

DESCRIPTION

COMPOSITION FOR FORMING PHOTOCATALYST FILM, AND SUBSTRATE
PROVIDED WITH PHOTOCATALYST FILM

5 TECHNICAL FIELD

The present invention relates to a composition for forming a photocatalyst film, which is capable of forming a photocatalyst film on the surface of various substrates, a photocatalyst film formed of such a composition, and a
10 substrate provided with a photocatalyst film, which has such a photocatalyst film.

BACKGROUND ART

It is known that when a photocatalyst is excited by light, an organic stain or the like deposited on the
15 surface of the photocatalyst will be decomposed and consequently, a hydrophilic surface will be realized. As a method for forming a photocatalyst film, pyrolysis has heretofore been known which is one type of dry system method (e.g. JP-A-11-512337). However, such a method has
20 had a problem that it is inferior to a wet system method in durability of the hydrophilic property.

Further, a method for forming a photocatalyst film by using a coating composition comprising a photocatalyst and silica, is also known (e.g. Japanese Patent 2756474).
25 However, the film employing silica by the above method was inferior in the durability of the hydrophilic property and had a problem that the stain-decomposing

function was low.

The present invention is to solve the above problems and has an object to provide a composition for forming a photocatalyst film, which is capable of forming a photocatalyst film which is capable of imparting an excellent hydrophilic property to the surface of a substrate and which is particularly excellent in the stain decomposing function, a photocatalyst film formed by such a composition, and a substrate provided with such a photocatalyst film. Further, it has an object to provide a composition for forming a photocatalyst film, which is capable of forming a photocatalyst film excellent in the durability of the hydrophilic property and also excellent in the abrasion resistance of the surface, a photocatalyst film formed of such a composition, and a substrate provided with such a photocatalyst film.

DISCLOSURE OF THE INVENTION

The present invention provides a composition for forming a photocatalyst film, which essentially comprises photocatalytic semiconductor microparticles, the following silica precursor and a medium:

Silica precursor: A silicic acid compound comprising 100 parts by mass of silicic acid and from 0.001 to 1 part by mass of an alkali metal ion.

Further, the present invention provides a photocatalyst film formed of the composition for forming

a photocatalyst film, on the surface of a substrate, and a substrate provided with a photocatalyst film, which has such a photocatalyst film.

BRIEF DESCRIPTION OF THE DRAWINGS

- 5 Fig. 1: Schematic cross-sectional view showing one embodiment of the substrate provided with a photocatalyst film of the present invention.

Meanings of reference numerals

- 10 10: Substrate provided with a photocatalyst film
 20: Substrate
 30: Photocatalyst film

MODE FOR CARRYING OUT THE INVENTION

- 15 In the present invention, the photocatalytic semiconductor microparticles are a material having a nature such that when irradiated with light having an energy larger than the energy difference between the valency electron band and the conduction electron band of the photocatalyst, it is capable of forming conductive electrons and electron holes by excitation of electrons
- 20 in the valency electron band. Such photocatalytic semiconductor microparticles may preferably be, for example, anatase type titanium oxide, rutile type titanium oxide, tin oxide, zinc oxide, tungsten trioxide, ferric oxide, or strontium titanate.

- 25 In the present invention, the average particle size of the photocatalytic semiconductor microparticles is one obtained by measuring agglomerated particle sizes of

microparticles in the composition by utilizing light scattering by means of a Microtrac UPA particle size distribution meter (manufactured by HONEYWELL Co.), and it is preferably from 5 to 90 nm, particularly preferably
5 from 40 to 70 nm. If the average particle size is too small, microparticles of the photocatalyst tend to be embedded in the formed photocatalyst film, whereby various effects of the photocatalyst tend to hardly develop. On the other hand, if the average particle size
10 is too large, the mechanical strength of the photocatalyst film thereby formed, tends to be inadequate, or the transparency may not be secured.

