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SURFACE TREATMENT METHOD AND  
MATERIAL TREATED BY THE METHOD



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BACKGROUND OF THE INVENTION

5 Field of the Invention

The present invention relates to a method of performing a treatment such as modification, deposition, or etching on the surface of a solid material and a material treated by the method and,  
10 more particularly, to a method of giving liquid repellency to a solid material surface and a material treated by the method.

More specifically, the present invention relates to a method of giving liquid repellency only  
15 to the surface of a solid material containing a polymer having on its side chain a single bonding group of a carbon atom and hydrogen atom, by dissociating hydrogen atoms from the solid material surface and at the same time substituting with a  
20 carbon fluoride  $C_nF_m$  ( $n = 1, 2, 3, \dots$ ,  $m = 2n, 2n + 1$ ) group, and a material treated by the method.

Related Background Art

Conventionally, a functional solid material has been so developed that its own physical properties  
25 are effectively utilized. However, various physical properties are required in device applications and the like, so it is becoming more and more difficult

for any single bulk material to well satisfy the required performance or characteristics. In particular, a fluorine resin is used in various purposes by making use of its characteristic features, such as inertness, water repellency, oil repellency, and resistance to scratching, resulting from low surface energy. For example, a fluorine resin is singly molded into parts and products having diverse shapes or used in the form of a film. Also, a fluorine resin film having one surface which is given hydrophilic nature is used to cover parts having various shapes. Furthermore, a fluorine resin is dissolved in a solvent and used in the form of a coating film. Thus, a fluorine resin is used in a wide variety of applications and hence regarded as one of very useful materials.

Even when this fluorine resin is in the form of a film, however, if a bulk region of a certain size is present in the film, in this bulk region the physical properties unique to the fluorine resin appear. For example, a low hardness decreases the cutting resistance, so the film is readily cut with a knife. In the case of molding, a high glass transition point decreases the flowability, and this makes precision molding difficult to perform. Also, in the case of solvent coating the material is limited to a fluorine polymer which dissolves in a

solvent, so the inertness, water repellency, oil repellency, and resistance to scratching do not reach the characteristics of PTFE. Additionally, a high curing temperature restricts the base material that  
5 can be coated. Furthermore, the original physical properties of a fluorine resin also pose problems: a large linear expansion coefficient causes deformation in a high-temperature environment, and a high chargeability limits uses in the vicinity of charge  
10 carriers.

If, therefore, it is possible, instead of processing a fluorine resin material itself, to add the characteristics of a fluorine resin only to surface region thereof while the original bulk  
15 physical characteristics of a base material made of an organic material or organic-inorganic composite material are fully utilized, a wider variety of functions can be achieved.

As this method, Japanese Patent Application  
20 Laid-Open No. 6-340759 discloses a method of modifying a plastic material having a C-H bond by exciting light. That is, this prior art reference describes a method by which, in an atmosphere of a compound or mixture which contains a first atom  
25 having a bond energy of 80.6 kcal/mol or more with respect to a hydrogen atom and a second atom or atomic group whose bond energy with respect to the

first atom is smaller than the optical energy of the  
exciting light, the interface between the plastic  
material and the compound or mixture is directly or  
indirectly irradiated with ultraviolet light having a  
5 photon energy of 80.6 kcal/mol or more. In this  
manner, the plastic material is dehydrogenated via  
the first atom and substituted with the second atom  
or atomic group. As the compound or mixture,  
fluorine compound examples are presented in Examples  
10 11, 27, and 31.

#### SUMMARY OF THE INVENTION

In the configuration of Japanese Patent  
Application Laid-Open No. 6-340759 described above,  
15 however, variations in the manufacturing conditions  
produce large variations in the performance of the  
contact angle owing to the substitution mechanism.  
Since this requires severe management of the  
manufacturing conditions, it is difficult to form  
20 highly stably surface-treated samples with high yield.

That is, the present inventors conducted  
experiments by the method described in (Example 2) of  
Japanese Patent Application Laid-Open No. 6-340759.  
Consequently, when a sample was irradiated with an  
25 ArF laser while being in close contact with an  
aqueous solution prepared by dissolving 2 g of boric  
acid ( $\text{H}_3\text{BO}_3$ ) in 50 cc of water, the aqueous boric

acid solution absorbed light upon ArF laser  
irradiation, and this worsened the efficiency of the  
substitution reaction. Additionally, the thickness  
of the aqueous boric acid solution sometimes produced  
5 variations in the substitution reaction.

