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SELF-CLEANING GLASS

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**SUMMARY**

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INTRODUCTION

Environmental purification using TiO₂ photocatalysts has attracted a great deal of attention with the increasing number of recent environmental problems in society. Recently, the application has been focused on purification and treatment of water and air, which are concerned in the protection of the environment, such as nature and life space. However, the use of conventional powder catalysts results in disadvantages in stirring during the reaction and in separation after the reaction. Preparation of the catalysts coated as thin films will make it possible to overcome these disadvantages and to extend the industrial applications, such as, uses in antibacterial ceramic tile and self-cleaning glass.

Titanium dioxide has been intensively investigated as a semiconductor photocatalyst since Fujishima and Honda discovered the photocatalytic splitting of water on TiO₂ electrodes without using electricity in 1972. This event marked the beginning of a new era in heterogeneous photocatalysis. Previous to this, several studies had been made on obtaining hydrogen from water using sunlight. In recent years, several applied researches on water and air purifications using decomposition effects of organic matters due to strong oxidation reducing power of photocatalyst have been made as demand for environmental protection rises.

All of these works originally got started in the late 1960s at the University of Tokyo in research on photoelectrochemical solar cells. For various reasons, the solid-state photovoltaic device has become the technology of choice. Ever since 1977 when Professor Allen J. Bard and co-workers at the University of Texas first examined the possibilities of using TiO₂ to decompose cyanide in water, there has been increasing interest in environmental applications.

Although many important fundamental results concerning titanium dioxide photocatalytic reaction have been clarified by such intensive works, there have been few successful industrial applications in environmental as well as photovoltaic applications. Most of these works utilized powder titanium dioxide as a material.

In order to avoid the use of powder, which has to be separated from the water after photocatalysis, we have been developing ways to apply TiO₂ coating on various materials such as glass or tiles to give the surface of these materials a self-cleaning function utilizing photocatalysis.

TITANIUM DIOXIDE

Titanium dioxide is one of the basic materials in everyday life. It has been widely used as white pigment in paints, cosmetics and foodstuffs. TiO₂ exists in three crystalline modifications: rutile, anatase, and brookite. Generally, titanium dioxide is a semiconducting material which can be chemically activated by light. The photoactivity of TiO₂ which is known for approx. 60 years is investigated extensively. For a long time there was a considerable problem especially what its application as pigment concerns. Under the influence of light the material tends to decompose organic materials. This effect leads to the well-known phenomenon of "paint chalking", where the organic components of the paint are decomposed as result of photocatalytic processes.
Titanium Dioxide is a very high-tonnage material and is the principal white pigment of commerce. The compound has an exceptionally high refractive index, great inertness, and a negligible colour, all qualities that make it close to an ideal pigment.

Figura 1

Titanium Dioxide is commercially available in two crystal structures - Anatase and Rutile. Rutile has a density of 4.2g/cc, while Anatase has a density of 3.9g/cc. This difference is explained by their different crystal structures. The Rutile modification is more closely packed than the Anatase crystal.

Compared with Rutile and Brookite, Anatase shows the highest photoactivity. Therefore, the TiO_2 used in industrial products is almost exclusively from the Rutile type. Although TiO_2 absorbs only approx. 5 % of the solar light reaching the surface of the earth, it is the best investigated semiconductor in the field of chemical conversion and storage of solar energy.

Rutile Titanium Dioxide pigments scatter light more efficiently and are more stable and durable than Anatase pigments. TiO_2 is unique in that it combines high refractive index with a high degree of transparency in the visible region of the spectrum. This combination affords the coatings formulator a route to highly opaque and bright whites or tints at minimum film thicknesses.
Figura 2 An Anatase crystal

Figura 2a Crystal structure of Anatase titanium dioxide

Picture courtesy of Amethyst Galleries, Inc

Figura 2b
Figura 3 A Rutile crystal

Figura 3a Crystal structure of Rutile titanium dioxide

Figura 3b
To understand why TiO₂ and especially Rutile TiO₂ offers such great advantages in hiding, it is only necessary to compare the refractive indices of Rutile and Anatase with those of other commercial white pigments and paint vehicles. The larger the difference between the refractive index of the pigment and that of the medium in which it is dispersed, the greater the refractive light scattering.

