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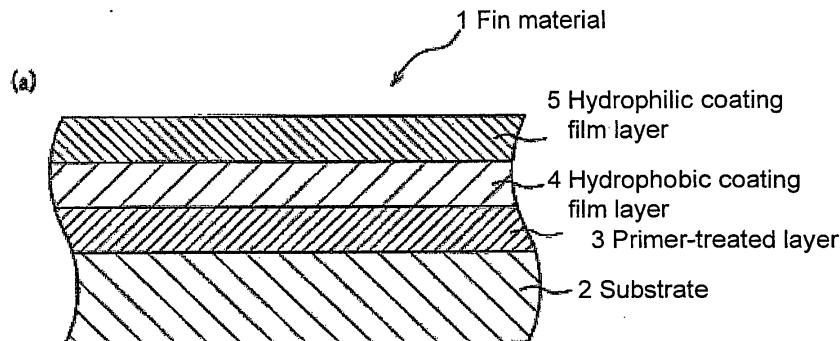
**(54) ALUMINUM FIN MATERIAL FOR HEAT EXCHANGER**

(57) The present invention provides a fin material for a heat exchanger, which can prevent odor emission and deterioration of hydrophilicity for a long period.

Disclosed in an aluminum fin material 1 for a heat exchanger includes a substrate 2, a primer-treated layer 3, a hydrophobic coating film layer 4 having a thickness of 0.1 to 10  $\mu\text{m}$ , and a hydrophilic coating film layer 5 having a thickness of 0.1 to 10  $\mu\text{m}$ , wherein the hydrophobic coating film layer 4 is made of at least one kind of a hydrophobic resin selected from the group consisting of an urethane-based resin, an epoxy-based resin, a polyester-based resin and a polyacrylic acid-based resin,

the hydrophilic coating film layer 5 is made of a hydrophilic resin, which has a sulfonic acid group or a sulfonyl acid group derivative, and also has at least one kind selected from the group consisting of a carboxyl group, carboxyl group derivative, a hydroxyl group and a hydroxyl group derivative, an existing ratio of S measured in a film thickness direction by high-frequency glow discharge optical emission spectroscopy is from 1 to 5 atomic % and an existing ratio of O is from 10 to 35 atomic %, and the total amount of impurities of the hydrophobic coating film layer 4 and the hydrophilic coating film layer 5 is 1% by mass or less.

Fig.1



**Description****BACKGROUND OF THE INVENTION**5 **Field of the Invention**

**[0001]** The present invention relates to an aluminum fin material made of aluminum or an aluminum alloy, in which a coating film is formed on the surface. More particularly, the present invention relates to an aluminum fin material, which is suited for use as a fin material for a heat exchanger of air conditioners.

10 **Description of the Related Art**

**[0002]** A heat exchanger is utilized in various fields such as room air conditioners, package air conditioners, refrigerated display cases, refrigerators, oil coolers, and radiators. In the heat exchanger of room air conditioners and package air conditioners, aluminum materials are used as the fin material because of excellent thermal conductivity and workability.

**[0003]** In the heat exchanger, in order to prevent deterioration of characteristics of the heat exchanger due to disturbing a ventilation caused by accumulation of dew condensation water produced upon a cooling operation between fins (fin materials), the surface of a fin material is subjected to a hydrophilic treatment for the purpose of enhancing fluidity of dew condensation water on the surface of the fin material. Furthermore, the surface of the fin material is subjected to a corrosion-resisting treatment for the purpose of preventing the occurrence of corrosion of fin material.

**[0004]** In the environment (indoor condition) in which air conditioners are used, various pollutants, for example, plasticizers such as diisooctyl phthalate, repelling materials such as lubricants for plastics (e.g. palmitic acid, stearic acid, paraffins, etc.), and odor materials such as acetaldehyde exist (reference: Proceeding of 18th Annual Conference of Japan Association on Odor Environment /June 2005, p3, "Study on Causative of Odor from Air Conditioners").

**[0005]** JP3,383,914B discloses, as means for preventing adhesion of these pollutants, an aluminum fin material for a heat exchanger, in which a corrosion-resistant film made of an inorganic oxide or an organic-inorganic composite compound is formed on a substrate made of aluminum or an aluminum alloy and a hydrophilic film made of a polyacrylic acid or polyacrylate containing a water-soluble resin having a hydroxyl group in the molecule is formed thereon, and then a water-soluble resin film made of a water-soluble resin having a hydroxyl group in the molecule is formed thereon.

**[0006]** In a fin material in the JP3,383,914B, hydrophilicity of both the hydrophilic film and the water-soluble resin film is enhanced by mixing with the water-soluble resin. Thus, fluidity of dew condensation water is enhanced and adhesion of pollutants is prevented. However, it is hard to maintain hydrophilicity of both films since the water-soluble resin is dissolved in dew condensation water, and thus adhesion of pollutants could not be prevented for a long period. Adhesion of pollutants is promoted since pollutants deteriorate hydrophilicity of both films, thus causing a problem that odor emission and deterioration of hydrophilicity caused by pollutants cannot be sufficiently prevented.

**[0007]** In the fin material, the corrosion-resistant film is formed on the substrate made of aluminum or an aluminum alloy, and a hydrophilic resin film and a water-soluble resin film, which have high affinity with water, are formed on the corrosion-resistant film. Therefore, dew condensation water easily penetrates into the corrosion-resistant film and thus it may corrode the substrate to form an aluminum oxide. The aluminum oxide moves into the hydrophilic resin film and the water-soluble resin coating film, resulting in adsorption and occlusion of pollutants, thus causing a problem that pollutants easily adhere and it is impossible to sufficiently prevent odor emission and deterioration of hydrophilicity.

**[0008]** In the fin material, inorganic oxides such as alumina, silica, titania, zeolite and a hydrate thereof were positively added to the hydrophilic film and the water-soluble resin film for the purpose of improving hydrophilicity. These inorganic oxides also had a problem that pollutants easily adhere on the surface of the fin material since they have the action of adsorbing and occluding pollutants, and thus odor emission and deterioration of hydrophilicity cannot be sufficiently prevented.

**SUMMARY OF THE INVENTION**

50 **[0009]** In light of the above problems, the present invention has been made and an object thereof is to provide a fin material for a heat exchanger, which can prevent odor emission and deterioration of hydrophilicity for a long period.

