by mass to 99% by mass of one or more types of fluororesin selected from the group consisting of PTFE, PFA, FEP, ethylene tetrafluoroethylene copolymer (ETFE), polychlorotrifluoroethylene (PCTFE), and polyvinylidene fluoride (PVDF), and from 20% by mass to 1% by mass of high-purity graphene.

[0028]

If the amount of high-purity graphene component is insufficient relative to the entire fluororesin coating layer, it is not possible to achieve desired antistatic property as well as corrosion resistance, chemical resistance, permeation resistance, heat resistance, durability, and the like. And, if the amount of the component is excessive, it cannot be well formed into a film.

[0029]

The above-mentioned fluororesin coating layer preferably has a thickness of from 200 μm to 2000 μm .

[0030]

If the thickness of the fluororesin coating layer is not sufficient, it is not possible to achieve corrosion resistance, chemical resistance, permeation resistance, heat resistance, and durability. If the thickness is excessive, bubbles are formed in the coating, or cracks or asperities are formed on the surface of the coating, which may result in loss of smoothness.

[0031]

The above-mentioned substrate is preferably steel, aluminum, nickel, chromium, manganese, molybdenum, titanium, and niobium, or alloy consisting of two or more types selected therefrom.

[0032]

These metals can suitably be used, since they are easy to roughen and easy to process and are less likely to deform and the like when baked.

[0033]

The above-mentioned primer layer is formed of a primer preferably containing from 65% by mass to 85% by mass of one or more types of fluororesin selected from the group consisting of PTFE, PFA, and FEP; and from 35% by mass to 15% by mass of chromic acid and phosphoric acid.

[0034]

It becomes possible to improve adhesion to the substrate when the primer comprises 15% by mass or more of chromic acid and phosphoric acid. If the primer comprises more than 35% by mass of chromic acid and phosphoric acid, the primer layer cannot be well formed into a film and is not preferable.

[0035]

When the coating is immersed in 200 ml of 3.6% by mass of hydrochloric acid for 24 hours, the amount of metal seepage is preferably very close to 0. Also, it is discovered that if the amount of metal seepage is, without limitation, from 3.0 μg to 15 μg per square meter surface area, the coating can generally preferably be adopted.

[0036]

The reason is that, if the coating has a very small amount of metal seepage such as from 3.0 μg to 15 μg , the problem is less likely to arise that metallic components of the filler seep out as metal ions to treatment liquids used in the process for manufacturing electronic components and precision instruments and remain as impurities in the electronic components and precision instruments, which results in degrading cleanliness of the electronic components and precision instruments. By solving this problem, the coating can suitably be used for devices for manufacturing electronic components and precision instruments (e.g., tanks for semiconductor manufacturing devices, etc.) without

spreading metal contamination upon manufacturing precision electronic instrument components used for electronic instruments and precision instruments.

[0037]

The above-mentioned substrate may be used for one or more types selected from the group consisting of members constituting devices for manufacturing electronic components and precision instruments (e.g., tanks for semiconductor manufacturing devices), chemical reaction tanks (reactors), filtration tanks, mixing tanks comprising impellers, reservoirs, or distillation tanks, or the like.

[0038]

Related is a production method for the coating of the present invention, wherein the method comprises steps of: degreasing to remove oil from the surface of a substrate; blasting to roughen the surface of the substrate after degreasing; forming a primer layer through applying a primer on the surface of the substrate after blasting, and drying or baking it to form a primer layer; and forming a fluororesin coating layer through applying a coating composition containing high-purity graphene and fluororesin on the primer layer, baking it, and performing the formation of the fluororesin coating layer one or more times.

[0039]

According to the related production method for the coating, it is possible to form a coating with high adhesion on the surface of the substrate since the method comprises the steps of degreasing, blasting, and forming a primer layer. It is also possible to produce a coating having a small amount of metal seepage while having excellent antistatic property, corrosion resistance, chemical resistance, permeation resistance, heat resistance, and durability, since the fluororesin coating layer is formed from a coating composition containing high-purity graphene and fluororesin. Furthermore, since the step of forming a fluororesin coating layer is performed one or more times, it is possible to form a fluororesin coating layer in a desired thickness.

[0040]

The above-mentioned high-purity graphene contained in the fluororesin coating layer comprises an amorphous carbon content of less than or equal to 5.0% by mass. The

content is preferably less than or equal to 5.0% by mass, and more preferably less than or equal to 3.0% by mass.

[0041]

The above-mentioned high-purity graphene contained in the fluororesin coating layer has an amorphous carbon content of less than or equal to 5.0% by mass, and when suitable high-purity graphene is used, it becomes possible to achieve a reduction in the amount of metal seepage while providing antistatic property.

[0042]

The above-mentioned high-purity graphene contained in the fluororesin coating layer is mixed with PET resin and solvent at a ratio of high-purity graphene: PET resin: solvent = 1:2:40 and stirred with a stirrer, which then is applied as a coating such that the thickness of the coating will be 15 μm and preferably, the surface resistivity measured by the 4-Probe method after being dried will be from $1.0 \times 10^2 \Omega/\text{sq}$ to $4.0 \times 10^2 \Omega/\text{sq}$. And, the surface resistivity could even be less than or equal to $1.0 \times 10^2 \Omega/\text{sq}$.