![Figura 4](image)

<table>
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<th>Material</th>
<th>Refractive Index</th>
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<tr>
<td>Rutile TiO₂</td>
<td>2.76</td>
</tr>
<tr>
<td>Anatase TiO₂</td>
<td>2.52</td>
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Refractive Index = \( \frac{\text{Speed of light in vacuum}}{\text{Speed of light in substance}} \)

**PROPERTIES OF TITANIUM DIOXIDE**

- Semiconductor transparent in the visible region of the spectrum
- Highly porous material that provides strong enhancement of the surface area (~1000) times
- High affinity of TiO₂ surface to many molecules leads to easy surface modification
- Low costs material, easy to produce in large quantities, chemically inert, non-toxic, biocompatible

TiO₂ has emerged as an excellent photocatalyst material and most recently the interest is shifted into the area of photoinduced hydrophilicity, which involves not only self-cleaning surfaces, but also antifogging ones. Ones of the most interesting aspects of TiO₂ is that
the types of photochemistry responsible for photocatalysis and hydrophilicity are completely different, even though both can occur simultaneously on the same surface. So glass coated with a thin film of titanium dioxide exhibits these two intriguing properties when illuminated with UV light:

- Photocatalytic (light-induced) breakdown of organic compounds that come into contact with it, making it self-degreasing
- Very high affinity for water, so that water does not bead up but forms a continuous sheet.

**SELF-CLEANING SURFACE**

In practice, surface cleaning of building materials like tiles, facades and glass panes causes considerable trouble, high consumption of energy and chemical detergents and, consequently, high costs. To realize self-cleaning material surfaces there are two principal ways: the development of so-called superhydrophobic or super-hydrophilic surfaces. What is hydrophobicity? Also termed hydrophobic, materials possessing this characteristic have the opposite response to water interaction compared to hydrophilic materials. Hydrophobic materials ("water hating") have little or no tendency to adsorb water and water tends to "bead" on their surfaces (i.e., discrete droplets). Hydrophobic materials possess low surface tension values and lack active groups in their surface chemistry for formation of "hydrogen-bonds" with water.

The wetting of a solid with water, where air is the surrounding medium, is dependent on the relation between the interfacial tensions (water/air, water/solid and solid/air). The ratio between these tensions determines the contact angle between a water droplet on a given surface. A contact angle of 0° means complete wetting, and a contact angle of 180° corresponds to complete non-wetting. Hydrophobic surfaces with low wettability and contact angles of about 100° are known for a long time. The higher this angle the lower is the value of the adhesion work. Decreasing of the contact angle leads to enlarged values of the adhesion work (hydrophilic surfaces).

By transferring the microstructure of selected plant surfaces to practical materials, super-hydrophobic surfaces could be developed. The water repellency of plant surfaces has been known for many years. That water-repellent surfaces also indicate self-cleaning properties has been completely overlooked. Recently, Barthlott et al. investigated and proved the correlation between the microstructure, wettability and contaminants in detail using lotus leaves. This was called the *Lotus Effect* because it can be demonstrated beautifully with the great leaves of the lotus plant. The microrough surfaces show contact angles higher than 130°. That means, the adhesion of water, as well as particles is extremely reduced. Water which contacts such surfaces will be immediately contracted to droplets. The particles of contaminants adhere to the droplet surfaces and are removed from the rough surface when the droplets roll off (fig. 5).
If TiO₂ of the Anatase type is exposed to UV light very low contact angles are obtained (<1°). These materials have the unique property of “attracting” rather than repelling water (super-hydrophilicity). The water lies flat on the surface in sheets instead of forming droplets. If the illumination is stopped, the super-hydrophilic behaviour of the TiO₂ surface is retained for approximately two days. Furthermore, UV illumination of titanium dioxide leads to the formation of powerful agents with the ability to oxidize and decompose many types of bacteria, organic and inorganic materials. In the following, the principles and potential applications of TiO₂ photocatalysis are discussed.