**[0010]** In order to achieve the above object, the first aspect of the invention includes a substrate made of aluminum or an aluminum alloy, a primer-treated layer made of an inorganic oxide or an organic-inorganic composite compound formed on the substrate, a hydrophobic coating film layer having a thickness of 0.1 to 10  $\mu\text{m}$  formed on the primer-treated layer, and a hydrophilic coating film layer having a thickness of 0.1 to 10  $\mu\text{m}$  formed on the hydrophobic coating film layer, wherein the hydrophobic coating film layer is made of at least one kind of a hydrophobic resin selected from the group consisting of an urethane-based resin, an epoxy-based resin, a polyester-based resin and a polyacrylic acid-based resin, the hydrophilic coating film layer is made of a hydrophilic resin, which has a sulfonic acid group or a sulfonic

acid group derivative, and also has at least one kind selected from the group consisting of a carboxyl group, a carboxyl group derivative, a hydroxyl group and a hydroxyl group derivative, and an existing ratio of S measured in a film thickness direction by high-frequency glow discharge optical emission spectroscopy is from 1 to 5 atomic % and an existing ratio of O is from 10 to 35 atomic %, and the total amount of at least one kind of alumina, silica, titania, zeolite and a hydrate thereof contained as impurities in the hydrophobic coating film layer and the hydrophilic coating film layer is 1% by mass or less.

[0011] With the above constitution, the hydrophobic coating film layer is made of a predetermined hydrophobic resin and is formed on the primer-treated layer, and thus dew condensation water penetrated through the hydrophilic coating film layer is blocked by the hydrophobic coating film layer, thereby suppressing penetration into the primer-treated layer. Consequently, contact between the dew condensation water and substrate at the portion, where the primer-treated layer is not sufficiently formed, is suppressed. When a resin having very high hydrophobicity such as a fluorine-based resin is used as the resin of the hydrophobic coating film layer, it becomes difficult to form and to adhere a hydrophilic layer serving as a finishing coat.

[0012] When the hydrophilic coating film layer is made of a hydrophilic resin having a predetermined functional group and each existing ratio of S and O is within a predetermined range, hydrophilicity of the aluminum fin material enhances and fluidity of dew condensation water on the surface of the aluminum fin material enhances. Consequently, if pollutants adhere on the surface of the aluminum fin material, pollutants are easily washed off (removed) with dew condensation water. Also, when the hydrophilic coating film layer is made of the hydrophilic resin having a sulfonic acid group or a sulfonic acid group derivative, polarity increases and, even if pollutants adhere thereon, pollutants are easily washed off with dew condensation water. Furthermore, when the hydrophilic coating film layer has a predetermined functional group, a rate of dissolution of the hydrophilic coating film layer into dew condensation water decreases as compared with a hydrophilic coating film layer made of a conventional water-soluble resin. The rate of dissolution further decreases when the hydrophilic coating film layer has a carboxyl group which is easily reactable with the hydrophobic coating film layer.

[0013] Furthermore, when the total amount of impurities contained in the hydrophobic coating film layer and the hydrophilic coating film layer is a predetermined value or less, adsorption and occlusion of pollutants by impurities are suppressed, and thus the amount of pollutants to be adhered on the surface of the fin material decreases.

[0014] The second aspect of the invention is characterized in that the hydrophilic coating film layer is made of the hydrophilic resin containing an antibacterial agent added thereto.

With the above constitution, fungicidal and antibacterial properties of the hydrophilic coating film layer are improved by adding the antibacterial agent to the hydrophilic resin.

[0015] The aluminum fin material for a heat exchanger according to the present invention includes the predetermined hydrophobic coating film layer and hydrophilic coating film layer, and thus odor is not emitted in the aluminum fin material and hydrophilicity of the aluminum fin material does not deteriorate. Also, mold and bacteria are not grown in the aluminum fin material by adding the antibacterial agent to the hydrophilic resin.

#### BRIEF DESCRIPTION OF THE DRAWINGS

##### [0016]

Fig. 1a is a sectional view schematically showing a cross section of an aluminum fin material for a heat exchanger according to the present invention, and Fig. 1b is a sectional view schematically showing a cross section of another aluminum fin material for a heat exchanger according to the present invention.

Fig. 2 is a graph showing analytical results of high-frequency glow discharge optical emission spectroscopy in the aluminum fin material for a heat exchanger according to the present invention.

[Description of Reference Numerals]

##### [0017]

- 1,1A: Fin material
- 2: Substrate
- 3: Primer-treated layer
- 4: Hydrophobic coating film layer
- 5: Hydrophilic coating film layer
- 6: Antibacterial agent

## DETAILED DESCRIPTION OF THE INVENTION

**[0018]** Embodiments of the aluminum fin material for a heat exchanger of the present invention will be described with reference to the accompanying drawings. Fig. 1a and Fig. 1b are sectional views schematically showing a cross section 5 of an aluminum fin material for a heat exchanger (hereinafter referred to as a fin material).

<Fin Material>

**[0019]** As shown in Fig. 1a, a fin material 1 comprises a substrate 2, a primer-treated layer 3 formed on the substrate 10 2, a hydrophobic coating film layer 4 formed on the primer-treated layer 3, and a hydrophilic coating film layer 5 formed on the hydrophobic coating film layer 4. The expression "on the substrate 2" as used herein means one or both surfaces (not shown) of the substrate 2. The respective essential components will now be described.

## Substrate

**[0020]** The substrate 2 is a sheet material made of aluminum or an aluminum alloy, and 1000 series aluminum defined 15 in JIS H4000, preferably aluminum of an alloy number 1200, is used since it is excellent in thermal conductivity and workability. In the aluminum fin material for a heat exchanger, a sheet having a thickness of about 0.08 to 0.3 mm is used taking account of strength, thermal conductivity and workability.

## Primer-Treated Layer

**[0021]** The primer-treated layer 3 is made of an inorganic oxide or an organic-inorganic composite compound. The inorganic oxide preferably contains chromium (Cr) or zirconium (Zr) as a main component and is formed by carrying out 25 a phosphoric chromate treatment, a zirconium phosphate treatment, or a chromic acid chromate treatment. In the present invention, the treatment is not limited thereto as long as it imparts corrosion resistance and, for example, the primer-treated layer 3 may be formed by conducting a zinc phosphate treatment or a phosphate/titanate treatment. The organic-inorganic composite compound is formed by carrying out a coating type chromate treatment or a coating type zirconium treatment, and includes an acryl-zirconium complex.

**[0022]** The primer-treated layer 3 preferably contains Cr or Zr in an amount within a range from 1 to 100 mg/m<sup>2</sup>. The thickness of the primer-treated layer 3 is preferably from 10 to 1,000 Å and may appropriately vary depending on the 30 purposes. Adhesion between the substrate 2 and a hydrophobic coating film layer 4 described below is improved and also corrosion resistance of the fin material 1 is improved by forming the primer-treated layer 3.

## Hydrophobic Coating Film Layer

**[0023]** The hydrophobic coating film layer 4 is made of at least one kind of a hydrophobic resin among a urethane-based resin, an epoxy-based resin, a polyester-based resin and a polyacrylic acid-based resin, and the thickness is from 0.5 to 10 µm.