Accordingly, the present inventors studied a  
substitution mechanism for efficiently performing  
substitution without any variations produced by the  
thickness of the aqueous boric acid solution or the  
10 like, and have found a novel substitution mechanism,  
thereby deriving a surface treatment stabilization  
method. In particular, the present inventors have  
found a method by which a physical property  
irreversible process logically holds in a method of  
15 adding high liquid repellency to the surface of a  
plastic material having a C-H bond in its surface  
layer.

It is an object of the present invention to  
provide a surface treatment method capable of  
20 extending application regions by maintaining both the  
surface characteristics and bulk characteristics, and  
capable of achieving both high liquid repellency and  
high productivity.

To achieve the above object, the present  
25 invention provides a surface treatment method of  
treating the surface of a material to be treated, by  
irradiating with light the material to be treated and

a mediating material in contact with each other,  
characterized in that the mediating material itself  
causes substantially no interaction upon irradiation  
with light, and the surface of the material to be  
5 treated is treated by provision of chemical reaction  
field, in which a substituent of the material to be  
treated and an atom or atomic group of the mediating  
material is induced by excitation at the same time,  
by irradiating with light by using the logical  
10 product of the contact interface between the material  
to be treated and the mediating material and the  
light irradiation region, thereby causing and  
progressing bonded state transition.

The method is also characterized in that bond  
15 energy by which the substituent induced by excitation  
from the material to be treated in the chemical  
reaction field is subjected to captive transition  
bonding by the atom or atomic group induced by  
excitation from the mediating material is larger than  
20 a larger one of bond energy between the substituent  
of the material to be treated and a matrix atom and  
bond energy between the atom or atomic group of the  
mediating material and the matrix atom.

The method is further characterized in that the  
25 light which irradiates the material to be treated and  
the mediating material has a wavelength having photon  
energy larger than a larger one of bond energy

between the substituent of the material to be treated and a matrix atom and bond energy between the atom or atomic group of the mediating material and the matrix atom.

5           Also, the present invention for achieving the above object is a method of treating the surface of a material to be treated having a single bonding group of a carbon atom and hydrogen atom on the surface, characterized in that while the material to be  
10   treated is in contact with a liquid mediating material which is an aggregate of a polymer having on its main chain an ether bonding group and a carbon fluoride  $C_nF_m$  ( $n = 1, 2, 3, \dots$ ,  $m = 2n$  or  $2n + 1$ ) group, the contact interface between the material to  
15   be treated and the mediating material is irradiated with ultraviolet radiation having a wavelength of 221.4 to 351.6 nm, thereby substituting a hydrogen atom in the single bonding group of a carbon atom and the hydrogen atom on the surface of the material to  
20   be treated with the carbon fluoride group in the mediating material, and modifying the surface of the material to be treated.

#### BRIEF DESCRIPTION OF THE DRAWINGS

25           Fig. 1 is a schematic view showing a means for performing a solid material surface treatment according to the present invention;

Fig. 2 is a graph showing the water repellency characteristics of an embodiment;

Fig. 3 is a graph showing the water repellency characteristics of a comparative example;

5        Fig. 4 is a view showing the mechanism of treating the surface of a material to be treated according to this embodiment;

Fig. 5 is a view showing the mechanism of treating the surface of a material to be treated  
10 according to the comparative example;

Figs. 6A, 6B and 6C are schematic views showing the surface conditions of the materials to be treated according to the embodiment and the comparative example; and

15        Fig. 7 is a schematic view of another means for performing the solid material surface treatment according to the present invention.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

20        The characteristic feature of the present invention will be described in detail below.

This characteristic feature of the present invention is to perform a surface treatment by providing a chemical reaction field, in which a  
25        substituent of a material to be treated is induced by excitation and at the same time an atom of atomic group of a mediating material which causes

substantially no interaction upon irradiation with  
light when used alone is induced by excitation, by  
irradiating with light the material to be treated and  
the mediating material in contact with each other by  
5 using the logical product of the contact interface  
between the material to be treated and the mediating  
material and the light irradiation region, thereby  
causing and progressing bonded state transition.

In the present invention, a material which when  
10 used alone causes substantially no interaction upon  
irradiation with light is used as the mediating  
material. Therefore, the energy obtained by  
irradiation with light is not used in excitation  
transition of the mediating material.