**BASIC PRINCIPLES OF HETEROGENEOUS PHOTOCATALYSIS**

Without reference to a special or specific mechanism, photocatalysis has also been described as the acceleration of the rate of a photoreaction by the presence of a catalyst; further, as a label to indicate that a catalyst may accelerate the photoreaction by interaction with a substrate either in its ground state or in its excited state and/or with the primary photoproduct, depending on the mechanism of the photoreaction. This description also encompasses photosensitization, yet such a process, defined officially as a process by which a photochemical or photophysical alteration occurs in one molecular entity as a result of initial absorption of radiation by another molecular entity—the photosensitizer. In absence of a catalytic active substance, the oxidation of the most hydrocarbons proceeds rather slowly, which can be explained by kinetic arguments. A photocatalyst decreases the activation energy of a given reaction. In the result of photoinduced processes often particles with strong oxidation and reduction ability occur. A heterogeneous photocatalytic system consists of semiconductor particles (photocatalyst), which are in close contact with a liquid or gaseous reaction medium. Exposing the catalyst to light excited states are generated which are able to initiate subsequent processes like redox reactions and molecular transformations. In fig. 7 a simplified reaction scheme of photocatalysis is
shown. Due to their electronic structure, which is characterized by a filled valence band (VB) and an empty conduction band (CB), semiconductors (metal oxides or sulfides as ZnO, CdS, TiO$_2$, Fe$_2$O$_3$, and ZnS) can act as sensitizers for light-induced redox processes. The energy difference between the lowest energy level of the CB and the highest energy level of the VB is the so-called band gap energy $E_g$. It corresponds to the minimum energy of light required to make the material electrically conductive.

Mobile charge carriers can be generated by three different mechanisms. Thermal excitation, photoexcitation and doping. If the band gap energy is sufficiently small (less than half an electron volt) thermal excitation can promote an electron from the valence band to the conduction band. In a similar manner, an electron can be promoted from the
valence band to the conduction band upon the absorption of a photon of light, photoexcitation, provided that $hn > E_{bg}$. The third mechanism of generating mobile charge carriers is doping. This charge transfer introduces conditions of non-balance, which lead to the reduction or to the oxidation of the species absorbed on the surface of the semiconductor.

When a photon with an energy of $hv$ exceeds the energy of the band gap an electron ($e^-$) is promoted from the valence band to the conduction band leaving a hole ($h^+$) behind. In electrically conducting materials, i.e. metals, the produced charge carriers are immediately recombined. In semiconductors a portion of this photoexcited electron-hole pairs diffuse to the surface of the catalytic particle (electron hole pairs are trapped at the surface) and take part in the chemical reaction with the adsorbed donor (D) or acceptor (A) molecules. The holes can oxidize donor molecules (1) whereas the conduction band electrons can reduce appropriate electron acceptor molecules (2).

$$D + h^+ \rightarrow D\bullet^+$$  \hspace{1cm} (1)

$$A + e^- \rightarrow A\bullet^-$$  \hspace{1cm} (2)

A characteristic feature of semiconducting metal oxides is the strong oxidation power of their holes $h^+$. They can react in an one-electron oxidation step with water (3) to produce the highly reactive hydroxyl radical (•OH). Both the holes and the hydroxyl radicals are very powerful oxidants, which can be used to oxidize most organic contaminants.

$$H_2O + h^+ \rightarrow •OH + H^+$$  \hspace{1cm} (3)
In general, air oxygen acts as electron acceptor (4) by forming the super-oxide ion $\bullet O_2^-$

$$O_2 + e^- \rightarrow \bullet O_2^-$$  \hspace{1cm} (4)

Super-oxide ions are also highly reactive particles, which are able to oxidize organic materials.

**TiO$_2$ AS PHOTOCATALYST**

In recent years semiconductor photocatalysis using TiO$_2$ has been applied to important problems of environmental interest like detoxification of water and of air. TiO$_2$ is a semiconductor with a band gap energy $E_g = 3.2$ eV. If this material is irradiated with photons of the energy $> 3.2$ eV (wavelength $< 388$ nm), the band gap is exceeded and an electron is promoted from the valence to the conduction band. Consequently, the primary process is the charge-carrier generation (5).

$$TiO_2 + h\nu \rightarrow h^+ + e^-$$  \hspace{1cm} (5)

The ability of a semiconductor to undergo photoinduced electron transfer to adsorbed particles is governed by the band energy positions of the semiconductor and the redox potentials of the adsorbates. The relevant potential level of the acceptor species is thermodynamically required to be below the conduction band of the semiconductor. Otherwise, the potential level of the donor is required to be above the valence band position of the semiconductor in order to donate an electron to the empty hole. The band-edge positions of several semiconductors are presented in fig. 9.

![Figura 9 Band-edge energies of typical semiconductors](image-url)
Reaction of oxidation-reduction may possibly occur as shown in fig.10. There is a 3.2eV of band gap between conductive and charging zones, when electrons (e\(^-\)) and holes (h\(^+\)) are irradiated by applying light. In general, the electrons and the holes recombine immediately and do not originate photocatalyst reaction, but they carry on through for a while and move up to the surface of the particles and react as shown below.