**[0024]** Formation of the hydrophobic coating film layer 4 suppresses dew condensation water penetrated into a hydrophilic coating film layer 5 described hereinafter from contacting with the substrate 2 even under a high humidity environment in an oxidative atmosphere. Consequently, generation of an aluminum oxide as a result of corrosion (oxidation) of the substrate 2 is suppressed and emission of cement odor peculiar to the aluminum oxide can be prevented. It is also possible to prevent that the aluminum oxide moves to the hydrophilic coating film layer 5 thereby causing 40 deterioration of hydrophilicity and durability, and to prevent that pollutants are adsorbed and occluded by the moved alumina thereby emitting odor.

**[0025]** The thickness of the hydrophobic coating film layer 4 is limited to a range from 0.1 to 10 µm by the following 50 reason. When the thickness is less than 0.1 µm, penetration of dew condensation water from the hydrophilic coating film layer 5 cannot be prevented, thereby causing odor emission and deteriorating the hydrophilicity of the fin material 1. In a conventional heat exchanger, a copper tube is often used as a heat exchanger tube formed by piercing the fin material 1. Accordingly, when the thickness of the hydrophobic coating film layer 4 is more than 10 µm, contact thermal resistance between the hydrophobic coating film and the copper tube increased and heat transfer performances may deteriorate. It is not preferred that the thickness of the hydrophobic coating film layer is more than 10 µm from an economical point of view. The thickness of the hydrophobic coating film layer 4 is preferably from 0.5 to 2 µm. Corrosion resistance and hydrophilicity of the fin material 1 are further enhanced by the thickness controlled within the above range.

**[0026]** The hydrophobic coating film layer 4 is preferably formed of a hydrophobic resin containing an organic crosslinking agent added thereto so as to improve durability of the hydrophobic coating film layer 4. The hydrophobic coating film layer 4 is preferably formed of a hydrophobic resin containing a surfactant and an organic crosslinking agent added

thereto so as to easily form the hydrophobic coating film layer 4 on the primer-treated layer 3 by coating.

[0027] The hydrophobic coating film layer 4 preferably has a constant electrical resistivity or less when immersed in an aqueous 1N-hydrochloric acid solution. Specifically, an interfacial impedance is preferably  $1 \times 10^2 \Omega \cdot \text{m}^2$  or more measured when an area of a sample (hydrophobic coating film layer 4) exposed in the aqueous 1N-hydrochloric acid solution is  $10 \text{ cm}^2$ , an AC amplitude voltage is 100 mV, and a frequency is from 10 mHz to 10 kHz. When the interfacial impedance of the hydrophobic coating film layer 4 is less than  $1 \times 10^2 \Omega \cdot \text{m}^2$ , the substrate 2 is corroded and the aluminum oxide is likely to be generated. Consequently, emission of odor is likely to be caused by the aluminum oxide.

[0028] The urethane-based resin as used herein is a compound which repeatedly has a urethane bond in the composition and can be obtained by reacting a polyisocyanate compound ( $\text{O}=\text{C}=\text{N}-\text{R}-\text{N}=\text{C}=\text{O}$ ) having two or more isocyanate groups with a polyol compound ( $\text{HO}-\text{R}'-\text{OH}$ ) having two or more hydroxyl groups, polyamine ( $\text{H}_2\text{N}-\text{R}''-\text{NH}_2$ ), or a compound having active hydrogen (-NH<sub>2</sub>, -NH, -CONH-, etc.) of water (R, R', R'': aliphatic, aromatic, etc.). The polyester-based resin as used herein is a polycondensate of a polyhydric carboxylic acid (dicarboxylic acid) and a polyalcohol (diol) and is basically obtained by reaction (dehydration condensation) of a polyalcohol (a compound having a plurality of alcoholic functional groups -OH) and a polyhydric carboxylic acid (a compound having a plurality of carboxylic acid functional groups -COOH).

#### Hydrophilic Coating Film Layer

[0029] The hydrophilic coating film layer 5 is made of a hydrophilic resin which has a sulfonic acid group or a sulfonic acid group derivative, and also has at least one kind of a carboxyl group, a carboxyl group derivative, a hydroxyl group and a hydroxyl group derivative, and the thickness is from 0.1 to 10  $\mu\text{m}$ . Examples of the sulfonic acid group derivative, the carboxyl group derivative and the hydroxyl group derivative include salts of monovalent metals such as sodium and potassium; salts of divalent metals such as calcium; and salts of an organic basic compound, such as ammonium salt.

[0030] The hydrophilic coating film layer 5 is made of a hydrophilic resin having a sulfonic acid group (a sulfonic acid group derivative), a carboxyl group and a hydroxyl group, and thus it exhibits hydrophilicity and fluidity of dew condensation water of the surface of the fin material is improved. Even if pollutants adhere to the surface of the fin material, pollutants can be washed off with dew condensation water. When the hydrophilic coating film layer 5 is made of a hydrophilic resin having a sulfonic acid group (a sulfonic acid group derivative), the resulting coating film layer has high polarity because of a difference in electronegativity between a main chain (a carbon chain) and a sulfonic acid group (a sulfonic acid group derivative) of the hydrophilic resin. Consequently, even if pollutants adhere, dew condensation water penetrates into the space between the coating film layer and pollutants, and thus pollutants are easily washed off.

[0031] The hydrophilic resin includes, for example, an acrylic acid/sulfonic acid-based monomer copolymer salt, a ligninsulfonic acid and a metal salt thereof, and a copolymer of styrenesulfonic acid-maleic acid. The hydrophilic resin may be a copolymer of a monomer having the above mentioned functional group (sulfonic acid group, sulfonic acid group derivative, carboxyl group, carboxyl group derivative, a hydroxyl group, a hydroxyl group derivative, etc.) as well as a blend with a polymer having a predetermined functional group. The polymer having a carboxyl group includes polyacrylic acid, and the polymer having a hydroxyl group includes polyvinyl alcohol.

[0032] In the hydrophilic coating film layer 5, an existing ratio of S measured in a film thickness direction by high-frequency glow discharge optical emission spectroscopy (GD-OES) is from 1 to 5 atomic %, and an existing ratio of O is from 10 to 35 atomic %. Namely, each existing ratio of S and O measured in the entire film thickness direction of the hydrophilic coating film layer 5 is within the above mentioned range. In other words, the region where existing ratios of S and O are within the mentioned ranges continuously exists in a film thickness direction (see Fig. 2).

[0033] Specifically, existing ratios of S and O are measured by the following procedure. The existing ratios of S and O are measured by argon sputtering at a pulse mode using a high-frequency glow discharge optical emission spectroscopic apparatus and carrying out spectral analysis of an emission lines in an argon plasma of S and O in the sputtered region. After argon sputtering is continued until it reaches the hydrophobic coating film layer 4, the existing ratios of S and O of the hydrophilic coating film layer 5 are measured.