15 Accordingly, no variations are produced in the  
substitution reaction by the thickness of the  
mediating material in contact with the material to be  
treated. So, the substitution reaction can be  
performed more efficiently.

20 Also, a chemical reaction field in which the  
substituent in the material to be treated is induced  
by excitation and at the same time the atom or atomic  
group in the mediating material is induced by  
excitation is provided by the contact interface  
25 between the material to be treated and the mediating  
material. This improves the efficiency of bonded  
state transition and makes efficient substitution

feasible.

This mechanism of treating only the surface of a material to be treated according to the present invention will be described in detail below with  
5 reference to Fig. 4.

This embodiment relates to an example in which a liquid mediating material which is an aggregate of a polymer having on its main chain an ether bonding group and a carbon fluoride  $C_nF_m$  ( $n = 1, 2, 3, \dots, m$   
10  $= 2n$  or  $2n + 1$ ) group is used as the mediating material which when used alone causes substantially no interaction upon irradiation with light, and a material having on its surface a single bonding group of a carbon atom and hydrogen atom is used as the  
15 material to be treated.

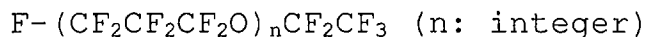
Fig. 4 is a view for explaining the mechanism of treating the surface of a material to be treated according to the present invention. Referring to Fig. 4, (1) indicates a mediating liquid material region;  
20 (2), a boundary region between a mediating liquid material and a material to be treated having a C-H group on its side chain; and (3), a region of the material to be treated. (a) to (c) in (1), (a) to (e) in (2), and (a) to (c) in (3) schematically  
25 represent photochemical reactions in the respective regions when these regions are irradiated with ultraviolet radiation.

In the present invention, an exposed, developed negative photosensitive resin containing an alicyclic epoxy resin as its main component is used as the material to be treated. Also, perfluoroether

5 (chemical name: perfluoropolyoxetane, trade name: DEMNUM (manufactured by DAIKIN INDUSTRIES, LTD.) is used as the mediating material.

A krypton fluorine excimer laser beam (114 kcal/mol) emitted from an ultraviolet laser  
10 oscillator and having an optical wavelength of 248.4 nm irradiates perfluoropolyether as a mediating material represented by the following formula.

Chemical formula of perfluoropolyether



15 The emitted ultraviolet radiation (excimer laser) is transmitted through the perfluoropolyether with no light absorption, and reaches the surface of a solid material 7 to be treated. However, in terms of quantum optics, the passing of ultraviolet photons  
20 strictly means that no photon energy absorption takes place; if an energy level which transits by absorbing photons exists, absorption of photons occurs to produce an action. That is, a photochemical reaction can be locally generated by providing an  
25 energetically stable level.

In the mediating liquid material, as indicated by (1)-(a), the energy exceeding the potential

barrier of the single bond energy of a carbon atom and oxygen atom is about 76 kcal/mol. When the ultraviolet wavelength is about 357 nm or less, the photon energy is about 76 kcal/mol or more, so this energy exceeds the potential barrier of the single bond energy of a carbon atom and oxygen atom as an ether group. Accordingly, as indicated by (1)-(b), an oxygen atom can dissociate as an ion from a carbon atom. However, an oxygen atom alone is unstable, so the life of an oxygen atom alone is short. Therefore, even when dissociating as an ion from a carbon atom, an oxygen atom immediately radiates a photon having the same energy to return to the original level ((1)-(c)). That is, when observed from the outside this is equivalent to induced radiation; a photon having the same phase, same polarized light, same wavelength, and same propagation direction is radiated, so the observation indicates that no changes have taken place. That is, this is equivalent to the occurrence of nothing.

In the material to be treated, on the other hand, as indicated by (3)-(a), the energy exceeding the potential barrier of the single bond energy of a carbon atom and hydrogen atom is 80.6 kcal/mol. When the ultraviolet wavelength is 351.6 nm or less, the photon energy is 80.6 kcal/mol or more, so this energy exceeds the potential barrier of the single

bond energy of a carbon atom and hydrogen atom. Accordingly, as indicated by (3)-(b), a hydrogen atom can dissociate as an ion from a carbon atom. However, a hydrogen atom alone is unstable, so the life of a  
5 hydrogen atom alone is short. Therefore, even when dissociating as an ion from a carbon atom, a hydrogen atom immediately radiates a photon having the same energy to return to the original level ((3)-(c)). That is, when observed from the outside this is  
10 equivalent to the occurrence of no change, similar to the above case.