![Figura 10 Oxidation-reduction reaction on the surface of TiO\(_2\)](image)

Absorbed water on the surface of titanium oxide is oxidized by the holes and then originates oxidative hydroxyl radical (•OH). Then the hydroxyl radical reacts to organic matters. If oxygen exists in this reaction process, radicals, which are intermediates of organic compounds, and oxygen molecules start off a radical chain reaction [(1) to (5)]. Eventually, the organic matters break down into carbon dioxide and water. On the other hand, the electron deoxidize and generate super oxide ion (•O\(_2^-\)) (5). It is conceivable that the superoxide ion produce peroxide, which comes to the intermediates of oxidative reaction, or generates water through hydrogen peroxide.

\[
\begin{align*}
\text{OH}^- + h^+ &\rightarrow \bullet \text{OH} \\
O_2 + e^- &\rightarrow \bullet \text{O}_2^-
\end{align*}
\]

Semiconductors are usually covered with hydroxyl groups on their surfaces as well as physisorbed water molecules. We know that the surface of TiO\(_2\) is promptly hydroxylated when the TiO\(_2\) is contact with water. On the other hand when water dissociates on a pure TiO\(_2\) surface two distinctive hydroxyl groups are formed. Assuming that Anatase particles consists of a mixture of these surface planes, complete surface coverage by OH\(^-\) should be around 5-15 OH\(^-\)/nm\(^2\) on room temperature.
The increase in the photocatalytic activity of TiO$_2$ films with the heat treatment time is due to the increase in Ti$^{3+}$ concentration occurring as a result of reduction of Ti$^{4+}$ to Ti$^{3+}$ by organic residues such as alcohol and unhydrolyzed alkoxide groups. However, once it is used up for the reduction of Ti$^{4+}$ or burnt out on further heating in air, the Ti$^{3+}$ concentration starts to decrease due to reoxidation of Ti$^{3+}$, resulting in the decrease in the photocatalytic activity. Moreover, it is easily expected that very long heating in air results in a decrease in the specific surface area, which also deteriorates the photocatalytic activity.

**Surface hydroxyl groups on TiO$_2$**

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**Physical adsorption of water**

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**Dissociation of water resulting two distinctive OHgroups**
of TiO₂ films. These phenomena are thought to be the major reason that the photocatalytic activity shows a maximum at 500°C for 1 h. It is already known that generally Anatase type photoactivates more efficiently than Rutile type does. The difference between the energy structures of both types is taken as an instance of the reason. Band gap of Anatase type is 3.2eV, and that of Rutile is 3.0eV. The position of conductive zone of Anatase type is 0.2eV higher. A characteristic of titanium is that it has a very deep valence band and enough oxidizability. But the position of conductive zone comes close to the reduction point of water and oxygen at some level, and titanium has a weak reducing power. Therefore general activity may be increased by using Anatase type which has a higher point of conductive zone. The heterogeneous photocatalytic oxidation with TiO₂ meets the following requirements what could make it competitive with respect to other processes oxidizing contaminants:

- A low-cost material is used as photocatalyst.
- The reaction is quite fast at mild operating conditions (room temperature, atmospheric pressure).
- A wide spectrum of organic contaminants can be converted to water and CO₂.
- No chemical reactants must be used and no side reactions are produced.

**PRACTICAL APPLICATIONS OF TiO₂ PHOTOCATALYSIS**

In fig. 12 the main areas of activity in titanium dioxide photocatalysis are shown. As already mentioned, in the last 10 years photocatalysis has become more and more attractive for the industry regarding the development of technologies for purification of water and air. Compared with traditional advanced oxidation processes the technology of photocatalysis is known to have some advantages, such as ease of setup and operation at ambient temperatures, no need for postprocesses, low consumption of energy and consequently low costs.

*Bactericidal Effects*

Photocatalyst is not adequate to break down large quantities of a substance at once, but it is highly effective in breaking down growing substances, which initially have a small quantity, such as bacteria and virus. The differences from a silver antibacterial agent are that an antibacterial agent can break down dead bacteria and toxin called endotoxic which is released after killing bacteria. Also, some dirt can be broken down by photocatalyst reaction so that it brings certain advantages of maintaining antibacterial spectrum without cleaning.