[0043]

It is possible to improve antistatic property of the coating and further prevent breakage due to static electricity by using high-purity graphene that satisfies the above-mentioned conditions.

[0044]

The coating has a volume resistivity of less than $10^8 \Omega$, and has antistatic property.

[0045]

It is preferable to further comprise a step of forming a top layer through applying fluororesin on the fluororesin coating layer and baking it to form a top layer.

[0046]

It becomes possible to produce a coating with a further reduced amount of metal seepage by comprising the step of forming an appropriate top layer. It also becomes possible to produce a coating that will prevent separation of high-purity graphene from the fluororesin coating layer by comprising the step of forming a top layer.

[0047]

In the above-mentioned step of forming a top layer, preferably one or more types of fluororesin selected from the group consisting of PTFE, PFA, FEP, ethylene tetrafluoroethylene copolymer (ETFE), polychlorotrifluoroethylene (PCTFE), and polyvinylidene fluoride (PVDF) are applied. In the above-mentioned step of forming a top layer, the above-mentioned top layer is formed preferably in a thickness of from 10 μm to 300 μm .

[0048]

It becomes possible to produce a coating that is more excellent in corrosion resistance, chemical resistance, permeation resistance, heat resistance, durability, and the like, and has a small amount of metal seepage, by applying one or more types of fluororesin selected from the group consisting of PTFE, PFA, FEP, ethylene tetrafluoroethylene copolymer (ETFE), polychlorotrifluoroethylene (PCTFE), and polyvinylidene fluoride (PVDF), and forming a suitable top layer. Also, if the thickness is not sufficient, the top layer cannot sufficiently prevent separation of high-purity graphene from the fluororesin coating layer. If the thickness is excessive, potential metal seepage due to the top layer increases.

[0049]

In the above-mentioned step of forming a fluororesin coating layer, the above-mentioned fluororesin coating layer is formed from a coating composition preferably containing from 80% by mass to 99% by mass of one or more types of fluororesin selected from the group consisting of PTFE, PFA, FEP, ethylene tetrafluoroethylene copolymer (ETFE), polychlorotrifluoroethylene (PCTFE), and polyvinylidene fluoride (PVDF), and from 20% by mass to 1% by mass of high-purity graphene.

[0050]

If the amount of high-purity graphene component is insufficient relative to the entire fluororesin coating layer, it is not possible to achieve desired antistatic property as well as corrosion resistance, chemical resistance, permeation resistance, heat resistance, durability, and the like. And, if the amount of the component is excessive, it cannot be well formed into a film.

[0051]

In the above-mentioned step of forming a fluororesin coating layer, the above-mentioned fluororesin coating layer is formed preferably in a thickness of from 200 μm to 2000 μm .

[0052]

If the thickness of the fluororesin coating layer is not sufficient, it is not possible to achieve corrosion resistance, chemical resistance, permeation resistance, heat resistance, and durability. If the thickness is excessive, bubbles are formed in the coating, or cracks or asperities are formed on the surface of the coating, which may result in loss of smoothness.

[0053]

The above-mentioned substrate is preferably steel, aluminum, nickel, chromium, manganese, molybdenum, titanium, and niobium, or alloy consisting of two or more types selected therefrom.

[0054]

These metals can suitably be used, since they are easy to roughen in the step of blasting and are less likely to deform and the like when baked.

[0055]

In the above-mentioned step of forming a primer layer, the above-mentioned primer layer is formed from a primer preferably containing from 65% by mass to 85% by mass of one or more types of fluororesin selected from the group consisting of PTFE, PFA, and FEP; and from 35% by mass to 15% by mass of chromic acid and phosphoric acid.

[0056]

It becomes possible to improve adhesion between the substrate and the primer layer by using the primer comprising 15% by mass or more of chromic acid and phosphoric acid. If a primer comprising more than 35% by mass of chromic acid and phosphoric acid is used, the primer layer cannot be well formed into a film and is not preferable.

[0057]

The above-mentioned substrate may be used for one or more types selected from the group consisting of members constituting devices for manufacturing electronic

components and precision instruments (e.g., tanks for semiconductor manufacturing devices), chemical reaction tanks (reactors), filtration tanks, mixing tanks comprising impellers, reservoirs, or distillation tanks, or the like.

[Effects of the Invention]

[0058]

According to the coating containing high-purity graphene and the production method for the coating of the present invention, it is possible to provide a coating having a small amount of metal seepage while having excellent antistatic property, corrosion resistance, chemical resistance, permeation resistance, heat resistance, durability, and the like, and a production method for the aforementioned coating.

[BRIEF DESCRIPTION OF DRAWINGS]

[0059]

[Fig. 1] Fig. 1 is a structural cross-sectional view of a coating in accordance with a first embodiment of the present invention.

[Fig. 2] Fig. 2 is a cross-sectional view illustrating a mixing tank in which a coating in accordance with an embodiment of the present invention is used.

[Fig. 3] Fig. 3 is a structural cross-sectional view of a coating in accordance with a second embodiment of the present invention.

[Fig. 4] Fig. 4 is a schematic plan view of a substrate coated with a coating in accordance with an embodiment of the present invention, used for a corrosion test of a coating, and it shows the state when adhesion is evaluated after the corrosion test.