[0034] When each existing ratio of S and O is less than the lower limit, the amount of a sulfonic acid group (a sulfonic acid group derivative), a carboxyl group and a hydroxyl group introduced into the hydrophilic resin is small, and hydrophilicity of the surface of the fin material and self-cleaning properties(washing-off properties) of pollutants deteriorate. In contrast, when the existing ratio is more than the upper limit, it becomes difficult to polymerize the hydrophilic resin so as to obtain the composition. To enable the region where each existing ratio of S and O is within the range mentioned above to continuously exist in a film thickness direction of the hydrophilic coating film layer 5, the hydrophilic resin polymerized so as to control each existing ratio of S and O within the mentioned range is formed on the hydrophobic coating film layer 4 by a coating (coating, baking, etc.) operation described hereinafter.

[0035] The thickness of the hydrophilic coating film layer 5 is limited to a range from 0.1 to 10  $\mu\text{m}$  by the following reason. When the thickness is less than 0.1  $\mu\text{m}$ , hydrophilicity and self-cleaning properties of the fin material 1 deteriorate. In contrast, when the thickness of the hydrophilic coating film layer is more than 10  $\mu\text{m}$ , further improvement in hy-

hydrophilicity and self-cleaning properties is not recognized. It is not preferred that the thickness of the hydrophilic coating film layer is more than 10  $\mu\text{m}$  from an economical point of view. The thickness of the hydrophilic coating film layer 5 is preferably from 0.5 to 2  $\mu\text{m}$ . Hydrophilicity and self-cleaning properties of the fin material 1 are further enhanced by the thickness controlled within the above range.

[0036] The hydrophilic coating film layer 5 is preferably formed of a hydrophilic resin containing an organic crosslinking agent added thereto so as to improve durability of the hydrophilic coating film layer 5. The hydrophilic coating film layer 5 is preferably formed of a hydrophilic resin containing a surfactant and an organic crosslinking agent added thereto so as to easily form the hydrophilic coating film layer 5 on the hydrophobic coating film layer 4 by coating.

[0037] The hydrophilic coating film layer 5 preferably has a surface which is as smooth as possible. When the surface of the hydrophilic coating film layer 5 has fine unevenness, the adsorption area of pollutants relatively increases and the amount of pollutants to be adsorbed (adhered) increases, and thus it becomes impossible to wash off pollutants with dew condensation water. Consequently, emission of odor is likely to be caused by pollutants.

[0038] It is preferred that the hydrophilic coating film layer 5 does not contain a nitrogen compound such as an acrylamide-based resin. When the hydrophilic coating film layer contains the nitrogen compound, the nitrogen compound is oxidized under a severe environment, and thus odor is likely to be emitted. The content of the nitrogen compound is preferably 1 atomic % or less in the measurement of an existing ratio of nitrogen by GD-OES.

#### Impurities in Coating Film

[0039] In the fin material 1 of the present invention, the total amount of at least one kind of alumina, silica, titania, zeolite and a hydrate thereof as impurities contained in the hydrophobic coating film layer 4 and the hydrophilic coating film layer 5 is preferably 1% by mass or less. When the fin material contains 1% by mass or more of impurities (at least one kind of alumina, silica, titania, zeolite and a hydrate thereof), pollutants are adsorbed and occluded, and thus odor or repelling (deterioration of hydrophilicity) of the surface of the fin material is likely to be caused. When the hydrophilic coating film layer 5 contains impurities, a continuous coating film layer is not formed and the effect of washing off pollutants decreases.

[0040] The total mass of impurities is measured by the following procedure. First, the hydrophobic coating film layer 4 and the hydrophilic coating film layer 5 are removed from the substrate 2 (the primer-treated layer 3) using fuming nitric acid. Both coating film layers thus removed are completely burned and the residue is poured into pure water. The mass of an insoluble matter which is not dissolved in pure water is measured and is taken as the total mass of impurities.

#### Other Embodiments of Fin Material

[0041] As shown in Fig. 1b, a hydrophilic coating film layer 5 of a fin material 1A is preferably made of a hydrophilic resin containing an antibacterial agent 6 added thereto. Explanation of other essential components is omitted since they are the same as in the fin material 1 (see Fig. 1a). The antibacterial agent may be soluble or insoluble in water. It is preferred to use an antibacterial agent, which is soluble or slightly soluble in water, so as to prevent deterioration of hydrophilicity of the hydrophilic coating film layer 5. Examples of the antibacterial agent, which is soluble in water, include sodium pyrithione, zinc pyrithione, chloroxylenol, thiabendazole, and methylisothiazoline. Examples of the antibacterial agent, which is insoluble in water, include copper pyrithione, carbendazine, and captan. It is preferred that the antibacterial agent does not contain the above-described impurities (at least one kind of alumina, silica, titania, zeolite and a hydrate thereof) or a nitrogen compound. It is preferred that the content of impurities is 1% by mass or less and the content of the nitrogen compound is 1 atomic % or less in the measurement of an existing ratio of nitrogen by GD-OES. The amount of the antibacterial agent to be added is preferably from 1 to 50% by mass based on the total mass of the hydrophilic coating film layer 5. When the amount is less than 1% by mass, fungicidal and antibacterial properties are likely to deteriorate. In contrast, when the amount is more than 50% by mass, hydrophilicity is likely to deteriorate.

[0042] The method for producing a fin material 1 (see Fig. 1a) of the present invention will now be described. The fin material 1 is produced by the following method.

#### Method for Production of Fin Material

[0043] (1) A primer-treated layer 3 made of an inorganic oxide or an organic-inorganic composite compound is formed by subjecting one or both surfaces of a substrate 2 made of aluminum or an aluminum alloy to a phosphoric chromate treatment or a zirconium phosphate treatment. The phosphoric chromate treatment or the zirconium phosphate treatment is carried out by coating a chemical treating solution on the substrate 2 using a spray. The coating amount is preferably within a range from 1 to 100 mg/m<sup>2</sup> in terms of Cr or Zr, and the thickness of a film to be formed is preferably from 10 to 1,000  $\text{\AA}$ . It is preferred that the surface of the substrate 2 is preliminarily degreased by spraying an aqueous alkali solution over the surface of the substrate 2 before forming the primer-treated layer 3. Adhesion between the substrate

2 and the primer-treated layer 3 is improved by degreasing.

[0044] (2) On the primer-treated layer 3 thus formed, a resin solution of at least one kind of an urethane-based resin, an epoxy-based resin, a polyester-based resin and a polyacrylic acid-based resin is coated and baked to form a hydrophobic coating film layer 4 on the primer-treated layer 3.

5 [0045] Coating is carried out by a conventionally known coating method using a bar coater or a roll coater. The coating amount is appropriately set so as to control the thickness of the hydrophobic coating film layer 4 within a range from 0.1 to 10  $\mu\text{m}$ . The baking temperature is appropriately set according to the resin solution to be coated. It is preferred that the surface of the primer-treated layer 3 is preliminarily degreased by spraying an aqueous alkali solution over the surface of the primer-treated layer 3 before forming the hydrophobic coating film layer 4. Adhesion between the primer-treated layer 3 and the hydrophobic coating film layer 4 is improved by degreasing.