However, by providing a new level (a so-called donor or acceptor level) at which oxygen atoms dissociated as ions are captured, absorption of  
15 ultraviolet photons occurs, and this can bring about a photochemical reaction. In the present invention, this capture level is provided on the surface of a solid material to be treated, i.e., on the contact interface between the mediating liquid material and  
20 the material to be processed having a C-H group on its side chain. This will be explained below. An organic material is formed on the surface of a solid material to be treated, and single bonds of carbon atoms and hydrogen atoms are present on the side  
25 chain of an organic material polymer (Fig. 6A). On the other hand, single bonds of oxygen atoms and carbon atoms are present in the mediating liquid

material in contact with the solid material. As indicated by (2)-(a), the energy exceeding the potential barrier of the single bond energy of a carbon atom and oxygen atom is about 76 kcal/mol.

5 Also, the potential barrier energy of the single bond of a carbon atom and hydrogen atom on the organic polymer side chain is 80.6 kcal/mol. When the ultraviolet wavelength is 351.6 nm or less, the photon energy is 80.6 kcal/mol or more. This energy  
10 exceeds the potential barrier of the single bond energy of a carbon atom and oxygen atom and also exceeds the potential barrier of the single bond energy of a carbon atom and hydrogen atom. That is, this energy induces dissociation of an oxygen atom  
15 and hydrogen atom. As indicated by (2)-(b), therefore, an oxygen atom and hydrogen atom dissociate as ions from carbon atoms.

The single bond energy of an oxygen atom and hydrogen atom is about 109 kcal/mol, i.e., larger  
20 than about 76 kcal/mol as the potential barrier energy of the single bond of a carbon atom and oxygen atom as an ether group, and larger than 80.6 kcal/mol as the potential barrier energy of the single bond of a carbon atom and hydrogen atom on the organic  
25 polymer side chain. Accordingly, when an oxygen atom and carbon atom form a single bond, the energy level potential drops to a deeper stable level. More

specifically, with respect to a dissociated oxygen atom and dissociated hydrogen atom, a transition-stable level is provided on the contact interface between the surface of the solid material to be  
5 treated and perfluoropolyether as the mediating liquid material.

As indicated by (2)-(c), an oxygen atom and hydrogen atom radiate photons having an energy of about 109 kcal/mol, generating a single bond of these  
10 oxygen atom and hydrogen atom.

In practice, the stable state of hydrogen H and oxygen O is pure water  $H_2O$ , so the photochemical reaction described so far occurs by consuming four ultraviolet photons of 351.6 nm or less.

15 If the ultraviolet photon energy is equal to or larger than about 109 kcal/mol as the single bond energy of an oxygen atom and hydrogen atom, an oxygen atom and hydrogen atom can of course dissociate as ions as indicated by (2)-(d). However, an oxygen  
20 atom and hydrogen atom alone are unstable, so the life of an oxygen atom alone is short. Therefore, even when dissociating as an ion, an oxygen atom immediately radiates a photon having the same energy to return to the original level ((2)-(e)). That is,  
25 when observed from the outside this is equivalent to the occurrence of no changes. Also, strictly speaking, it is impossible, according to the

Heisenberg uncertainty principle, to observe an ion dissociation process within a very short time; an appropriate explanation is to express this as "unknown" by the quantum theory.

5           At the same time, perfluoropolyether as the mediating liquid material loses ether groups on its main chain, so carbon fluoride groups ( $C_3F_6$  or  $C_3F_7$ ) remain. On the other hand, carbon active groups remain on the surface of the solid material to be  
10 treated. This forms an environment in which the carbon fluoride groups unavoidably chemically bond to the carbon active groups on the surface of the solid material. Consequently, the surface of the solid material is fluorinated to achieve water repellency  
15 (Fig. 6B).

          As a supplementary explanation, the single bond energy of carbon atoms is about 84 kcal/mol. Therefore, when a wavelength of about 336 nm or less is used as ultraviolet radiation to be emitted,  
20 carbon atoms unstably transit between dissociation and bonding, and carbon fluoride chemically bonds to the surface of the solid material in the most stable state in which this carbon fluoride is decomposed or combined to any state in a  $C_nF_m$  ( $n = 1, 2, 3, \dots, m =$   
25  $2n$  or  $2n + 1$ ) group.