The silica precursor in the present invention is a silicic acid compound containing from 0.001 to 1 part by
15 mass, preferably from 0.001 to 0.2 part by mass, more preferably from 0.001 to 0.15 part by mass, of an alkali metal ion, per 100 parts by mass of silicic acid. The concentration of the alkali metal ion is one measured by an ICP emission spectrometry by means of e.g. SPS4000
20 manufactured by Seiko Instruments Inc. The alkali metal ion is not particularly limited, and one type may be employed or two or more types may be employed. The alkali metal ion is preferably sodium ion or lithium ion. Further, the silicic acid compound is meant for a
25 compound to form a silica film upon application of post treatment as described hereinafter.

The silica precursor is preferably a product

obtained by removing a part of the alkali metal ion from an alkali metal salt of silicic acid. For example, such a product can be obtained by a method of reducing the alkali metal ion from an alkali metal salt of silicic acid by means of a cation exchange resin. The amount of the alkali metal ion to be reduced, can be adjusted by controlling the amount of the cation exchange resin to be used, the contact time, the contact method, etc.

As the cation exchange resin, a strongly acidic cation exchange resin (RSO_3H type) or a weakly acidic cation exchange resin (RCOOH type) may, for example, be used. However, from the viewpoint of the reaction rate, it is preferred to use the strongly acidic cation exchange resin.

In the composition for forming a photocatalyst film of the present invention, the concentration of the alkali metal ion is preferably from 1 to 80 ppm, particularly preferably from 1 to 40 ppm, more preferably from 1 to 20 ppm, as calculated by mass based on the composition for forming a photocatalyst. If the concentration of the alkali metal ion is too small, the stability and the hydrophilic property of the composition tend to deteriorate, and if it is too large, the stability of the composition tends to remarkably deteriorate.

The alkali metal salt of silicic acid may be at least one member selected from the group consisting of sodium silicate, lithium silicate and potassium silicate

and is particularly preferably sodium silicate and/or lithium silicate.

As sodium silicate, materials differing in the compositional ratio of $\text{SiO}_2/\text{Na}_2\text{O}$ are known, and any
5 material may be used without any particular limitation. Among them, a material having a small content ratio of Na_2O is preferred. As commercially available sodium silicate, sodium silicate No. 1 (molar ratio of $\text{SiO}_2/\text{Na}_2\text{O}$: 2.0 to 2.3; sodium silicate No. 1 is a
10 tradename, manufactured by Nippon Chemical Industrial Co., Ltd., the same applies to No. 2 to No. 4), sodium silicate No. 2 (the same molar ratio: 2.4 to 2.7), sodium silicate No. 3 (the same molar ratio: 3.0 to 3.3), or sodium silicate No. 4 (the same molar ratio: 3.7 to 3.9)
15 may be mentioned. Particularly preferred is sodium silicate No. 3 or No. 4 having a small content ratio of Na_2O .

As lithium silicate, materials differing in the compositional ratio of $\text{SiO}_2/\text{Li}_2\text{O}$ are known, and any
20 material may be used without any particular limitation. Among them, a material having a small content ratio of Li_2O is preferred. As commercially available lithium silicate, lithium silicate 35 (molar ratio of $\text{SiO}_2/\text{Li}_2\text{O}$: 3.5; lithium silicate 35 is a tradename, manufactured by
25 Nippon Chemical Industrial Co., Ltd., the same applies to 45 and 75), lithium silicate 45 (the same molar ratio: 4.5) or lithium silicate 75 (the same molar ratio: 7.5)

may be mentioned. Particularly preferred is lithium silicate 75 having a small content ratio of Li_2O .