[Detailed Description of the Invention]

[0060]

Hereinafter, a coating containing high-purity graphene and a production method for the coating in accordance with the present invention are described in detail.

[0061]

The only term, coating, described herein refers to a coating in accordance with the present invention.

[0062]

Also, a coating composition herein refers to a coating composition used for forming a fluororesin coating layer.

[0063]

<First Embodiment>

Fig. 1 is a cross-sectional view of a coating (10) in accordance with a first embodiment. The coating (10) in accordance with the first embodiment is a coating (10) comprising a substrate (1); a primer layer (2) formed on the surface of the substrate (1); and one or more fluororesin coating layers (3) formed on the primer layer (2).

[0064]

As the substrate (1), steel, aluminum, nickel, chromium, manganese, molybdenum, titanium, and niobium, or alloy consisting of two or more types selected therefrom is used.

[0065]

Such substrate (1) may be used for one or more types selected from the group consisting of members constituting devices for manufacturing electronic components and precision instruments (e.g., tanks for semiconductor manufacturing devices), chemical reaction tanks (reactors), filtration tanks, mixing tanks (100) comprising impellers (101), reservoirs, or distillation tanks, or the like. As an example, Fig. 2 shows a mixing tank (100) in which the coating (10) is used. When used in the mixing tank (100) in Fig. 2, the substrate (1) is provided as a member constituting the outer frame of the mixing tank (100), and the coating (10) is formed on the inner surface of the mixing tank (100). Not only the inner surface of the mixing tank (100), but also other portions such as impellers (101), which are in contact with chemicals added in the mixing tank (100), may be coated with the coating (10).

[0066]

A production method for the coating (10) in accordance with this embodiment comprises a step of degreasing to remove oil from the surface of the substrate (1) before forming the primer layer (2) on the surface of the substrate (1). The step of degreasing may be performed by a method, including but not limited to, baking the substrate (1) without other components.

[0067]

The production method comprises a step of blasting to roughen the surface of the substrate (1), subsequently to the step of degreasing. The step of blasting may be performed by a method, including but not limited to, sandblasting, shotblasting, and/or gritblasting, using a metal such as alumina and steel, glass, sand, or the like.

[0068]

Through these steps, it is possible to remove impurities such as oil and deposits from the surface of the substrate (1) and enhance adhesion between the substrate (1) and the primer layer (2).

[0069]

Subsequently, as a step of forming a primer, a primer is applied on the surface of the substrate (1) that went through the step of blasting and is dried or baked to form the primer layer (2). This step of forming a primer layer may be performed once, or may be repeated multiple times. The baking in the step of forming a primer layer is set as appropriate, depending on the material of the substrate (1), the type of the primer layer (2), and the like.

[0070]

The primer is fluororesin containing chromic acid and phosphoric acid. Preferably, one or more types of fluororesin selected from the group consisting of PTFE (polytetrafluoroethylene), PFA (tetrafluoro ethylene perfluoroalkyl vinyl ether copolymer) and FEP (tetrafluoro ethylene hexafluoropropylene copolymer) are used as this fluororesin.

[0071]

The primer preferably contains from 65% by mass to 85% by mass of fluororesin; and from 35% by mass to 15% by mass of chromic acid and phosphoric acid.

[0072]

It becomes possible to improve adhesion between the substrate (1) and the primer layer (2) by using the primer comprising 15% by mass or more of chromic acid and phosphoric acid. If a primer comprising more than 35% by mass of chromic acid and phosphoric acid is used, the primer layer (2) cannot be well formed into a film and is not preferable.

[0073]

As a step of forming a fluororesin coating layer, a fluororesin coating composition containing high-purity graphene is applied on the primer layer (2) and is baked to form a fluororesin coating layer (3). The step of forming a fluororesin coating layer may be repeated multiple times to form multiple fluororesin coating layers (3).

[0074]

The conditions in the step of forming a fluororesin coating layer are not particularly limited, and are set as appropriate, depending on the material of the substrate (1), the type of the fluororesin coating layer (3), and the like. Such baking may be performed using, for example, an electric oven, a gas oven, or the like. The fluororesin coating composition may be dried after being applied and before being baked. Drying may be performed under appropriate conditions.

[0075]

The above-mentioned high-purity graphene contained in the fluororesin coating layer (3) contains less amorphous carbon compared to common graphene, and can suitably be used as a filler (filler material). By containing suitable high-purity graphene in the fluororesin coating layer (3), it is possible to provide a coating (10) having a small amount of metal seepage while having excellent antistatic property.

[0076]

The above-mentioned high-purity graphene contained in the fluororesin coating layer (3) has an amorphous carbon content of less than or equal to 5.0 % by mass. The content is preferably less than or equal to 5.0% by mass, and more preferably less than or equal to 3.0% by mass.

[0077]

The above-mentioned high-purity graphene contained in the fluororesin coating layer (3) is mixed with PET resin and solvent at a ratio of high-purity graphene: PET resin: solvent = 1:2:40 and stirred with a stirrer, which then is applied as a coating such that the thickness will be 15 μm and preferably, the surface resistivity measured by the 4-Probe method after being dried will be from $1.0 \times 10^2 \text{ } \Omega/\text{sq}$ to $4.0 \times 10^2 \text{ } \Omega/\text{sq}$. And, the surface resistivity could even be less than or equal to $1.0 \times 10^2 \text{ } \Omega/\text{sq}$.