*Air Purification and Odour Elimination*

Elimination of NOₓ by coating wall surfaces of express highways with titanium oxide has been started in Osaka. Such an approach is not necessarily effective when used in open air, and a key point is riding on how NOₓ is added to titanium oxide coatings. A grand project of air purification coating all large constructions and exterior walls with titanium oxide has also been considered. Also, advanced implements for air purification and odour elimination by applying UV light to a titanium oxide treated filter of air purification equipment used indoors have been considered. Dirt, which is stuck on a filter, can be broken down by photocatalyst, so that filter replacement is not required.
**Self-cleaning Functions**

The material surface is kept clean when quantities of UV light exceed that of absorbed dirt on a surface. Due to super hydrophilic property, which is described below, dirt hardly adheres, and even if it does, it can be easily rinsed in water. Toshiba Lighting & Technology Co. field tested on road and tunnel illuminating glassware, and the test demonstrated diminution of dirt by auto emissions. Since maintenance of road illumination requires a large amount of labour and considerable expense and is a cause of traffic jams on highways, the use of illumination using TiO\(_2\) photocatalyst is expected to be widespread from now on. Also, applications of TiO\(_2\) photocatalyst to fluoropolymer tent materials used for Tokyo Dome or exterior wall cements for wall materials are considered.

**Super Hydrophilic and Lipophilic Properties**

Exposing UV light to a surface of TiO\(_2\) gives very high hydrophilic properties when the contact angle of water is five degree and below. This status remains for a few hours to a week and then involutes slowly. This phenomenon is likely to be understood as having hydrophilic properties by breaking down due to photocatalyst reaction where absorbed dirt of organic matter on a surface of TiO\(_2\) becomes hydrophobic. However, a whole new phenomenon taking place on the surface of TiO\(_2\) can be presumed according to several experiments. Moreover, we found that the surface after exposing also has super lipophilicity that has a high affinity to oil. Both water-based and oil-based dirt hardly adhere on such amphipathic surface, and even if it does, dirt can easily be rinsed in water. In addition to self-cleaning effects, anticlouding effects for windows and glass clouded over with condensation have been considered as applications of super hydrophilic properties. Such applications include bathroom mirrors, car windows, and fender mirrors.

![Figure 12 Major areas of activity in titanium dioxide photocatalysis](image-url)
HYDROPHILICITY AND SUPER-HYDROPHILICITY

Contact Angle

For a given droplet on a solid surface: the contact angle is a measurement of the angle formed between the surface of a solid and the line tangent to the droplet radius from the point of contact with the solid. The contact angle is related to the surface tension by the Young's equation through which the behaviour of specific liquid-solid interactions can be calculated. A contact angle of zero results in wetting, while an angle between 0° and 90° results in spreading of the drop (due to molecular attraction). Angles greater than 90° indicate the liquid tends to bead or shrink away from the solid surface. (i.e., fig.13)

![Figure 13](image)

Hydrophilicity

Also called hydrophilic, is a characteristic of materials exhibiting an affinity for water. Hydrophilic literally means "water-loving" and such materials readily adsorb water. The surface chemistry allows these materials to be wetted forming a water film or coating on their surface. Hydrophilic materials also possess a high surface tension value and have the ability to form "hydrogen-bonds" with water. TiO₂ acquires superhydrophilic properties after UV illumination. In this case, electrons and holes are still produced, but they react in a different way. The electrons tend to reduce the Ti(IV) cations to the Ti(III) state, and the holes oxidize the O₂⁻ anions. In the process, oxygen atoms are ejected, creating oxygen vacancies (fig.14). Water molecules can then occupy these oxygen vacancies, producing adsorbed OH groups, which tend to make the surface hydrophilic. The longer the surface is illuminated with UV light, the smaller the contact angle for water becomes; after about 30° min or so under a moderate intensity UV light source, the contact angle approaches zero, meaning that water has a tendency to spread perfectly across the surface.
Figura 14 Mechanism of photo-induced hydrophilicity

In the usual environment, a surface of material repels the water to a certain extent. Fig. 15 shows the shape of the waterdrops on the surfaces of glass, resin and hydrophobic resin.