10 [0046] (3) On the surface of the hydrophobic coating film layer 4 thus formed, a resin solution of a hydrophilic resin is coated and then baked to form a hydrophilic coating film layer 5 on the hydrophobic coating film layer 4, and thus a fin material 1 is obtained. Coating is carried out by a conventionally known coating method using a bar coater or a roll coater. The coating amount is appropriately set so as to control the thickness of the hydrophilic coating film layer 5 within a range from 0.1 to 10  $\mu\text{m}$ . The baking temperature is appropriately set according to a resin solution to be coated. As shown in Fig. 1b, when the hydrophilic coating film layer 5 of the fin material 1A is formed of a hydrophilic resin containing an antibacterial agent 6 added thereto, baking is carried out at a baking temperature at which the antibacterial agent 6 is not decomposed.

20 EXAMPLES

[0047] While best mode for carrying out the present invention is described above, a description will now be made about Examples in which the effect of the present invention was confirmed.

25 Examples 1 to 9

[0048] A fin material 1 (Examples 1, 3 to 9) and fin material 1A (Example 2) shown in Fig. 1a and Fig. 1b were made so as to confirm the effect of the present invention. As the substrate 2, a 0.1 mm thick aluminum sheet made of aluminum of an alloy number 1200 defined in JIS H4000 was used.

30 [0049] The surface of the aluminum sheet was subjected to a phosphoric chromate treatment for formation of a primer-treated layer 3. As a chemical treating solution, ALUSURF® 401/45 manufactured by NIPPON PAINT Co., Ltd., phosphoric acid, and chromic acid were used. At this time, the thickness of the primer-treated layer 3 was 400 Å (a value measured by a fluorescent X-ray method was 20 mg/m<sup>2</sup> in terms of Cr).

35 As a treatment for formation of another primer-treated layer 3, a coating type zirconium treatment was carried out. As a treating solution, SURFCOAT® 147/148 manufactured by NIPPON PAINT Co., Ltd. was used. At this time, the thickness of the primer-treated layer was 40 mg/m<sup>2</sup> in terms of Zr.

[0050] On the primer-treated layer 3, a predetermined amount of a coating material for a hydrophobic coating film layer was coated and then baked. As shown in Table 1, any one of an urethane-based resin coating material (an urethane modified resin emulsion HITECK® S-6254, manufactured by TOHO Chemical Industry Co., LTD.), an epoxy-based resin coating material (ADEKA® Resin EM series EM-0434AN, manufactured by ADEKA CORPORATION), an acryl-based resin coating material (a polyacrylate ester copolymer JURYMER® AT-210, manufactured by NIHON JUNYAKU Co., Ltd.), and a polyester-based resin coating material (Nichigo POLYESTER® WR-960, manufacture by Nippon Synthetic Chemical Industry Co., Ltd.) was used as the coating material for a hydrophobic coating film layer. Baking was carried out at the baking temperature so as to control an arrival temperature of an aluminum sheet to 160°C. Thus, a hydrophobic coating film layer 4 having the thickness shown in Table 1 was formed.

45 [0051] On the hydrophobic coating film layer 4, a predetermined amount of an aqueous resin solution of a mixture of a polymer having a sulfonic acid group alone, and polyacrylic acid or polyvinyl alcohol (completely saponified type) (each having an average molecular weight of 100,000) was coated and then baked. At this time, 0.01% by mass of a polyoxethylene alkyl phenyl ether phosphoric acid was added to the hydrophilic coating film layer 5 so as to improve coatability. Baking was carried out at the baking temperature so as to control an arrival temperature of an aluminum sheet to 200°C. Thus, a hydrophobic coating film layer 5 having the thickness shown in Table 1 was formed, and thus a fin material 1 (Examples 1, 3 to 9) and a fin material 1A (Example 2) were obtained. In the fin material 1A (Example 2), a resin solution containing an antibacterial agent added thereto was used. As the antibacterial agent, zinc pyrithione (average particle diameter: 0.37  $\mu\text{m}$ ) was used and added to the resin solution in the amount shown in Table 1. An average particle diameter of zinc pyrithione was measured by a laser diffraction scattering type particle size distribution analyzer (SK LASER MICRON SIZER LMS-24, manufactured by SEISHIN ENTERPRISE CO., LTD.) using water as a dispersion and screw dispersion as a dispersion method.

55 [0052] Each existing ratio of S and O in the hydrophilic coating film layer 5 was measured by argon sputtering at a

5 pulse mode (frequency: 300 HZ, duty cycle: 0.3125) by a high-frequency glow discharge optical emission spectroscopic apparatus (JY-5000RF, manufactured by HORIBA, Ltd.) using the fin material 1 (Examples 1, 3 to 9) and the fin material 1A (Example 2). The total amount of impurities of the coating film layer (hydrophobic coating film layer 4 and hydrophilic coating film layer 5) was measured by the mentioned method, in which insoluble matters of the combustion residue of the coating film was measured. Combustion was carried out by placing a coating material of a hydrophilic coating film component in a crucible and heating in a heating furnace in an air atmosphere at 500°C for one hour. The results are shown in Table 1. Analytical results of Examples 1 are shown in Fig. 2.

10 Comparative Examples 1 to 8

15 [0053] As references of Examples, fin materials of Comparative Examples 1 to 8 were also made. Fin materials were made in the same manner as in Example 1, except that each existing ratio of S and O of the hydrophilic coating film layer is less than the lower limit of the first aspect of the invention in Comparative Example 1, the thickness of hydrophilic coating film layer is less than the lower limit in Comparative Example 2, the thickness of hydrophobic coating film layer is less than the lower limit in Comparative Example 3, and the total amount of impurities contained in the coating film layer exceeds the upper limit in Comparative Examples 4. In the same manner as in Example 1, each existing ratio of S and O of the hydrophilic coating film layer and the total amount of impurities of the coating film layer were measured. The results are shown in Table 1. The hydrophilic coating film layer is made of a compound which contains oxygen but does not contain sulfur in Comparative Examples 6, a compound which contains sulfur but does not contain oxygen in Comparative Examples 7, or a compound which is not subjected to a primer treatment in Comparative Examples 8.

20 [0054] Next, the fin materials of Examples 1 to 9 and Comparative Examples 1 to 8 were exposed to the environment of a temperature of 49°C and a humidity of 98%RH or higher for 300 hours and then immersed in running tap water (1,000 cc/min) for 240 hours, assuming corrosion in a high humidity atmosphere and a long-period cooling operation. 25 A pollutant adhesion test was then carried out by the following procedure, and hydrophilicity and odor were evaluated. The results are shown in Table 1.

Pollutant Adhesion Test

30 [0055] Using stearic acid as a repelling material and formaldehyde as an odor material, these reagents (1 g each) were placed on the bottom of a desiccator having a volume of 6 liter. Each sample material measuring 5 cm x 10 cm cut from the fin material was suspended over the reagents. After the desiccator was heated at 100°C for 24 hours and air-cooled to room temperature, the sample material was taken out, immersed in pure water for one minute and dried at room temperature. Then, hydrophilicity and odor were evaluated by the following procedure.