[0078]

It is possible to improve antistatic property of the coating (10) and further prevent breakage due to static electricity by using high-purity graphene that satisfies the above-mentioned conditions.

[0079]

The coating (10) has a volume resistivity of less than $10^8 \Omega$, and has antistatic property.

[0080]

As fluororesin of the coating composition applied on the fluororesin coating layer (3), one or more types of fluororesin selected from the group consisting of PTFE (polytetrafluoroethylene), PFA (tetrafluoro ethylene perfluoroalkyl vinyl ether copolymer), FEP (tetrafluoro ethylene hexafluoropropylene copolymer), ethylene tetrafluoroethylene copolymer (ETFE), polychlorotrifluoroethylene (PCTFE), and polyvinylidene fluoride (PVDF) may be used.

[0081]

In the step of forming a fluororesin coating layer, the fluororesin coating layer (3) is formed from a coating composition preferably containing from 80% by mass to 99% by mass of fluororesin; and 20% by mass to 1% by mass of high-purity graphene.

[0082]

If the amount of high-purity graphene component is insufficient relative to the entire fluororesin coating layer (3), it is not possible to achieve desired antistatic property as well as corrosion resistance, chemical resistance, permeation resistance, heat resistance, durability, and the like. And, if the amount of the component is excessive, it cannot be well formed into a film.

[0083]

In the step of forming a fluororesin coating layer, the fluororesin coating layer (3) is formed preferably in a thickness of from 200 μm to 2000 μm .

[0084]

If the thickness of the fluororesin coating layer (3) is not sufficient, it is not possible to achieve corrosion resistance, chemical resistance, permeation resistance, heat resistance, and durability. If the thickness is excessive, bubbles are formed in the coating,

or cracks or asperities are formed on the surface of the coating, which may result in loss of smoothness.

[0085]

The coating (10) produced through the above-mentioned steps has excellent antistatic property, corrosion resistance, chemical resistance, permeation resistance, heat resistance, durability, and the like.

[0086]

Furthermore, the coating (10) produced through the above-mentioned steps has a small amount of metal seepage. As for the amount of metal seepage, it is discovered that when the coating (10) is immersed in 200 ml of 3.6% by mass of hydrochloric acid for 24 hours, if the amount of metal seepage is, for example, but without limitation, from 3.0 μg to 15 μg per square meter surface area, the coating (10) can generally preferably be adopted.

[0087]

<Second Embodiment>

Fig. 3 is a cross-sectional view of a coating (20) in accordance with a second embodiment of the present invention. The coating (20) in accordance with the second embodiment further comprises a top layer (4) on the surface of the fluororesin coating layer (3) of the coating (10) in accordance with a first example. That is, in the second embodiment, the fluororesin coating layer (3) is a layer constituting a middle layer (interlayer) of the coating (20).

[0088]

In the second embodiment, in order to form the top layer (4), the production method further comprises a step of forming a top layer through applying fluororesin on the fluororesin coating layer (3) and baking it to form the top layer (4). The baking in the step of forming a top layer is set as appropriate, depending on the material of the substrate (1), the type of the top layer (4), and the like.

[0089]

It becomes possible to produce the coating (20) with a further reduced amount of metal seepage by comprising the step of forming a top layer. It also becomes possible

to produce the coating (20) that will prevent separation of high-purity graphene from the fluororesin coating layer (3), by comprising the step of forming a top layer.

[0090]

Fluororesin used in the step of forming a top layer is preferably one or more types of fluororesin selected from the group consisting of PTFE (polytetrafluoroethylene), PFA (tetrafluoro ethylene perfluoroalkyl vinyl ether copolymer), FEP (tetrafluoro ethylene hexafluoropropylene copolymer), ethylene tetrafluoroethylene copolymer (ETFE), polychlorotrifluoroethylene (PCTFE), and polyvinylidene fluoride (PVDF). By these, it becomes possible to produce the coating (20) that is excellent in corrosion resistance, chemical resistance, permeation resistance, heat resistance, durability, and the like, and has a small amount of metal seepage.

[0091]

Without limitation, in the step of forming a top layer, the top layer (4) is formed preferably in a thickness of 10 μm to 300 μm . If the thickness is not sufficient, the top layer (4) cannot sufficiently prevent separation of high-purity graphene from the fluororesin coating layer (3). If the thickness is excessive, potential metal seepage due to the top layer (4) increases.

[Examples]

[0092]

Hereinafter, Examples are shown to evaluate the coating of the present invention, so that the effects of the present invention will be clarified. However, the present invention should not be understood to be limited to the aspects shown in the following Examples.

[0093]

<1. Coating Production>

[0094]

(Example 1)

Stainless steel (SUS304, 6 mm thick, 200 mm square) was used as a substrate. Stainless steel was degreased through heating and baking it without other components at about 400°C, and then it was shotblasted with #60 alumina. A chromic acid-based

primer was spray-applied on the surface of the degreased and blasted substrate to form a primer layer.

[0095]

Subsequently, a coating composition comprising 3% by mass of high-purity graphen xGnP® R-10 (manufactured by XG Sciences, Inc.) and the remaining, PFA, was applied on the primer layer by an electrostatic powder coating method, to achieve a coating film with a thickness of 300 µm. This coating was called Example 1.