          As another supplementary explanation, the single bond energy of carbon atoms is about 84

kcal/mol. Therefore, when a wavelength of about 336 nm or less is used as ultraviolet radiation, carbon atoms unstably transit between dissociation and bonding in a direction in which the entropy increases, and carbon fluoride chemically bonds to the surface of the solid material by forming a network in the most stable state in which this carbon fluoride is decomposed or recombined to any state in a  $C_nF_m$  ( $n = 1, 2, 3, \dots$ ,  $m = 2n$  or  $2n + 1$ ) group and the Gibbs free energy is a minimum.

(Comparative Example)

Fig. 5 is a view showing the mechanism of treating the surface of a material to be treated according to a comparative example. (1) indicates a mediating liquid material region; (2), the boundary region between a mediating liquid material and a material to be treated having a C-H group on its side chain; and (3) a region of the material to be treated. Fig. 5 schematically represents photochemical reactions occurring in these regions when they are irradiated with ultraviolet light.

This comparative example is the same as the embodiment except that the ultraviolet laser oscillator 1 emits an argon fluorine excimer laser beam (147 kcal/mol) having an optical wavelength of 193 nm.

The reactions occurring in (1) and (3) are the

same as in the embodiment.

In the reaction in (2), the level at which a hydrogen atom dissociated as an ion is captured by an oxygen atom, i.e., at which absorption of ultraviolet photons occurs to bring about a photochemical reaction, is provided by the surface of a solid material to be treated, as in the embodiment.

However, the use of light having an ultraviolet wavelength of 221.4 nm or less, i.e., the use of light having a photon energy of about 128 kcal/mol or more as in this comparative example makes the photochemical reaction unstable. Since the photon energy of an argon fluorine excimer laser beam having an optical wavelength of 193 nm is 147 kcal/mol, this beam has a photon energy larger than 128 kcal/mol described above.

That is, this energy is larger than about 128 kcal/mol as the single bond energy of a carbon atom and fluorine atom. In addition, about 136 kcal/mol as the single bond energy of a carbon atom and fluorine atom is larger than about 109 kcal/mol as the single bond energy of an oxygen atom and hydrogen atom, so the former energy drops to a deeper potential level and becomes more stable. Consequently, a fluorine atom captures a hydrogen atom as indicated by (2) in Fig. 5. For this reason, an ether group loses a transition state to be

captured and chemically bonds to the surface of the solid material to change the characteristic in a direction in which the hydrophilic nature increases.

The characteristic is not saturated but  
5 exhibits a peak value in accordance with the number of irradiation pulses, presumably because the characteristic appearance process is delayed since the potential barrier of the dissociation energy of a carbon-fluorine single bond is higher than that of  
10 the dissociation energy of a carbon-oxygen single bond of an ether group.

When thus compared with the comparative example, the point of this embodiment is as follows. To reliably give liquid repellency to the surface of a  
15 solid material to be treated, it is necessary to emit light (light having a photon energy of about 80.6 kcal/mol or more) having a wavelength which gives photon energy higher than 80.6 kcal/mol as the energy of dissociation, from carbon, of a hydrogen atom as a  
20 substituent of the material to be treated, and about 76 kcal/mol as the energy of dissociation, from carbon, of an oxygen atom as an atom or atomic group of the mediating material. This makes it possible to reliably dissociate hydrogen atoms from the material  
25 to be treated and oxygen atoms from the mediating material, and emit light (light having a photon energy of about 128 kcal/mol or less) whose photon

energy is lower than the dissociation energies of a carbon atom and fluorine atom, thereby preventing fluorine atoms from capturing hydrogen atoms.

That is, the point of this embodiment is to  
5 prevent the process of the comparative example by setting the wavelength of ultraviolet light to be emitted within the range of 221.4 to 351.6 nm.

In this embodiment, a liquid material which is an aggregate of a polymer having on its main chain an  
10 ether bonding group and a carbon fluoride  $C_nF_m$  ( $n = 1, 2, 3, \dots, m = 2n$  or  $2n + 1$ ) group is used as the mediating material, and a material having on its surface a single bond of a carbon atom and hydrogen atom is used as the material to be treated. However,  
15 as the material to be treated, it is also possible to use an aggregate of an organic material containing a polymer having on its side chain a single bonding group of a carbon atom and hydrogen atom, or a mixture of an inorganic material and an organic  
20 material containing a polymer having on its side chain a single bonding group of a carbon atom and hydrogen atom.