35 Hydrophilicity

40 [0056] 1 µl of pure water was dropped on the sample material and then a contact angle  $\theta$  of the obtained water droplet was measured by a goniometer (Model CA-X250, manufactured by Kyowa Interface Science Co., Ltd.). The case where the contact angle  $\theta$  is 30° or less was rated "Good (G)", while the case where the contact angle  $\theta$  is 30° or more was rated "Poor (P)".

Odor

45 [0057] Sensory evaluation of odor was carried out using, as a standard, the sample material in a state before subjecting to the pollutant adhesion test. The case where panelists feel odor was rated "Poor (P)", while the case where panelists feel no odor was rated "Good (G)".

50 [0058] With respect to only the fin material 1A of Example 2, fungicidal and antibacterial properties were evaluated by the following procedure.

Fungicidal and Antibacterial Properties

55 [0059] Fungicidal and antibacterial properties were evaluated by a test according to the glass ring method described in "Sadako YAMADA et al.: Quick Method for Antifungal Activity Test of Surface of Solid Material" (in Japanese), Anti-bacterial and Fungicidal Properties, Vol. 31, No. 11, PP.711-717 (2003)". A mixture of three kinds of molds such as black mold (Aspergillus niger), green mold (Penicillium chrysogenum) and black sooty mold (Cladosporium cladosporioides) was used as the mold. The results are evaluated by six grades shown in Table 2. The case where a score is 4 or more was rated "Good (G)", while the case where a score is 3 or less was rated "Poor (P)".

[0060]

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Table 1

|                       | Primer treatment       | Coating material of hydrophobic coating film layer | Thickness of hydrophobic coating film layer (μm) | Hydrophilic coating film layer                 |                          |   |     |     |   |
|-----------------------|------------------------|--|--|--|--------------------------|---|-----|-----|---|
|                       |                        |  |  | 1) SO <sub>3</sub> Na group-containing polymer | 2) Additive polymer kind | Mass ratio to (1)                               | S   | O   | Hydrophilic resin (% by mass)                 |
| Example 1             | Phosphoric chromate    | Urethane-based coating material                    | 1.8  | 0.3  | Resin (1)                | Resin A   | 0.1 | 2.8 | 21  |
| Example 2             | Phosphoric chromate    | Urethane-based coating material                    | 1  | 1  | Resin (2)                | None  | 0   | 2.0 | 15  |
| Example 3             | Phosphoric chromate    | Epoxy-based coating material                       | 1  | 1  | Resin (3)                | Resin A   | 0.5 | 4.5 | 30  |
| Example 4             | Phosphoric chromate    | Acrylic coating material                           | 1  | 1  | Resin (1)                | None  | 0   | 2.0 | 15  |
| Example 5             | Phosphoric chromate    | Polyester-based coating material                   | 1  | 1  | Resin (1)                | Resin B   | 0.2 | 2.0 | 15  |
| Example 6             | Coating type zirconium | Epoxy-based coating material                       | 1  | 1  | Resin (1)                | Resin A   | 0.5 | 2.0 | 15  |
| Example 7             | Phosphoric chromate    | Epoxy-based coating material                       | 1  | 9.5  | Resin (1)                | Resin A   | 3.5 | 1.2 | 15  |
| Example 8             | Phosphoric chromate    | Epoxy-based coating material                       | 9.5  | 1  | Resin (1)                | Resin A   | 0.5 | 2.0 | 15  |
| Example 9             | Phosphoric chromate    | Epoxy-based coating material                       | 0.2  | 1  | Resin (1)                | Resin A   | 0.5 | 2.0 | 15  |
| Comparative Example 1 | Phosphoric chromate    | Urethane-based coating material                    | 1  | 1  | Resin (1)                | Resin A   | 5   | 0.5 | 5   |
| Comparative Example 2 | Phosphoric chromate    | Urethane-based coating material                    | 1.8  | 0.05   | Resin (1)                | Resin A   | 0.1 | 2.8 | 21  |
| Comparative Example 3 | Phosphoric chromate    | Urethane-based coating material                    | 0.05   | 1  | Resin (1)                | Resin A   | 0.1 | 2.8 | 21  |
| Comparative Example 4 | Phosphoric chromate    | Urethane-based coating material                    | 1.8  | 0.3  | Resin (1)                | Resin A   | 0.1 | 2.8 | 21  |
| Comparative Example 5 | None                   | -  | -  | Resin (1)                                      | None                     | 0   | 10  | 40  | Hydrophilic coating film layer was not formed |
| Comparative Example 6 | Phosphoric chromate    | Urethane-based coating material                    | 1.8  | 0.3  | None                     | Equivalent mixture of resin A and resin B       |     | 21  | 100   |
| Comparative Example 7 | Phosphoric chromate    | Urethane-based coating material                    | 1.8  | 0.3  | None                     | Mixture of polyethylene resin and sulfur powder |     | 0   | 100   |
| Comparative Example 8 | None                   | Urethane-based coating material                    | 1  | 1  | Resin (3)                | Resin A   | 0.5 | 2.0 | 15  |
|                       |                        |  |  |  |                          |   |     | 70  | -   |

Table 1 (Continued)

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|                          | Total amount<br>of<br>impurities<br>(% by mass) | Evaluation results |                         |      | Fungicidal and<br>antibacterial<br>properties |
|--------------------------|---|--------------------|-------------------------|------|---|
|                          |   | Hydrophilicity     | Pollutant adhesion test | Odor |   |
| Example 1                | Less than 1                                     | G                  | G                       | G    | -   |
| Example 2                | Less than 1                                     | G                  | G                       | G    | G   |
| Example 3                | Less than 1                                     | G                  | G                       | G    | -   |
| Example 4                | Less than 1                                     | G                  | G                       | G    | -   |
| Example 5                | Less than 1                                     | G                  | G                       | G    | -   |
| Example 6                | Less than 1                                     | G                  | G                       | G    | -   |
| Example 7                | Less than 1                                     | G                  | G                       | G    | -   |
| Example 8                | Less than 1                                     | G                  | G                       | G    | -   |
| Example 9                | Less than 1                                     | G                  | G                       | G    | -   |
| Comparative<br>Example 1 | Less than 1                                     | P                  | P                       | P    | -   |
| Comparative<br>Example 2 | Less than 1                                     | P                  | P                       | P    | -   |
| Comparative<br>Example 3 | Less than 1                                     | P                  | P                       | P    | -   |
| Comparative<br>Example 4 | 2   | P                  | P                       | P    | -   |
| Comparative<br>Example 5 | -   | -                  | -                       | -    | -   |
| Comparative<br>Example 6 | Less than 1                                     | P                  | P                       | P    | -   |
| Comparative<br>Example 7 | Less than 1                                     | P                  | P                       | P    | -   |
| Comparative<br>Example 8 | Less than 1                                     | P                  | P                       | P    | -   |

1) SO<sub>3</sub>Na group-containing polymer

- Resin (1): Acrylic acid/sulfonic acid-based monomer copolymer salt (AQUALIC GL, manufactured by NIPPON SHOKUBAI CO., LTD.)  
 Resin (2): Calcium ligninsulfonate (SANX® C, manufactured by NIPPON PAPER CHEMICALS CO., LTD.)  
 Resin (3): Styrenesulfonic acid-maleic acid copolymer (VERSA® TL3, manufactured by Nippon NSC, Ltd.)