[0096]

(Example 2)

A primer layer and a fluororesin coating layer were formed on the surface of a substrate through the same procedure as Example 1. In Example 2, further, PFA was applied on the surface of the fluororesin coating layer to form a top layer with a film thickness of 300 µm. This coating was called Example 2.

[0097]

(Comparative Example 1)

A coating was produced in the same manner, except that graphene xGnP® H-15 (manufactured by XG Sciences, Inc.) was used instead of high-purity graphene xGnP® R-10 (manufactured by XG Sciences, Inc.) in Example 1. This coating was called Comparative Example 1.

[0098]

(Comparative Example 2)

A coating was produced in the same manner, except that graphene xGnP® M-15 (manufactured by XG Sciences, Inc.) was used instead of high-purity graphene xGnP® R-10 (manufactured by XG Sciences, Inc.) in Example 1. This coating was called Comparative Example 2.

[0099]

(Comparative Example 3)

A coating was produced in the same manner, except that graphene xGnP® C300 (manufactured by XG Sciences, Inc.) was used instead of high-purity graphene xGnP® R-10 (manufactured by XG Sciences, Inc.) in Example 1. This coating was called Comparative Example 3.

[0100]

The following Table 1 shows high-purity graphene and graphene used in Examples 1 and 2 and Comparative Examples 1-3, and respective characteristics.

[0101]

[Table 1]

	Example 1	Example 2	Comparative Example 1	Comparative Example 2	Comparative Example 3
Graphene	xGnP® R-10	xGnP® R-10	xGnP® H-15	xGnP® M-15	xGnP® C300
Amorphous Carbon Content (%) by mass)	1.48	1.48	6.64	16.76	3.56
BET Specific Surface (m ² /g)	40	40	60	130	300
Surface Resistivity (Ω/sq)	1.6x10 ²	1.6x10 ²	4.8x10 ²	1.8x10 ³	5.0x10 ⁴

[0102]

<2. Corrosion Test>

[0103]

A corrosion test was conducted on the above-mentioned coatings of Examples 1 and 2 and Comparative Examples 1-3 with a Yamazaki method lining tester LA-15 (manufactured by Yamazaki Seiki Laboratories Co., Ltd.).

[0104]

In the corrosion test, the Yamazaki method lining tester LA-15 was enclosed with the above-mentioned coatings of Examples 1 and 2 and Comparative Examples 1-3, and the top half was filled with 5% hydrochloric acid.

And, the top half was kept away from being in 5% hydrochloric acid, and was kept in a state of being exposed to vapor due to the heat from the heater. The bottom half of the corrosion resistant member that was directly immersed in 5% hydrochloric acid was called a liquid phase portion and the top half that was not directly immersed in 5% hydrochloric acid was called a gas phase portion, and these two portions were together called an immersed portion. This was left at below 100°C for 28 days, and the following evaluations were conducted.

[0105]

Specifically, the evaluations were conducted in terms of the following five items (a) to (f).

[0106]

(a) Volume Resistivity

Volume resistivity of each coating before exposure to hydrochloric acid was measured, so that antistatic property, which is one of the characteristics of the coating, would be measured. The coatings of Examples 1 and 2 and Comparative Examples 1-3 were created, and volume resistivity was measured with a High Resistivity Meter, Hiresta.

[0107]

(b) Initial Adhesion

A peel strength test was conducted as per JIS K 5400 on each coating before exposure to hydrochloric acid, per the range of 5 mm width, so that initial adhesion to the substrate would be evaluated. Specific adhesion was entered in the following Table 2, and when breakage was found in the coating, the phrase "coating breakage" was entered. A peel strength test was conducted on the portion not immersed in hydrochloric acid like the portion *E* in Fig. 4, so that initial adhesion to the substrate was evaluated.

[0108]

(c) Blister (Swelling) Formation Area

The area of the blister after 28 days was measured, and the ratio of the blister formation area to the test area was calculated. As for the portions in which generally densely blisters are formed or coating film gaps are formed, the areas of the individual swellings were not totaled but such ranges were counted as blister formation areas.

[0109]

(d) Time Until Blister (Swelling) Formation

The time period until blister formation was measured. In this test, blister formation was entered on a weekly basis since the test was suspended after each week and the coating was broken down and checked.

[0110]

(e) Permeation Amount

The amount of hydrochloric acid permeation in the coating was measured, compared to before the test (day 0). When the amount of permeation was measured, an electronic even balance was used for measurement.

[0111]

(f) Residual Adhesion

Residual adhesion to the substrate after 28 days was evaluated through a peel strength test as per JIS K 5400. Since each coating was divided into a gas phase portion and a liquid phase portion, adhesion was measured in each portion, and adhesion of the gas phase was entered in the upper section and adhesion of the liquid phase was entered in the lower section in the row of adhesion after 28 days in Table 2. Also, the measurement value (N/5mm) of the peel strength test was entered in Table 2, and when breakage was found in the coating, the phrase "coating breakage" was entered. Each coating was measured twice, on the right side and on the left side as in Fig. 4, and *A* and *B* fall under the gas phase portion and *C* and *D* fall under the liquid phase portion. The numerical values of two measurements were combined and entered.