A preferred example of the mediating material is a polymer consisting of  $-C_nF_{2n}-O-$ .

25 Also, as an ultraviolet light source for emitting such ultraviolet radiation, it is possible to use an excimer light source such as KrF, XeCl, XeF,

XeBr, or Xel.

In this embodiment, light is emitted with the material to be treated in contact with the liquid mediating material. However, if the mediating  
5 material has a low molecular weight, as shown in Fig. 7, a surface treatment can also be performed by emitting light through a window 12 while the material to be treated is in contact with the mediating material in a gaseous state in a chamber 11.

10 (Example 1)

Fig. 1 is a schematic view of a means for giving liquid repellency to the surface of a solid material by fluorination according to the present invention.

15 This means gives liquid repellency to one surface of a solid material 7 to be treated. The solid material 7 is set via spacers 6 to have a gap of about 20 to 100  $\mu\text{m}$  from the surface of a window 3. This solid material 7 is pressed by a weight of 100 g,  
20 as a pressing member 8, so as not to move.

By using this means shown in Fig. 1, an exposed, developed negative photosensitive material (its main components are described in Table 1) containing an alicyclic epoxy resin as its main ingredient was used  
25 as the solid material 7, and perfluoropolyether (DEMNUM (trade name: manufactured by DAIKIN INDUSTRIES, LTD.) was used as a mediating liquid

material 5 to be supplied between the solid material  
7 and the window 3 by a mediating liquid supply means  
4. In addition, a krypton fluorine excimer laser  
beam having an optical wavelength of 248.4 nm was  
5 used as ultraviolet radiation to be emitted which was  
light 10 emitted from a light emitting means 1 and  
reflected by a reflecting plate 2 to the interface  
between the solid material 7 and the mediating liquid  
material 5. Fig. 2 shows the water repellency  
10 characteristics in this case.

Table 1

| Item                              | Product name                            | Parts by weight |
|-----------------------------------|-----------------------------------------|-----------------|
| Alicyclic epoxy resin             | EHPE (DAICEL CHEMICAL INDUSTRIES, LTD.) | 100             |
| Added resin                       | 1,4-HFAB (Central Glass Co., Ltd.)      | 20              |
| Silane coupling agent             | A-187 (Nihon Uniker K.K.)               | 5               |
| Photocation polymerizing catalyst | SP170 (ASAHI DENKA KOGYO K.K.)          | 2               |

In the embodiment, the NOVALine KrF laser apparatus manufactured by Lambdaphysics was used as a laser apparatus.

As can be seen from Fig. 2, when the laser irradiation fluence was 20 to 120 mJ/cm<sup>2</sup>/pulse, the contact angle of pure water increased to a larger water repellency in accordance with the irradiation exposure amount. This pure water contact angle was saturated at about 120° and did not increase or decrease after that even when the exposure amount was increased. Although not plotted on the graph in Fig. 2, when the fluence was 40 mJ/cm<sup>2</sup>/pulse, a pure water contact angle of about 120° was obtained by about 8,000 laser irradiation pulses; when the fluence was 20 mJ/cm<sup>2</sup>/pulse, a pure water contact angle of about 120° was obtained by about 50,000 laser irradiation pulses.

(Example 2)

Similar to Example 1, the means explained in Fig. 1 was used to perform a surface treatment under the same conditions as in Example 1 by using polystyrene as a material 7 to be treated. Consequently, the contact angle of pure water increased to a larger water repellency, was saturated at about 120°, and did not increase or decrease after that even when the exposure amount was increased.

(Example 3)

Similar to Example 1, the means explained in Fig. 1 was used to perform a surface treatment under the same conditions as in Example 1 by using

polyimide as a material 7 to be treated.

Consequently, the contact angle of pure water increased to a larger water repellency, was saturated at about  $120^{\circ}$ , and did not increase or decrease after  
5 that even when the exposure amount was increased.  
(Example 4)

Similar to Example 1, the means explained in Fig. 1 was used to perform a surface treatment under the same conditions as in Example 1 by using  
10 polysulfone as a material 7 to be treated. As a consequence, the contact angle of pure water increased to a larger water repellency, was saturated at about  $120^{\circ}$ , and did not increase or decrease after that even when the exposure amount was increased.  
15 (Example 5)

Similar to Example 1, the means explained in Fig. 1 was used to perform a surface treatment under the same conditions as in Example 1 by using, as a material 7 to be treated, an exposed and developed  
20 negative photosensitive resin (its main components are described in Table 1) containing as its main ingredient an alicyclic epoxy resin containing a silicon filler, as a mixture of an inorganic material and an organic material containing a polymer having  
25 on its side chain a single bonding group of a carbon atom and hydrogen atom. As a consequence, the contact angle of pure water increased to a larger

water repellency, was saturated at about 120°, and did not increase or decrease after that even when the exposure amount was increased.