Hydrophilicity of a material can be represented with a contact angle of water with the material. The contact angles of water with inorganic materials, such as glass are 20°-30°. Also, the contact angles of water with usual resins and hydrophobic resins, such as silicone resin or fluorocarbon polymer, are 70°-90° and more than 90°, respectively. Until now, there are few materials that have the contact angle of water less than 10°, except water absorptive materials or activated surface using interface activator. However, these materials have little durability and the low contact angle values do not last for a long time. Our modified TiO₂ photocatalyst thin film has interesting property of super-hydrophilicity. At first, the contact angle of water with the TiO₂ thin film is several tens degrees. Then, by the irradiation of UV light, the contact angle decreases gradually, and at last, it reaches 0°. After that, the contact angle remains only several degrees for scores of hours without the irradiation of UV light. Besides, even if the contact angle increases, it easily decreases again only by the irradiation of UV light. Therefore, the modified TiO₂ thin film is the first truly practical material that realizes the super-hydrophilicity. Fig. 16 shows the change of the contact angle of water with a TiO₂-silicone thin film by UV irradiation. Before UV irradiation, the contact angle with the film is more than 90°, then it gradually decreases to 0° with UV irradiation and the film never repels water. Now, we are theoretically studying the rationale of this phenomena.
The super-hydrophilicity should be caused by the function of photocatalyst. As TiO$_2$ photocatalyst decomposes hydrophobic molecules those originally existing on the surface of material, very thin film of physisorbed water forms on the surface. We presume that the water thin film is the origin of the super-hydrophilicity. Belove the schematic diagram of presumed super-hydrophilicizing mechanism is showed:

**STEP 1**: Chemisorbed water on the surface of TiO$_2$ is so unstable that it is stabilized with an adsorption of hydrophobic molecule (fig.17).

**STEP 2**: With irradiation of light, photocatalyst decomposes hydrophobic molecule and chemisorbed water is exposed to the surface (fig.18).
STEP 3: Exposed chemisorbed water physisorbs and bonds with another water (fig.19).

![Figure 19](image)

**Figura 19**

STEP 4: Physisorbed water is taken in the structure by the surface diffusion and stabilized (fig.20).

![Figure 20](image)

**Figura 20**

**APPLICATION OF SUPER-HYDROPHILIC PROPERTIES WITH THE PHOTOCATALYST**

The super-hydrophilic properties with the photocatalyst are quite useful in various fields in our society. We suggest some applications of super-hydrophilic materials as follows.

*Anti-fogging property*

The steam fogs a mirror and a glass easily, because moisture in the air is cooled down and numerous waterdrops form on the surface of the usual materials. However, utilizing the super-hydrophilic coating, the water cannot exist in the shape of a drop, but spreads flatly on the super-hydrophilic surface. Fig.21 shows the dependence of the anti-fogging ability on the contact angle of water.
Recently, the opposite way to remove waterdrops from the surface of material has been proposed. For example, super-hydrophobic coating is applied for windshield to remove the waterdrops easily. However, super-hydrophobic surface cannot stop fogging of the windshield unless the waterdrops is removed with wind power or vibration. On the contrary, the super-hydrophilic surface never fogs on condition of no wind nor vibration. Applying the super-hydrophilic photocatalyst for a surface of a mirror or a glass, they remain the clear surface without fogging semipermanently. Fig. 22 shows the difference of the fogging with steam between normal glass and the photocatalyst coated glass.

![Normal glass vs. Photocatalyst coated glass](image)

**Figura 22**

Though the normal glass fogs with steam, the super-hydrophilic glass remains transparent. In this way, the super-hydrophilic technology easily realizes the anti-fogging glass products and mirrors with low costs.

Contact angle measurements were performed to examine the surface wettability change of the Anatase polycrystalline sample upon UV illumination. Fig. 23 shows time dependence of the water contact angle upon UV illumination (fig. 23a) and in the dark (fig. 23b). The power density UV is 1 mW/cm² in this experiment. As shown in the figure, water contact angle decreases with illumination time when is irradiated by UV. Three hours are sufficient to give rise to a highly hydrophilic surface. The final contact angle with water was almost zero. When the contact angle becomes lower than 58, the antifogging property is observed on the steamed surface. Fig. 23b shows the time dependence of the water contact angle of the sample in the dark. The initial contact angle was almost zero after complete hydrophilization by enough UV illumination. The surface reconverted the hydrophobic state.
gradually. We reported previously that the conversion from hydrophobic to hydrophilic is explained by assuming that the surface $\text{Ti}_4^+$ sites are photoreduced to the $\text{Ti}_3^+$ state accompanying oxygen vacancy, and dissociative water adsorption on the vacancy site. This process is considered to be substantially the same as the surface reduction processes of $\text{Ti}_4^+$ to $\text{Ti}_3^+$ induced by Ar ion sputtering, electron beam exposure, and high energy UV light.

![Graph showing time dependence of water contact angle](image)

**Figura 23** Time dependence of the water contact angle in ambient atmosphere:

- a) upon UV illumination;
- b) in the dark.