[0112]

Results of evaluation of the corrosion test were entered in Table 2.

[0113]

[Table 2]

	Example 1	Example 2	Comparative Example 1	Comparative Example 2	Comparative Example 3
(a) Volume Resistivity (Ω)	$\leq 10^6$	$\leq 10^6$	$\geq 10^{11}$	$\leq 10^6$	$\geq 10^{11}$
(b) Initial Adhesion (N/5mm)	12.7-16.0 coating breakage	12.8-16.0 coating breakage	19.0-20.6 coating breakage	12.1-15.3 coating breakage	15.8-20.5 coating breakage
(c) Blister Formation Area After 28 Days (%)	0	0.03	16.7	7.8	77.3
(d) Time Until Blister Formation (weeks)	4	4	2	2	1
(e) Permeation Amount (Δ mg/cm ²)	0.48	0.65	1.1	0.81	0.73
(f) Adhesion After 28 Days (gas phase) (N/5mm)	14.9-16.4 coating breakage	14.4-17.9 coating breakage	12.2-18.2 coating breakage	11.0-14.9 coating breakage	2.5-16.6 coating breakage
(f) Adhesion After 28 Days (liquid phase) (N/5mm)	14.3-16.7 coating breakage	13.0-15.7 coating breakage	7.0-16.9 coating breakage	8.5-14.0 coating breakage	2.3-16.7 coating breakage

[0114]

As shown in Table 2, Comparative Examples 1 and 3 do not satisfy the requirement of a volume resistivity of less than $10^8 \Omega$ to provide antistatic property.

Comparative Example 2 had antistatic property, yet it had a shorter time period until blister formation and a larger blister formation area, compared to Examples 1 and 2. In addition, Comparative Example 2 had low residual adhesion and a greater permeation amount after the corrosion test.

[0115]

As shown in Table 2, Examples 1 and 2 had a longer time period until blister formation after the corrosion test and a smaller blister formation area, compared to Comparative Examples 1-3, while having antistatic property. In addition, Examples 1 and 2 had high residual adhesion after the corrosion test. And, Examples 1 and 2 had a smaller permeation amount.

[0116]

Therefore, it can be said that the present invention is a coating excellent in antistatic property, corrosion resistance, chemical resistance, permeation resistance, heat resistance, and durability, and a production method for the aforementioned coating.

[0117]

<3. Metal Seepage Test>

A metal seepage test was conducted on the coatings of Examples 1 and 2 and Comparative Examples 1-3 produced in the above-mentioned production of the coatings.

[0118]

In the metal seepage test, each coating (with a surface area of $3.8 \times 10^{-3} \text{m}^2$) of Examples 1 and 2 and Comparative Examples 1-3 was, after being washed, immersed in 200 ml of 3.6% by mass of hydrochloric acid for 24 hours. Then, the metal concentration in the immersion liquid was measured with an Inductivity Coupled Plasma-Mass Spectrometer (manufactured by Agilent Technologies, Inc.).

[0119]

Results of evaluation of the metal seepage test were entered in Table 3.

[0120]

[Table 3]

Element	Amount of Seepage ($\mu\text{g}/\text{m}^2$)				
	Example 1	Example 2	Comparative Example 1	Comparative Example 2	Comparative Example 3
Ag	<0.15	<0.15	<0.15	<0.15	<0.15
Al	1.2	<0.51	1.2	0.96	1.2
Ca	22	5.5	13	31	4.1
Cr	<1.8	<1.8	2.6	<1.8	<1.8
Cu	<1.5	<1.5	<1.5	<1.5	<1.5
Fe	3.0	<2.0	42	5.8	4.5
K	<2.5	<2.5	<2.5	<2.5	<2.5
Na	0.30	<0.25	0.36	0.66	0.25
Ni	<0.50	<0.50	1.1	<0.50	<0.50
Zn	3.5	<0.76	2.6	9.5	1.4

[0121]

In Table 3, Comparative Example 3 also had a small amount of metal seepage. Yet, as shown in Table 2, it had high volume resistivity as a coating and did not achieve antistatic property, and thus, it could not satisfy the performance requirements. Thus, Examples 1 and 2 were found to have a smaller amount of metal seepage, compared to Comparative Examples 1-3, while having antistatic property. As such, it can be said that the coating and the production method for the aforementioned coating in accordance with the present invention are useful.

[Industrial Applicability]

[0122]

The present invention can provide a coating having a small amount of metal seepage while having excellent antistatic property, corrosion resistance, chemical

resistance, permeation resistance, heat resistance, durability, and the like, and a production method for the aforementioned coating.

[0123]

Since the present invention has a small amount of metal seepage, for example, there will not arise the problem that metallic components of the filler seep out as metal ions to treatment liquids used in the process for manufacturing electronic components and precision instruments, which results in degrading cleanliness of the electronic components and precision instruments, and it can suitably be used for devices for manufacturing electronic components and precision instruments (e.g., tanks for semiconductor manufacturing devices), chemical reaction tanks (reactors), filtration tanks, mixing tanks comprising impellers, reservoirs, or distillation tanks, or the like.