The composition for forming a photocatalyst film of the present invention preferably contains a surfactant which has mainly two functions. The first function is to secure wettability of the composition to the substrate, and the second function is to increase the hydrophilic property of the photocatalyst layer formed by using the composition. The type of the surfactant is not particularly limited, but a nonionic surfactant is preferably employed from the viewpoint of the dispersion stability. Particularly preferred is a compound wherein the hydrophilic portion is a polyoxyalkylene and the hydrophobic portion is a fluorinated organic group (for example, a compound (hereinafter referred to as surfactant Q) represented by $\text{C}_8\text{F}_{17}\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}(\text{CH}_2\text{CH}_2\text{O})_x(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_y\text{H}$ ($x:y=70:30$, $x+y=5.72$, average molecular weight: 800)). Or, a compound wherein the hydrophilic portion is a polyoxyalkylene and the hydrophobic portion is a methylpolysiloxane (for example, "L-77", tradename, manufactured by NIPPON UNICAR CO., LTD.) is preferred.

In the composition for forming a photocatalyst film of the present invention, the silica precursor is preferably contained in an amount of from 25 to 900 parts by mass, particularly preferably from 50 to 400 parts by mass, per 100 parts by mass of the photocatalytic

semiconductor microparticles. Further, in a case where it contains a surfactant, it is preferred that the surfactant is contained in an amount of from 0.1 to 10 parts by mass per 100 parts by mass of the photocatalytic semiconductor microparticles.

If the concentration of the silica precursor is too large, the durability of the hydrophilic property of the resulting photocatalyst film will be low, and if it is too small, no adequate hydrophilic property will be imparted to the resulting photocatalyst film. Further, if the proportion of the surfactant is too large, the outer appearance of the resulting photocatalyst film tends to be impaired, and the durability of the hydrophilic property will be low, and if it is too small, the coating property of the composition will not be improved, and the hydrophilic property of the photocatalyst film will be low.

The composition for forming a photocatalyst film of the present invention contains a medium. The medium is not particularly limited, a medium containing water is preferred, and it may contain a solvent. Such a solvent is primarily used for dilution, and the composition is preferably in the form of a solution. As such a solvent, a polar solvent such as a lower alcohol, a nitrogen-containing solvent or a sulfur-containing solvent, is preferred, and particularly preferred is a lower alcohol. Two or more solvents may be used. As the medium,

particularly preferred is water.

The total amount of the photocatalytic semiconductor microparticles and the silica precursor in the composition for forming a photocatalyst film of the present invention may be determined depending upon the coating method and the desired thickness of the photocatalyst film. Such a total amount is preferably from 0.5 to 50 parts by mass, particularly preferably from 0.5 to 15 parts by mass, especially preferably from 0.5 to 5 parts by mass, per 100 parts by mass of the composition for forming a photocatalyst film, in view of the stability of the composition, the economical efficiency, etc.

The composition for forming a photocatalyst film of the present invention may contain a functional additive. The functional additive may, for example, be a coloring dye, a pigment, an ultraviolet absorber, an antioxidant or oxide microparticles other than the photocatalytic semiconductor microparticles in the present invention (such as phosphorus pentoxide or magnesium oxide; the average particle size is preferably at most 200 nm).

By using the composition for forming a photocatalyst film of the present invention, a substrate provided with a photocatalyst film is prepared by coating the composition on the surface of the substrate to form a photocatalyst film. In the photocatalyst film, the silica precursor has already been converted to silica,

but partially, silanol groups may remain.

The silica precursor is considered to have silanol groups in the compound, i.e. have a structure represented by $\text{SiO}_s(\text{OH})_t$ (wherein each of s and t is an integer of at least 0, provided $s+t=4$) (provided that in such a structure, an oxygen atom which does not constitute a hydroxyl group, is chemically bonded to another silicon atom), and from such a silica precursor, silica will be formed by a dehydration condensation reaction.

10 In the present invention, by means of a known wet system, the composition for forming a photocatalyst film can be coated on the surface of a substrate to form a substrate 10 provided with a photocatalyst film, wherein a photocatalyst film 30 is formed on a substrate 20, as shown in Fig. 1. As the wet system method, a coating method such as spray coating, brush coating, manual coating, spin coating, dip coating, coating by various printing systems, curtain flow coating, die coating or flow coating, may, for example, be preferably mentioned.