## 2) Additive polymer

- Resin A: Polyacrylic acid (JURYMER® AC10S, manufactured by NIHON JUNYAKU Co., Ltd.)  
 Resin B: Polyvinyl alcohol (NM11®, manufactured by Nippon Synthetic Chemical Industry Co., Ltd.)

[0061]

Table 2

| Evaluation of fungicidal and antibacterial properties | Growth state   |
|---|--|
| 1   | Spores are grown on nearly the entire surface.   |
| 2   | Between 1 and 3  |
| 3   | Generation of spores is slightly observed.   |
| 4   | Spores are not generated, but growth of the spawns is observed on nearly the entire surface. |
| 5   | Spores are not generated, but growth of spawns is slightly observed.                         |
| 6   | Growth of spawns is not observed.  |

[0062] The results shown in Table 1 and Table 2 revealed that the fin materials of Examples 1 to 9, which satisfy the aspect of the invention, are excellent in hydrophilicity and odor as compared with those of Comparative Examples 1 to 8, which do not satisfy the aspects. The results also revealed that the fin material of Example 2 also has fungicidal and antibacterial properties.

### Claims

1. An aluminum fin material for a heat exchanger, comprising:

a substrate made of aluminum or an aluminum alloy,  
 a primer-treated layer made of an inorganic oxide or an organic-inorganic composite compound formed on the substrate,  
 a hydrophobic coating film layer having a thickness of 0.1 to 10  $\mu\text{m}$  formed on the primer-treated layer, and  
 a hydrophilic coating film layer having a thickness of 0.1 to 10  $\mu\text{m}$  formed on the hydrophobic coating film layer, wherein  
 the hydrophobic coating film layer is made of at least one kind of a hydrophobic resin selected from the group consisting of an urethane-based resin, an epoxy-based resin, a polyester-based resin and a polyacrylic acid-based resin,  
 the hydrophilic coating film layer is made of a hydrophilic resin, which has a sulfonic acid group or a sulfonic acid group derivative, and also has at least one kind selected from the group consisting of a carboxyl group, a carboxyl group derivative, a hydroxyl group and a hydroxyl group derivative, and an existing ratio of S measured in a film thickness direction by high-frequency glow discharge optical emission spectroscopy is from 1 to 5 atomic % and an existing ratio of O is from 10 to 35 atomic %, and  
 the total amount of at least one kind of alumina, silica, titania, zeolite and a hydrate thereof contained as impurities in the hydrophobic coating film layer and the hydrophilic coating film layer is 1% by mass or less.

2. The aluminum fin material for a heat exchanger according to claim 1, wherein the hydrophilic coating film layer is made of the hydrophilic resin containing an antibacterial agent added thereto.