If a TiO$_2$ film coated on the surface of common soda-lime glass shows a high photocatalytic activity. It is known, however, that the diffusion of Na$^+$ ions into the nascent TiO$_2$ film from the SL-glass substrates during heat treatment process significantly deteriorates the photocatalytic activity. Fujishima and Narasinga have prepared TiO$_2$ thin films on different substrates, such as quartz, soda lime glass (SLG), and SiO$_2$-precoated SLG (SiO$_2$/SLG) substrates via the spray pyrolysis method, and showed that the TiO$_2$ coated on SiO$_2$/SLG had much higher catalytic activity than that of TiO$_2$ films coated on bare SLG.
Self-Cleaning Windows

Coating technology has provided tremendous consumer benefits to homeowners and the residential construction industry. Tempered glass improves safety, while low-E glass helps homeowners stay warmer in winter, cooler in the summer resulting in lower energy costs. Now, self-cleaning glass is available and is designed to make homeowners’ lives easier.

SunClean™ Self-Cleaning glass makes lives easier:
SunClean glass

The self-cleaning property of SunClean glass is made possible by a durable, transparent coating of titanium dioxide (TiO$_2$) applied during the manufacturing process. The application process, patented by PPG, makes the coating an integral part of the outer glass surface, providing homeowners with a durable, long-lasting product.

<table>
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<th>Feature</th>
<th>Benefit</th>
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<tbody>
<tr>
<td>Photocatalysis</td>
<td>• Slowly breaks down and loosens organic dirt on glass surface.</td>
</tr>
<tr>
<td></td>
<td>• Helps to keep organic materials from building up on the glass surface that can deteriorate the hydrophilic properties</td>
</tr>
<tr>
<td>Hydrophilicity</td>
<td>• Water sheeting action provides more efficient rinsing of the glass surface</td>
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<tr>
<td></td>
<td>• Allows the glass surface to dry naturally with minimal spotting and streaking.</td>
</tr>
<tr>
<td></td>
<td>• Accelerates glass surface drying</td>
</tr>
<tr>
<td>Thermal optical features</td>
<td>• UV transmittance is reduced by about 40% vs. a clear glass window.</td>
</tr>
<tr>
<td></td>
<td>• The outward appearance of SunClean glass appears slightly brighter.</td>
</tr>
<tr>
<td></td>
<td>• Solar heat gain coefficient (S.H.G.C.) is improved about 0.05 points as compared to regular glass</td>
</tr>
<tr>
<td>Durable coating applied by PPG patented process</td>
<td>• Durable long lasting coating</td>
</tr>
</tbody>
</table>

In a photocatalytic process, ultraviolet (UV) light from the sun energizes the SunClean Self-Cleaning glass to help slowly break down and loosen dirt. Since UV light is abundant even on cloudy days or in shaded areas, this process works non-stop throughout the day.

![Figura 26](image)

The coating also has a hydrophilic property that makes water droplets spread out, or sheet, across the surface of the glass. When rain or a light spray from a garden house hits the window, the water carries away the loosened dirt. This sheeting action, which works throughout the day and overnight, helps the window dry quickly with minimal spotting or streaking.
SunClean glass is a coated glass product with photocatalytic and hydrophilic properties that combine to make windows easier to maintain. The transparent SunClean glass coating is applied to hot glass during the forming process, where it forms a strong, durable bond with the glass surface. The photocatalytic property of the coating is triggered by the sun’s ultraviolet light (UV), and works to slowly break down and loosen organic dirt. At the same time, the coating’s hydrophilic property breaks down water beads and causes water to sheet over the glass, which helps to rinse away loosened dirt.

The self-cleaning attributes of this product are quite effective in reducing the everyday dirt and grime that accumulates on the exterior surface, meaning windows will be easier to clean. However, inorganic materials, such as paint, will continue to require hand cleaning. Also, if the glass becomes heavily soiled or does not become clean under your specific exposure conditions and circumstances, then it will be necessary to clean the glass manually. Of course, the interior surface will need to be cleaned like any other window glass.

From the exterior, windows with SunClean glass appear brighter. From inside, they look the same.

PPG defines self-cleaning glass as a product that has three distinct characteristics. First, the glass has a durable, long-lasting coating that has been fused into the glass at high temperatures during the glass manufacturing process. Second, the coating exhibits photocatalytic properties, i.e., it will slowly decompose organic material. Third, the same coating also exhibits hydrophilic properties, i.e., it will cause water to sheet over the coated surface and dry with minimal spotting and streaking. Other companies offering "self-cleaning" glass products should be evaluated as to whether their products provide these three distinct characteristics.