20 After coating the composition for forming a photocatalyst film, it is preferred to apply post treatment for the purpose of removing the medium or increasing the hardness of the photocatalyst film. Such post treatment may, for example, be drying or heating at room temperature, or irradiation or heating with 25 electromagnetic waves such as ultraviolet rays or electron rays. The heating is preferably carried out

within a range of from 50 to 700°C, particularly from 100 to 350°C, for from 5 to 60 minutes, taking into consideration the durability of the substrate.

Especially in a case where the substrate is made of a material having low heat resistance such as an organic resin, or a low molecular weight compound in the substrate is likely to diffuse out of the substrate by heating, it is preferred to carry out irradiation with electromagnetic waves such as ultraviolet rays or electron rays, as such post treatment.

In the present invention, the thickness of the resulting photocatalyst film can be controlled by adjusting the concentration of the composition for forming a photocatalyst film, the type of the solvent, the coating conditions, the post treatment conditions, etc. With respect to the thickness of the photocatalyst film, if it is too thick, there will be a drawback that the film is likely to have cracks or interference fringes, or if scratches are formed, such scratches are highly visible, and if it is too thin, the desired photocatalytic performance may not sufficiently be obtained. Taking into consideration the economical efficiency as well, the thickness of the photocatalyst film is preferably from 10 to 300 nm, particularly preferably from 10 to 150 nm.

The substrate to be used in the present invention is not particularly limited. The shape of the substrate is

not limited to a flat plate and may have a curvature over the entire surface or a part thereof. As the substrate to be used in the present invention, a transparent substrate of e.g. glass or an organic resin, is preferred.

5 As such glass, soda lime glass to be used mainly for a plate glass or glass for automobiles, may be mentioned. As the above-mentioned organic resin, a resin such as polycarbonate, an acrylic resin, polyethylene, polypropylene or polyethylene terephthalate, may, for

10 example, be mentioned. Further, in order to increase the strength of the organic resin, a silicone hard coating may be applied to the surface of the resin. Further, in a case where a transparent substrate of e.g. glass or organic resin, is used as the substrate, the visible

15 light transmittance (JIS R3106 (1998)) of the substrate provided with a photocatalyst film, is preferably at least 70% from the viewpoint of the see-through property.

Pretreatment may be applied to the substrate. As such pretreatment, discharge treatment such as plasma

20 treatment, corona treatment, UV treatment or ozone treatment, chemical treatment employing an acid or alkali, or physical treatment employing an abrasive, may, for example, be mentioned. By such pretreatment, wettability of the composition to the substrate may be improved, the

25 composition can be uniformly coated, or the adhesion of the formed photocatalyst film to the substrate may be improved. Especially in a case where the substrate is an

organic resin, it is preferred to carry out such pretreatment. It is usually particularly effective that the pretreatment is carried out by ultraviolet ray irradiation by means of a low pressure mercury lamp, to
5 be used for modification of plastics.

Further, such pretreatment and the above-mentioned post treatment are influential substantially over the performance of the resulting film, and accordingly it is necessary to optimize the respective treating conditions.
10 For example, by post treatment by means of irradiation with ultraviolet rays, it is possible not only to accelerate the dehydration polycondensation reaction to accelerate the curing of the film, but also to improve the adhesion between the substrate surface and the
15 composition. Thus, in a case where the adhesion to the substrate can be improved by such post treatment, no pretreatment will be required. Excessive pretreatment may rather deteriorate the substrate and may bring about deterioration of the performance.