[Description of Symbols]

[0124]

- | | |
|--------|---------------------------|
| 1 | Substrate |
| 2 | Primer Layer |
| 3 | Fluororesin coating layer |
| 4 | Top layer |
| 10, 20 | Coating |

AMENDED CLAIMS under Article 19**WHAT IS CLAIMED IS:**

1. A coating, comprising:
 - a substrate;
 - a primer layer formed on a surface of the substrate; and
 - one or more fluororesin coating layers formed on the primer layer,wherein the substrate is steel, aluminum, nickel, chromium, manganese, molybdenum, titanium, or niobium, or alloy consisting of two or more types selected therefrom,
 - wherein the one or more fluororesin coating layers contain fluororesin and high-purity graphene,
 - wherein the high-purity graphene has an amorphous carbon content of less than or equal to 5.0% by mass, and
 - wherein the high-purity graphene is mixed with PET resin and solvent at a ratio of high-purity graphene: PET resin: solvent = 1:2:40 and stirred with a stirrer, which then is applied as a coating, and a surface resistivity of the coating is from $1.0 \times 10^2 \Omega/\text{sq}$ to $4.0 \times 10^2 \Omega/\text{sq}$.
2. A coating, comprising:
 - a substrate;
 - a primer layer formed on a surface of the substrate; and
 - one or more fluororesin coating layers formed on the primer layer,wherein the primer layer contains from 65% by mass to 85% by mass of one or more types of fluororesin selected from the group consisting of PTFE, PFA, and FEP, and from 35% by mass to 15% by mass of chromic acid and phosphoric acid,
 - wherein the one or more fluororesin coating layers contain fluororesin and high-purity graphene,
 - wherein the high-purity graphene has an amorphous carbon content of less than or equal to 5.0% by mass, and
 - wherein the high-purity graphene is mixed with PET resin and solvent at a ratio of

high-purity graphene: PET resin: solvent = 1:2:40 and stirred with a stirrer, which then is applied as a coating, and a surface resistivity of the coating is from $1.0 \times 10^2 \Omega/\text{sq}$ to $4.0 \times 10^2 \Omega/\text{sq}$.

3. A coating, comprising:
 - a substrate;
 - a primer layer formed on a surface of the substrate; and
 - one or more fluororesin coating layers formed on the primer layer,
 - wherein the one or more fluororesin coating layers contain fluororesin and high-purity graphene,
 - wherein the high-purity graphene has an amorphous carbon content of less than or equal to 5.0% by mass, and
 - wherein the high-purity graphene is mixed with PET resin and solvent at a ratio of high-purity graphene: PET resin: solvent = 1:2:40 and stirred with a stirrer, which then is applied as a coating, and a surface resistivity of the coating is from $1.0 \times 10^2 \Omega/\text{sq}$ to $4.0 \times 10^2 \Omega/\text{sq}$,
 - wherein the coating further comprising a top layer formed on the one or more fluororesin coating layers,
 - wherein the top layer containing one or more types of fluororesin selected from the group consisting of PTFE, PFA, FEP, ETFE, PCTFE, and PVDF, and
 - wherein the top layer has a thickness of from 10 μm to 300 μm .
4. A coating according to claim 1 or 2, further comprising a top layer formed on the one or more fluororesin coating layers.
5. A coating according to claim 4, wherein the top layer contains one or more types of fluororesin selected from the group consisting of PTFE, PFA, FEP, ETFE, PCTFE, and PVDF, and wherein the top layer has a thickness of from 10 μm to 300 μm .
6. A coating according to any one of claims 1 to 5, wherein the one or more fluororesin coating layers contain from 80% by mass to 99% by mass of one or more types of

fluororesin selected from the group consisting of PTFE, PFA, FEP, ETFE, PCTFE, and PVDF, and from 20% by mass to 1% by mass of high-purity graphene.

7. A coating according to any one of claims 1 to 6, wherein the one or more fluororesin coating layers have a thickness of from 200 μm to 2000 μm .
8. A coating according to any one of claims 2 to 7, wherein the substrate is steel, aluminum, nickel, chromium, manganese, molybdenum, titanium, or niobium, or alloy consisting of two or more types selected therefrom.
9. A coating according to any one of claims 1 and 3 to 8, wherein the primer layer is formed of a primer containing from 65% by mass to 85% by mass of one or more types of fluororesin selected from the group consisting of PTFE, PFA, and FEP, and from 35% by mass to 15% by mass of chromic acid and phosphoric acid.
10. A coating according to any one of claims 1 to 9, wherein when the coating is immersed in 200 ml of 3.6% by mass of hydrochloric acid for 24 hours, an amount of metal seepage is from 3.0 μg to 15 μg per square meter surface area of the coating.
11. A coating according to any one of claims 1 to 10, wherein the substrate is used for one or more types selected from the group consisting of members constituting devices for manufacturing electronic components and precision instruments, chemical reaction tanks (reactors), filtration tanks, mixing tanks comprising impellers, reservoirs, and distillation tanks.
12. A coating according to any one of claims 1 to 11, wherein the high-purity graphene has an amorphous carbon content of less than or equal to 3.0% by mass.
13. A production method for a coating, the method comprising steps of:
degreasing to remove oil from a surface of a substrate;
blasting to roughen the surface of the substrate after degreasing;

forming a primer layer through applying a primer on the surface of the substrate after the step of blasting, and drying or baking it to form a primer layer; and forming a fluoro-resin coating layer through applying a coating composition containing high-purity graphene and fluoro-resin on the primer layer, baking it, and performing formation of a fluoro-resin coating layer one or more times, wherein the substrate is steel, aluminum, nickel, chromium, manganese, molybdenum, titanium, or niobium, or alloy consisting of two or more types selected therefrom, wherein the high-purity graphene has an amorphous carbon content of less than or equal to 5.0% by mass, and wherein the high-purity graphene is mixed with PET resin and solvent at a ratio of high-purity graphene: PET resin: solvent = 1:2:40 and stirred with a stirrer, which then is applied as a coating, and a surface resistivity of the coating is from $1.0 \times 10^2 \Omega/\text{sq}$ to $4.0 \times 10^2 \Omega/\text{sq}$.