Fig.1

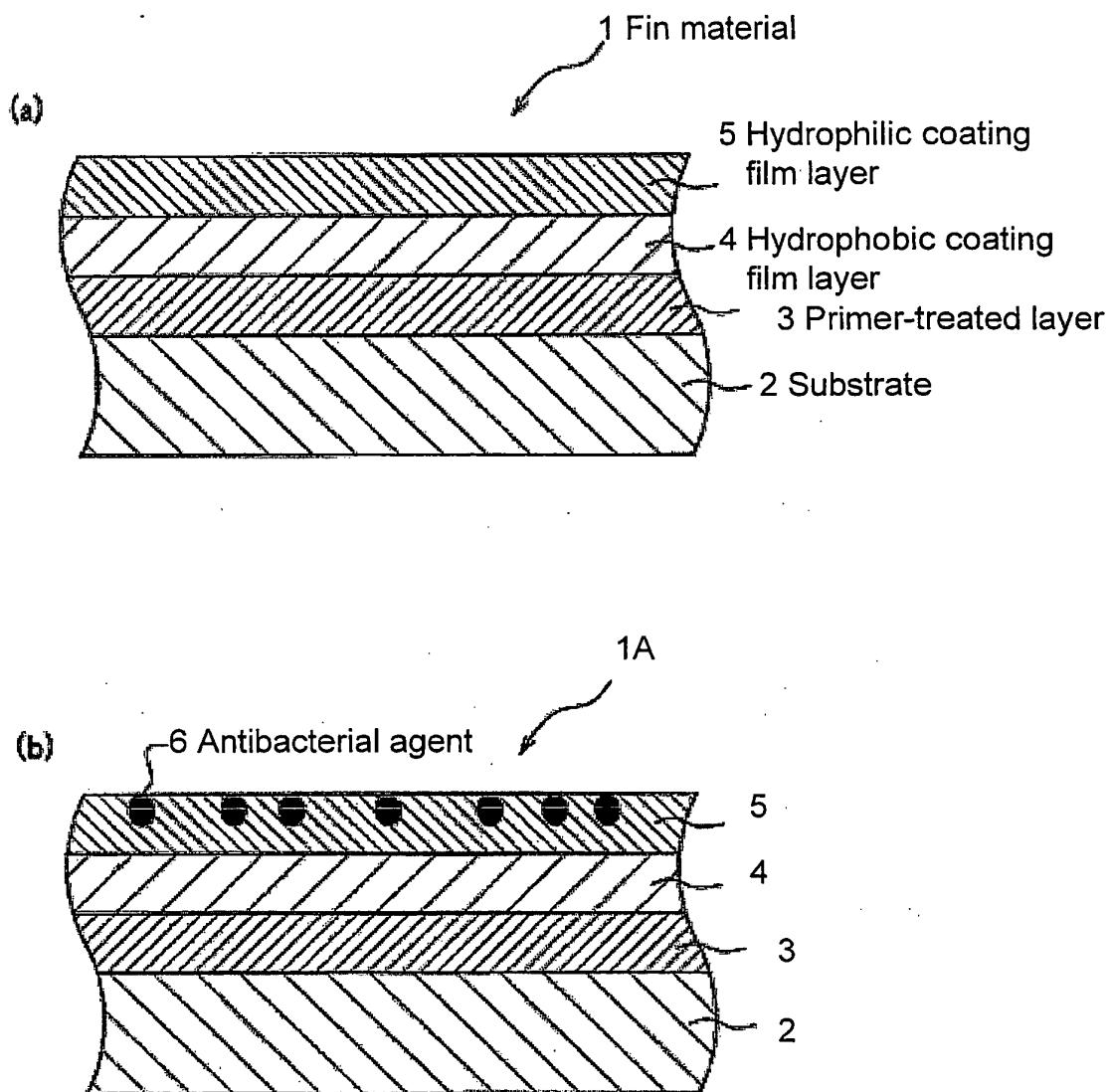
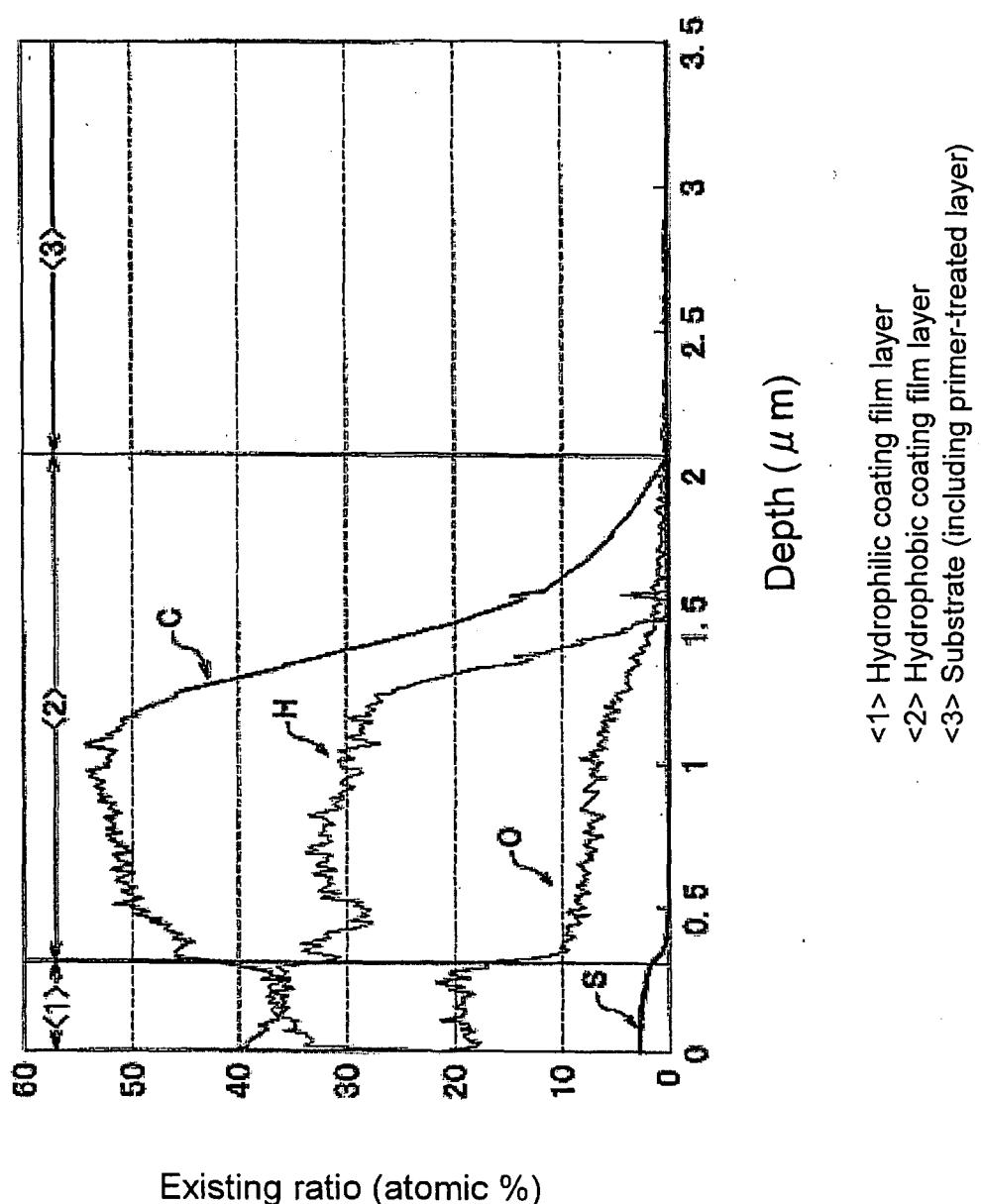


Fig.2

Depth ( $\mu\text{m}$ )

- <1> Hydrophilic coating film layer
- <2> Hydrophobic coating film layer
- <3> Substrate (including primer-treated layer)

Existing ratio (atomic %)

| INTERNATIONAL SEARCH REPORT   |  | International application No.<br>PCT/JP2008/052409                            |
|---|--|---|
| A. CLASSIFICATION OF SUBJECT MATTER<br>F28F13/18(2006.01)i, C23C22/07(2006.01)i, C23C22/36(2006.01)i, F28F19/04 (2006.01)i  |  |   |
| According to International Patent Classification (IPC) or to both national classification and IPC   |  |   |
| B. FIELDS SEARCHED<br>Minimum documentation searched (classification system followed by classification symbols)<br>F28F13/18, C23C22/07, C23C22/36, F28F19/04   |  |   |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched<br>Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2008<br>Kokai Jitsuyo Shinan Koho 1971-2008 Toroku Jitsuyo Shinan Koho 1994-2008   |  |   |
| Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  |  |   |
| C. DOCUMENTS CONSIDERED TO BE RELEVANT  |  |   |
| Category*   | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No.   |
| Y   | JP 2000-171191 A (Nihon Parkerizing Co., Ltd., Samsung Electronics Co., Ltd.), 23 June, 2000 (23.06.00), Claim 1; Par. Nos. [0004], [0013] to [0026]; Fig. 1<br>(Family: none) | 1, 2  |
| Y   | JP 2007-2288 A (Nippon Steel Corp.), 11 January, 2007 (11.01.07), Par. Nos. [0014], [0015], [0020] to [0022]<br>(Family: none)   | 1, 2  |
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| <input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.  |  |   |
| <p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> |  |   |
| Date of the actual completion of the international search<br>13 May, 2008 (13.05.08)  |  | Date of mailing of the international search report<br>20 May, 2008 (20.05.08) |
| Name and mailing address of the ISA/<br>Japanese Patent Office  |  | Authorized officer  |
| Facsimile No.   |  | Telephone No.   |

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## INTERNATIONAL SEARCH REPORT

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| International application No.<br>PCT/JP2008/052409 |
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| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |  |                       |
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**REFERENCES CITED IN THE DESCRIPTION**

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**Patent documents cited in the description**

- JP 3383914 B [0005] [0006]

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- Proceeding of 18th Annual Conference of Japan Association on Odor Environment. *Study on Causative of Odor from Air Conditioners*, June 2005, 3 [0004]
- **Sadako YAMADA et al.** Quick Method for Antifungal Activity Test of Surface of Solid Material" (in Japanese). *Antibacterial and Fungicidal Properties*, 2003, vol. 31 (11), 711-717 [0059]