20 The substrate provided with a photocatalyst film of the present invention is excellent in the hydrophilic property of the surface and also excellent in transparency, and thus is preferably employed as a component for transportation equipments or as a component
25 for buildings. As the component for transportation equipments, a body, a window glass, a mirror, a cover plate or the like for various display devices, for an

electric car, an automobile, a ship or boat, or an aircraft, may, for example, be mentioned. As the component for buildings, an outer wall, a sealant portion, a window glass, or a structure such as a bridge or tunnel, may, for example, be mentioned. Further, as other applications, cover glass for illumination, a sound-shielding wall, etc. may be mentioned.

The substrate provided with a photocatalyst film of the present invention is excellent in the hydrophilic property of its surface and thus has an anti-fogging property whereby water drops deposited on the surface will spread wettingly so that the surface will not be fogged. Further, an organic stain will be decomposed at the surface. Further, by irradiation of light on the surface, the performance in the decomposition of the organic stain will be further improved. Still further, when raindrops by raining will flow down on the surface, the stain will simultaneously flow down (i.e. a self-cleaning effect). The substrate provided with a photocatalyst film of the present invention is expected to have effects for e.g. securing the visibility, maintenance of the beautiful appearance or reduction of maintenance costs.

The photocatalyst film formed of the composition for forming a photocatalyst film of the present invention is superior in the maintenance of the hydrophilic property or in the performance for decomposition of a stain, to a

coating film formed from a composition employing a product having a structure represented by $\text{SiO}_p(\text{OH})_q(\text{OR})_r$ (wherein each of p and q is an integer of at least 0, r is an integer of at least 1, provided that $p+q+r=4$)

5 (provided that in such a structure, an oxygen atom other than the hydroxyl group, is chemically bonded to another silicon atom) obtained by hydrolysis of $\text{Si}(\text{OR})_4$ (R: alkyl group) as a conventional alkoxysilane.

The substrate provided with a photocatalyst film of
10 the present invention may have another film between the substrate and the photocatalyst film. As such another film, an alkali barrier layer (a layer for the purpose of preventing diffusion of alkali metal to the photocatalyst film in a case where the substrate is an alkali metal-
15 containing glass) may, for example, be mentioned.

EXAMPLES

The present invention will be described in further detail with reference to Examples (Examples 1 to 7 and 10 to 12) and Comparative Examples (Examples 8 and 9).

20 Samples were evaluated by the following methods. The evaluation results are shown in Table 1.

Hydrophilic property

Immediately after the preparation of a sample, the contact angle of water at the initial stage before
25 irradiation of light, was measured.

Durability of the hydrophilic property

A sample was maintained in an environment where no

light was irradiated, for one week from immediately after the preparation of the sample, whereupon the contact angle of water was measured. The contact angle is preferably at most 20° , more preferably at most 10° , from the viewpoint of durability of the hydrophilic property.

Stain decomposition performance

Oleic acid was deposited on a sample immediately after its preparation, to obtain a stained surface, of which the contact angle of water was about 70° . On the surface, black light (center wavelength: 365 nm) was irradiated for 6 hours with an intensity of 0.5 mW/cm^2 , whereupon the contact angle of water was measured. A contact angle of at most 10° , more preferably at most 6° , is preferred from the viewpoint of the antifouling property.

Film strength

A sample was subjected to a Taber abrasion test (number of abrasion times: 100 times, load: 4.9 N). Before and after the abrasion test, the haze value was measured (measuring instrument: direct reading haze computer, manufactured by Suga Shikenki K.K.), and the change was obtained. A change of at most 3%, is preferred from the viewpoint of abrasion resistance.

Antifouling property

A sample immediately after its preparation, was exposed outdoors for 1 month, whereupon the fouling degree was visually observed (little fouling observed: ○,

slight fouling was observed: Δ , substantial fouling observed: $\times$).

Anti-fogging property

A breath was blown to a sample immediately after its
5 preparation, whereby the presence or absence of fogging was visually observed (no fogging observed: $\bigcirc$, fogging observed: $\times$).

EXAMPLE 1

Soda lime glass plate (100 mm $\times$ 100 mm, thickness:
10 3.5 mm) was prepared, and its surface was polished with cerium oxide, then washed with distilled water and dried to obtain a pre-treated glass plate.