14. A production method for a coating, the method comprising steps of:

degreasing to remove oil from a surface of a substrate;
 blasting to roughen the surface of the substrate after degreasing; and
 forming a primer layer through applying a primer on the surface of the substrate after the step of blasting, and drying or baking it to form a primer layer,
 wherein in the step of forming a primer, the primer layer is formed from a primer containing from 65% by mass to 85% by mass of one or more types of fluoro-resin selected from the group consisting of PTFE, PFA, and FEP, and from 35% by mass to 15% by mass of chromic acid and phosphoric acid,
 the method further comprising a step of forming a fluoro-resin coating layer through applying a coating composition containing high-purity graphene and fluoro-resin on the primer layer, baking it, and performing the step of forming a fluoro-resin coating layer one or more times,
 wherein the high-purity graphene has an amorphous carbon content of less than or equal to 5.0% by mass, and
 wherein the high-purity graphene is mixed with PET resin and solvent at a ratio of high-purity graphene: PET resin: solvent = 1:2:40 and stirred with a stirrer, which

then is applied as a coating, and a surface resistivity of the coating is from $1.0 \times 10^2 \Omega/\text{sq}$ to $4.0 \times 10^2 \Omega/\text{sq}$.

15. A production method for a coating, the method comprising steps of:
 degreasing to remove oil from a surface of a substrate;
 blasting to roughen the surface of the substrate after degreasing;
 forming a primer layer through applying a primer on the surface of the substrate after the step of blasting, and drying or baking it to form a primer layer; and
 forming a fluoro-resin coating layer through applying a coating composition containing high-purity graphene and fluoro-resin on the primer layer, baking it, and performing formation of a fluoro-resin coating layer one or more times,
 wherein the high-purity graphene has an amorphous carbon content of less than or equal to 5.0% by mass, and
 wherein the high-purity graphene is mixed with PET resin and solvent at a ratio of high-purity graphene: PET resin: solvent = 1:2:40 and stirred with a stirrer, which then is applied as a coating, and a surface resistivity of the coating is from $1.0 \times 10^2 \Omega/\text{sq}$ to $4.0 \times 10^2 \Omega/\text{sq}$,
 the method further comprising a step of forming a top layer through applying fluoro-resin on the fluoro-resin coating layer and baking it to form a top layer,
 wherein in the step of forming a top layer, one or more types of fluoro-resin selected from the group consisting of PTFE, PFA, FEP, ETFE, PCTFE, and PVDF are applied, and
 wherein the top layer is formed in a thickness of from 10 μm to 300 μm .
16. A production method for a coating according to claim 13 or 14, further comprising a step of forming a top layer through applying fluoro-resin on the fluoro-resin coating layer and baking it to form a top layer,
17. A production method for a coating according to claim 16, wherein in the step of forming a top layer, one or more types of fluoro-resin selected from the group consisting of PTFE, PFA, FEP, ETFE, PCTFE, and PVDF are applied, and wherein

the top layer is formed in a thickness of from 10 μm to 300 μm .

18. A production method for a coating according to any one of claims 13 to 17, wherein in the step of forming a fluororesin coating layer, the fluororesin coating layer is formed from a coating composition containing from 80% by mass to 99% by mass of one or more types of fluororesin selected from the group consisting of PTFE, PFA, FEP, ETFE, PCTFE, and PVDF, and from 20% by mass to 1% by mass of high-purity graphene.
19. A production method for a coating according to any one of claims 13 to 18, wherein in the step of forming a fluororesin coating layer, the fluororesin coating layer is formed in a thickness of from 200 μm to 2000 μm .
20. A production method for a coating according to any one of claims 13 to 19, wherein the substrate is steel, aluminum, nickel, chromium, manganese, molybdenum, titanium, or niobium, or alloy consisting of two or more types selected therefrom.
21. A production method for a coating according to any one of claims 13 and 15 to 20, wherein in the step of forming a primer, the primer layer is formed from a primer containing from 65% by mass to 85% by mass of one or more types of fluororesin selected from the group consisting of PTFE, PFA, and FEP, and from 35% by mass to 15% by mass of chromic acid and phosphoric acid.
22. A production method for a coating according to any one of claims 13 to 21, wherein the substrate is used for one or more types selected from the group consisting of members constituting devices for manufacturing electronic components and precision instruments, chemical reaction tanks (reactors), filtration tanks, mixing tanks comprising impellers, reservoirs, and distillation tanks.
23. A production method for a coating according to any one of claims 13 to 22, wherein the high-purity graphene has an amorphous carbon content of less than or equal to

3.0% by mass.