(Example 6)

5           Similar to Example 1, the means explained in Fig. 1 was used to perform a surface treatment under the same conditions as in Example 1 by using, as a material 7 to be treated, polystyrene containing a glass filler, as a mixture of an inorganic material  
10 and an organic material containing polymer having on its side chain a single bonding group of a carbon atom and hydrogen atom. Consequently, the contact angle of pure water increased to a larger water repellency, was saturated at about 120°, and did not  
15 increase or decrease after that even when the exposure amount was increased.

(Example 7)

          Similar to Example 1, the means explained in Fig. 1 was used to perform a surface treatment under  
20 the same conditions as in Example 1 by using polyimide containing a glass filler as a material 7 to be treated. Consequently, the contact angle of pure water increased to a larger water repellency, was saturated at about 120°, and did not increase or  
25 decrease after that even when the exposure amount was increased.

(Example 8)

Similar to Example 1, the means explained in Fig. 1 was used to perform a surface treatment under the same conditions as in Example 1 by using polysulfone containing a glass filler as a material 7 to be treated. Consequently, the contact angle of pure water increased to a larger water repellency, was saturated at about 120°, and did not increase or decrease after that even when the exposure amount was increased.

10 (Comparative Example)

By using the means shown in Fig. 1 as in Example 1, an exposed and developed negative photosensitive material (its main components are described in Table 1) containing an alicyclic epoxy resin as its main ingredient was used as a material 15 to be treated, perfluoropolyether (DEMNUM (trade name: manufactured by DAIKIN INDUSTRIES, LTD.) was used as a mediating liquid material 5, and an argon fluorine excimer laser beam having an optical wavelength of 193 nm (photon energy = about 147 kcal/mol) was used as ultraviolet radiation to be emitted. Fig. 3 shows the water repellency characteristics in this case.

As can be seen from Fig. 3, when the laser irradiation fluence was 20 to 120 mJ/cm<sup>2</sup>/pulse, the contact angle of pure water once increased to a larger water repellency and reached about 120° in

accordance with the irradiation exposure amount.  
However, this contact angle decreased when the  
exposure amount was increased after that. Although  
not plotted on the graph in Fig. 3, even when the  
5 fluence was 20 mJ/cm<sup>2</sup>/pulse, the pure water contact  
angle reached its peak of about 120° when the number  
of laser irradiation pulses was about 10,000, and  
decreased when the number of laser irradiation pulses  
was about 20,000.

10 In each of the examples and comparative example  
described above, 500 samples were continuously formed  
and their contact angles were measured. Consequently,  
samples having contact angles of 120° or more  
accounted for 98% in each example and accounted for  
15 75% in the comparative example.

This is presumably because the ultraviolet dose  
was reduced by gas deterioration of the excimer laser  
oscillator owing to the continuous processing.  
However, each example of the present invention had a  
20 region in which a surface treatment could be  
performed with stable performance regardless of  
changes in the dose.

The surface conditions in this state were  
analyzed by ESCA. As a consequence, in each example  
25 of the present invention the surfaces were as shown  
in Fig. 6B, whereas in the comparative example some  
surfaces were as shown in Fig. 6C. As is evident

from these surface conditions, the surface of the comparative example had a portion in which no fluorine atoms were present, and the water repellency deteriorated only in this portion compared to the  
5 examples of the present invention. Note that Fig. 6A is a schematic view showing the surface condition of a material to be treated before substitution.

Note also that when a photomask patterned by using a metal film such as a chromium film or by  
10 using a dielectric substance interference reflecting film is used as the window 3, only predetermined portions of the surface of the solid material 7 to be treated can be given liquid repellency.