To 37.5 g of water, 12.5 g of sodium silicate No. 4 (tradename, manufactured by Nippon Chemical Industrial
15 Co., Ltd., SiO_2 : 23.35 mass%, Na_2O : 6.29 mass%, molar ratio of $\text{SiO}_2/\text{Na}_2\text{O}$: 3.83) was added, and further, 30 g of strongly acidic cation exchange resin ("SK1BH", tradename, manufactured by Mitsubishi Chemical Corporation) was added, followed by stirring at room temperature for 10
20 minutes to prepare a deionized sodium silicate solution (sodium ion was 0.12 part by mass, per 100 parts by mass of silicic acid).

Further, to 32.1 g of 2-propanol, 9 g of an aqueous dispersion (solid concentration: 10 mass%) of anatase
25 type titanium oxide microparticles (average particle size: 56 nm, hereinafter referred to as photocatalyst A) and 8.9 g of the deionized sodium silicate solution, were

added, and further, a surfactant "L-77" (tradename, manufactured by NIPPON UNICAR CO., LTD.) was added so that it would be 100 ppm based on the liquid amount, to obtain coating liquid 1 (sodium ion concentration: 12 ppm).

2 mL of the obtained coating liquid 1 was dropped on the surface of the above-mentioned pretreated glass plate and coated by a spin coating method, followed by baking in an atmospheric atmosphere at 200°C for 60 minutes to obtain a sample having a photocatalyst film having a thickness of 80 nm.

EXAMPLE 2

To 36.07 g of water, 13.93 g of lithium silicate 75 (tradename, manufactured by Nippon Chemical Industrial Co., Ltd., SiO₂: 21.54 mass%, Li₂O: 1.43 mass%, molar ratio of SiO₂/Li₂O: 7.49) was added, and further, 30 g of "SK1BH" was added, followed by stirring at room temperature for 10 minutes to prepare a deionized lithium silicate solution (lithium ion was 0.13 part by mass, per 100 parts by mass of silicic acid).

Further, to 32.1 g of 2-propanol, 9 g of photocatalyst A and 8.9 g of the deionized lithium silicate solution were added, and further, "L-77" was added so that it would be 100 ppm based on the liquid amount, to obtain coating liquid 2 (lithium ion concentration: 13 ppm). Using the obtained coating liquid 2, a sample having a photocatalyst film having a

thickness of 83 nm, was obtained in the same manner as in Example 1.

EXAMPLE 3

To 32.1 g of 2-propanol, 10.5 g photocatalyst A and
5 6.69 g of the deionized sodium silicate solution as in
Example 1, were added, and further, "L-77" was added so
that it would be 100 ppm based on the liquid amount, to
obtain coating liquid 3 (sodium ion concentration: 7 ppm).
Using the obtained coating liquid 3, a sample having a
10 photocatalyst film having a thickness of 82 nm, was
obtained in the same manner as in Example 1.

EXAMPLE 4

To 32.1 g of 2-propanol, 4.5 g photocatalyst A and
15 15.6 g of the deionized sodium silicate solution as in
Example 1, were added, and further, "L-77" was added so
that it would be 100 ppm based on the liquid amount, to
obtain coating liquid 4 (sodium ion concentration: 23
ppm). Using the obtained coating liquid 4, a sample
having a photocatalyst film having a thickness of 83 nm,
20 was obtained in the same manner as in Example 1.

EXAMPLE 5

A sample was obtained in the same manner as in
Example 1 except that in Example 1, surfactant Q was
employed instead of "L-77".

25 EXAMPLE 6

In Example 1, instead of baking in an atmospheric
atmosphere at 200°C for 60 minutes, baking was carried

out in an atmospheric atmosphere at 300°C for 30 minutes to obtain a sample.