The coating will provide photocatalytic and hydrophilic properties as described above given that it has been properly energized by ultraviolet light ("UV") and is not masked from UV exposure, including, but not limited to, materials on the glass that block UV or that isolate the coating. If hard water or water with high mineral content gets on the glass, it may require special cleaning procedures, since such water would likely contain inorganic material that the coating would not remove by the self-cleaning process.

SunClean glass is warranted by PPG in performance and functionality directly and only to customers who process or sell SunClean glass as a component for a final use application. Each manufacturer providing a product using SunClean glass will warrant the performance of its product as to self-clean and all other aspects (including overall product cleaning recommendations) to its own customers and consumers as it deems appropriate under the circumstances. The manufacturer's product warranty is an important consideration to assess when selecting a product using self-cleaning glass as a component.
Self-cleaning glass has been described as an impossible dream. Yet, following an intensive research and development program by Pilkington – inventors of the universally used float glass process, and the world's leading glass manufacturer – new Pilkington Activ™ does just that.

How does Pilkington ActivTM Self-Cleaning Glass do it? By using outdoor daylight – which is abundant even on cloudy days – to keep windows clean with a two-step process:

1. Pilkington ActivTM Self-Cleaning Glass actively attacks dirt, with a special PhotoActivTM surface that uses energy from the sun to actually break down, loosen and destroy dirt and other organic matter.
2. And, when it rains, the water sheets off the ActivTM surface, so windows dry without spots and streaks.

So under most conditions, natural rain is sufficient to keep your windows clean. And in dry weather, a quick spray with the hose will achieve the same results. Either way, Pilkington ActivTM Self-Cleaning Glass dramatically reduces window cleaning, providing crisp, clear vistas.

The secret is Pilkington's advanced pyrolytic technology, applying the Pilkington ActivTM Self-Cleaning Glass pyrolytic surface to clear float glass via an on-line chemical vapor deposition process. As a result, the advanced properties of Pilkington ActivTM Self-Cleaning Glass are integral to the glass surface – not just a coating that can peel, separate or disintegrate over time, or be damaged by liquid glass cleaners.

The proper application of Pilkington ActivTM Self-Cleaning Glass is with the Pilkington ActivTM Self-Cleaning Glass surface glazed to the exterior of the building (first surface glazing), in either a monolithic or insulating glass unit. The Pilkington ActivTM Self Cleaning Glass surface requires several days exposure to daylight to be activated.
Product Features

SELF-CLEANING PROPERTIES: reduces the need for window-washing. In dry weather, just a quick spray of the hose will do.

NEVER NEEDS RE-TREATING: because the pyrolytic self-cleaning surface is an inherent part of the glass, not a coating that washes away.

ENVIRONMENTALLY FRIENDLY, in its application, installation and use, and requiring less cleaning, no chemical cleaners and less detergent.

DURABLE PYROLYTIC SURFACE minimizes rubs and scratches. Plus it won’t peel, discolor or wear off, ensuring long-term self-cleaning performance.

COLOR NEUTRAL for compatibility with all home styles and an unspoiled exterior aesthetic.

UV CONTROL PROPERTIES, providing 20% reduction in the transmission of damaging ultraviolet energy (additional performance data noted below).

EASILY FABRICATED, it can be handled, cut, insulated, laminated and tempered using standard float glass techniques, and no edge deletion is required. In addition, unlimited shelf life provides long-term storage, minimal inventory loss and assured availability.
IDEAL FOR new construction, replacement and renovation applications. AVAILABLE IN thicknesses ranging from 3/32” (2.5 mm) to ¼” (6 mm) and glass sizes up to 130” x 204” (3.300 mm x 5.180 mm).

Figura 30
SGG AQUACLEAN

The self-cleaning coating on SGG AQUACLEAN keeps the glass clean longer than standard glass, especially in cases where the glass is exposed to the rain. The potential savings will depend on a number of factors: extent and type of pollution, rain, and wind exposure, etc. On average, the number of cleaning operations can be divided by a factor of 2 to 3, which means a savings of at least 50% on the total maintenance bill.

**Domestic Applications:**
- Windows and doors.
- Skylights and overhead glazing.
- Winter gardens.
- Balustrades.

**Commercial Application:**
- Glazed building facades and curtain walls.
- Windows and doors.
- Exterior shop fronts/display panels.
- Atria glazing.
- Street furniture.
- Greenhouses.

The SGG AQUACLEAN glass range includes 6 m x 3.21 m sheets of flat glass available in thicknesses of 3, 4, 5, 6 and 8 mm.

![Diagram showing the effect of cleaning](image)

**Figura 31**