As has been explained above, the present  
15 inventors studied the substitution mechanism and have found a novel substitution mechanism, thereby deriving a surface treatment stabilization method capable of efficiently performing substitution, with the above configuration, without producing any  
20 variations in the surface treatment due to the thickness of a mediating material in contact with a material to be treated. In particular, the present inventors have found a method by which a physical property irreversible reaction process logically  
25 holds in a method of adding high liquid repellency to the surface of a plastic material having a C-H bond in its surface layer. Additionally, application

regions are extended by maintaining both the surface characteristics and bulk characteristics.

WHAT IS CLAIMED IS:

1. A surface treatment method of treating the surface of a material to be treated, by irradiating with light the material to be treated and a mediating  
5 material in contact with each other,

wherein the mediating material itself causes substantially no interaction upon irradiation with light, and the surface of the material to be treated is treated by provision of a chemical reaction field,  
10 in which a substituent of the material to be treated and an atom of atomic group of the mediating material is induced by excitation at the same time, by irradiating with light by using the logical product of the contact interface between the material to be  
15 treated and the mediating material and the light irradiation region, thereby causing and progressing bonded state transition.

2. A method according to claim 1, wherein the  
20 mediating material is a liquid.

3. A method according to claim 1, wherein the mediating material is a gas.

25 4. A method according to claim 1, wherein bond energy by which the substituent induced by excitation from the material to be treated in the chemical

reaction field is subjected to captive transition bonding by the atom or atomic group induced by excitation from the mediating material is larger than a larger one of bond energy between the substituent  
5 of the material to be treated and a matrix atom and bond energy between the atom or atomic group of the mediating material and the matrix atom.

5. A method according to claim 1, wherein the  
10 light which irradiates the material to be treated and the mediating material has a wavelength having photon energy larger than a larger one of bond energy between the substituent of the material to be treated and a matrix atom and bond energy between the atom or  
15 atomic group of the mediating material and the matrix atom.

6. A method of treating the surface of a material to be treated having a single bonding group  
20 of a carbon atom and hydrogen atom on the surface,  
wherein while the material to be treated is in contact with a liquid mediating material which is an aggregate of a polymer having on a main chain thereof an ether bonding group and a carbon fluoride  $C_nF_m$  ( $n$   
25  $= 1, 2, 3, \dots$ ,  $m = 2n$  or  $2n + 1$ ) group, the contact interface between the material to be treated and the mediating material is irradiated with ultraviolet

radiation having a wavelength of 221.4 to 351.6 nm,  
thereby substituting a hydrogen atom in the single  
bonding group of a carbon atom and the hydrogen atom  
on the surface of the material to be treated with the  
5 carbon fluoride group in the mediating material, and  
modifying the surface of the material to be treated.

7. A method according to claim 6, wherein the  
material to be treated is an aggregate of an organic  
10 material containing a polymer having on a side chain  
thereof a single bonding group of a carbon atom and  
hydrogen atom.

8. A method according to claim 6, wherein the  
15 material to be treated is a mixture of an inorganic  
material and an organic material containing a polymer  
having on a side chain thereof a single bonding group  
of a carbon atom and hydrogen atom.

20 9. A method according to claim 6, wherein the  
mediating material is a polymer consisting of  $-C_nF_{2n}-$   
 $O-$ .

10. A method according to claim 6, wherein the  
25 mediating material is  $F-(CF_2CF_2CF_2O)_nCF_2CF_3$  (n:  
integer).

11. A method according to claim 6, wherein an ultraviolet light source for the ultraviolet irradiation is an excimer light source selected from the group consisting of KrF, XeCl, XeF, XeBr, and XeI.

5

12. A method according to claim 6, wherein when the material to be treated contains as a main component thereof a polymer having a single bond of carbon atoms as a main chain thereof, an ultraviolet  
10 dose for the ultraviolet irradiation is not less than  $16 \text{ mJ/cm}^2$  in a treatment at an ultraviolet wavelength of 221.4 nm and not less than  $10 \text{ mJ/cm}^2$  in a treatment at an ultraviolet wavelength of 351.6 nm.

15 13. A method according to claim 6, wherein the surface of the material to be treated is irradiated with the ultraviolet radiation from the side of the mediating material via a photomask formed by patterning a metal film into a predetermined pattern  
20 on a substrate which is transparent to the ultraviolet wavelength.

14. A method according to claim 13, wherein a substrate of the photomask is a material selected  
25 from the group consisting of synthetic quartz, rock crystal, calcium fluoride, magnesium fluoride, sapphire, and diamond.

15. A material of which surface is treated by  
a method according to claim 1.

16. A material of which surface is treated by  
5 a method according to claim 6.