EXAMPLE 7

In Example 1, instead of baking in an atmospheric
5 atmosphere at 200°C for 60 minutes, baking was carried out in an atmospheric atmosphere at 650°C for 5 minutes to obtain a sample.

EXAMPLE 8 (Comparative Example)

To 90 g of ethanol, 5 g of tetramethoxysilane was
10 added, followed by stirring for 10 minutes. Then, 5 g of an aqueous nitric acid solution (1 mass%) was gradually added to obtain a hydrolyzed product B of tetramethoxysilane.

To 32.1 g of 2-propanol, 9 g photocatalyst A and 8.9
15 g of the above hydrolyzed product B were added, and further, "L-77" was added so that it would be 100 ppm based on the liquid amount, to obtain coating liquid 8 (sodium ion concentration: 0 ppm).

Using the obtained coating liquid 8, a sample having
20 a photocatalyst film having a thickness of 80 nm, was obtained in the same manner as in Example 1.

EXAMPLE 9 (Comparative Example)

To 32.1 g of 2-propanol, 9 g photocatalyst A and 8.9
g of sodium silicate No. 4 (sodium ion was 26.9 parts by
25 mass per 100 parts by mass of silicic acid) were added, whereby precipitate was formed, and it was impossible to obtain a coating liquid.

EXAMPLE 10

A polycarbonate resin plate (100 mm × 100 mm, thickness: 5.0 mm) provided with a silicone hard coating, was prepared, and its hard coating surface was washed
5 with distilled water and then dried to obtain a pretreated polycarbonate plate.

2 mL of coating liquid 1 obtained in Example 1 was dropped on the surface of the pretreated polycarbonate plate and coated by a spin coating method. Then,
10 ultraviolet rays were irradiated for 5 minutes by means of a low pressure UV irradiation apparatus (PL7-200, manufactured by Sen Engineering K.K.) with a distance between the lamp and the resin plate being 2 cm, to obtain a sample having a photocatalyst film having a
15 thickness of 80 nm. Here, the ultraviolet rays are meant for high energy ultraviolet rays (hereinafter referred to as UV-C) having main wavelengths of 253.7 nm and 184.9 nm, by a low pressure mercury lamp.

EXAMPLE 11

20 A sample was obtained in the same manner as in Example 10 except that in Example 10, after washing and drying the polycarbonate resin plate provided with a silicone hard coating, UV-C was irradiated for 2 minutes by means of the above-mentioned low pressure UV
25 irradiation apparatus to obtain the pretreated polycarbonate plate.

EXAMPLE 12

In Example 10, instead of irradiating UV-C for 5 minutes, ultraviolet rays were irradiated for 5 minutes by means of a metal halide lamp (M03-L31, manufactured by EYEGRAPHICS Co., Ltd.) with a distance between the lamp and the above resin plate being 10 cm, to obtain a sample having a photocatalyst film having a thickness of 80 nm. Here, the metal halide lamp is meant for a lamp having a high output of ultraviolet rays having longer wavelength than the low pressure mercury lamp at a level of from 300 to 450 nm.

Table 1

Ex.	Hydro-philic property	Durability of hydro-philic property	Stain decomposition performance	Film strength	Anti-fouling property	Anti-fogging property
1	3°	8°	5°	2.1	○	○
2	4°	6°	4°	2.1	○	○
3	4°	12°	3°	2.8	○	○
4	3°	7°	5°	1.8	○	○
5	1°	6°	5°	2.1	○	○
6	5°	11°	5°	1.2	○	○
7	5°	10°	5°	0.8	○	○
8	3°	23°	46°	4.6	△	○
10	3°	6°	5°	2.2	○	○
11	4°	8°	5°	2.0	○	○
12	3°	7°	4°	2.4	○	○

INDUSTRIAL APPLICABILITY

According to the present invention, a composition for forming a photocatalyst film can be obtained which is

capable of imparting an excellent hydrophilic property to the surface of a substrate. Further, by means of the composition for forming a photocatalyst film of the present invention, a photocatalyst film excellent in a hydrophilic property can be formed at a low temperature, and the surface of a substrate provided with such a photocatalyst film will be excellent in the hydrophilic property. Further, the photocatalyst film formed by means of the composition for forming a photocatalyst film of the present invention, is particularly excellent in the stain decomposition performance, and the durability of the hydrophilic property is long. Accordingly, the surface can be maintained to be always clean.

The surface of a substrate formed by means of the composition for forming a photocatalyst film of the present invention and having an excellent hydrophilic property imparted, is excellent in the droplet falling property, the antifogging property, the antifouling property and the abrasion resistance. Namely, the hydrophilic property is imparted to the surface of the substrate, whereby waterdrops deposited on the surface of the substrate will spread wettingly, and the surface will not be fogged. Further, by irradiation of light such as sunlight, decomposition of a stain (particularly decomposition of an organic stain) will be accelerated. Further, when e.g. by raining, water falls down on the surface of an article, an inorganic stain will also

simultaneously fall down (self cleaning effect).

CLAIMS:

1. A composition for forming a photocatalyst film,
which essentially comprises photocatalytic semiconductor
microparticles, the following silica precursor and a
5 medium:

Silica precursor: A silicic acid compound comprising
100 parts by mass of silicic acid and from 0.001 to 1
part by mass of an alkali metal ion.

2. The composition for forming a photocatalyst film
10 according to Claim 1, wherein the average particle size
of the photocatalytic semiconductor microparticles is
from 5 to 90 nm.

3. The composition for forming a photocatalyst film
according to Claim 1 or 2, wherein the concentration of
15 the alkali metal ion in the composition for forming a
photocatalyst is from 1 to 80 ppm as calculated by mass
based on the composition for forming a photocatalyst.

4. The composition for forming a photocatalyst film
according to Claim 1, 2 or 3, wherein the silica
20 precursor is formed by removing a part of the alkali
metal ion from an alkali metal salt of silicic acid.

5. The composition for forming a photocatalyst film
according to Claim 1, 2 or 3, wherein the silica
precursor is formed by removing a part of the alkali
25 metal ion from an alkali metal salt of silicic acid by
means of a cation exchange resin.

6. The composition for forming a photocatalyst film

according to Claim 4 or 5, wherein the alkali metal salt of silicic acid is sodium silicate and/or lithium silicate.

7. The composition for forming a photocatalyst film
5 according to any one of Claims 1 to 6, wherein the silica precursor is contained in an amount of from 25 to 900 parts by mass per 100 parts by mass of the photocatalytic semiconductor microparticles.

8. The composition for forming a photocatalyst film
10 according to any one of Claims 1 to 7, wherein the total amount of the photocatalytic semiconductor microparticles and the silica precursor is from 0.5 to 50 parts by mass per 100 parts by mass of the composition for forming a photocatalyst film.

15 9. A photocatalyst film formed of the composition for forming a photocatalyst film as defined in any one of Claims 1 to 8, on the surface of a substrate.

10. A photocatalyst film formed by applying pretreatment to the surface of a substrate, coating the composition
20 for forming a photocatalyst film as defined in any one of Claims 1 to 8 on said surface and then applying post treatment.

11. The photocatalyst film according to Claim 10,
wherein the post treatment is irradiation of
25 electromagnetic waves.

12. The photocatalyst film according to Claim 9, 10 or 11, wherein the thickness of the photocatalyst film is

from 10 to 300 nm.

13. A substrate provided with a photocatalyst film, which has the photocatalyst film as defined in any one of Claims 9 to 12, on the surface of a substrate.

5 14. The substrate provided with a photocatalyst film according to Claim 13, wherein the substrate is made of glass or an organic resin.

15. The substrate provided with a photocatalyst film according to Claim 13 or 14, wherein the visible light
10 transmittance of the substrate provided with a photocatalyst film is at least 70%.