

Development of the Organic-inorganic Hybrid Super-hydrophilic Layer

Sumiaki YAMASAKI*, Satoshi TANAKA*, Makoto FUKUDA*, Yuuichiro MURAYAMA**, Yoshiaki KONDO**, Hideki OGASAWARA**, and Osamu UCHIDA***

Abstract

FUJIFILM Corporation has developed a novel super-hydrophilic layer using organic-inorganic hybrid technology. Different from photocatalyst TiO_2 , our hydrophilic layer shows super-hydrophilicity when stored in a dark room for a long time, and has various properties such as anti-clouding, self-cleaning, and hard surface. In addition, it can be applied to various materials (glass, resin metal), and has many other uses.

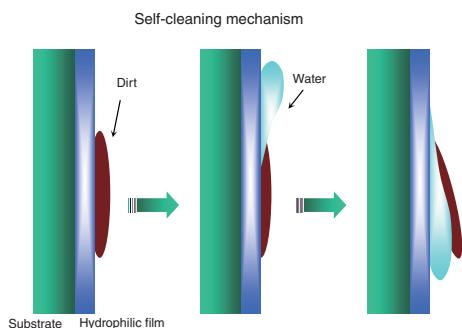
1. Introduction

A super hydrophilic surface is a “surface extremely wettable by water” with a contact angle of 10 degrees or less (Fig. 1). One of the most commonly known examples is a coating material using a photocatalyst (TiO_2). This material

exhibits super hydrophilicity under UV light. It is attracting attention as an anti-stain material that is easily cleaned with water because of its super hydrophilicity¹⁾. In addition to anti-stain quality, hydrophilicity is known to bring about many effects. More and more hydrophilic products are being launched for various applications (Fig. 2).



Fig. 1 Comparison between hydrophilic surface and hydrophobic surface.



Effects of hydrophilicity

- (1) Anti-fog (Prevents fogging)
- (2) Self-cleaning / easy-cleaning (Cleans dirt)
- (3) Quick dry (Drops spread)
- (4) Cooling (Takes the heat of vaporization)
- (5) Draining / water distribution (Very thin water film)
- (6) Water absorptive (Enhanced wettability)
- (7) Resistant to snow and ice accretion
- (8) Biocompatible
- (9) Antistatic
- (10) Enhancement in coating material performances

Fig. 2 Hydrophilic effects.

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* Synthetic Organic Chemistry Laboratories
Research & Development Management Headquarters
FUJIFILM Corporation
Nakanuma, Minamiashigara, Kanagawa 250-0193, Japan
** Industrial Products Division

FUJIFILM Corporation

Ohgi-cho, Odawara, Kanagawa 250-0001, Japan
*** Procurement Division
FUJIFILM Corporation
Akasaka, Minato-ku, Tokyo 107-0052, Japan

FUJIFILM has developed an original “super hydrophilic film that has a strong molecular bridge structure”²⁾, making the most of its functional polymer design/synthesis technology honed in the development and manufacturing of graphic materials and nanocomposite technology.

This report describes the method of making the super hydrophilic film, its structure, features of the properties, and uses of the features.

2. Structure of Super Hydrophilic Film

The super hydrophilic film has an “elaborate molecular bridge structure” inside the film. The hydrophilic group is oriented toward the outermost surface by delicate hydrophilicity/hydrophobicity control (Fig. 3). This structure gives the film the following features.

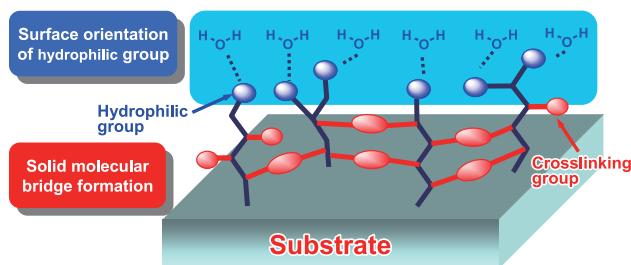


Fig. 3 Image of super-hydrophilic layer.

(1) As the hydrophilic group is oriented toward the outermost surface, a free water layer is easily formed on the surface. Although the mechanism is yet to be defined, an additive controls the surface hydrophilicity (Fig. 4). When a hydrophilic film does not contain an additive, the initial contact angle of a water droplet is around 40 degrees. As immersed in water for a long time, the hydrophilic group is oriented toward the surface and super hydrophilicity is exhibited. When a hydrophilic film contains an additive, it exhibits super hydrophilicity without immersion in water. The additive is considered to help to orient the hydrophilic group toward the surface.

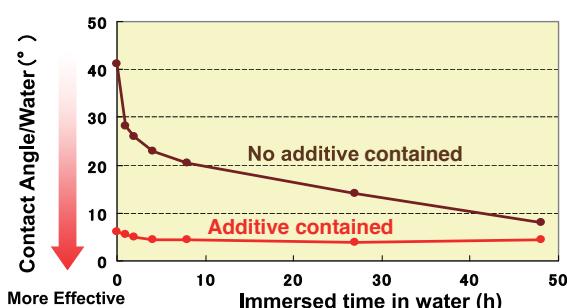


Fig. 4 Effect of additive.

- (2) The elaborate molecular bridge structure makes a strong film that will not be swollen by water. Organic and inorganic materials fused into a hybrid form the elaborate molecular bridge structure, which makes a high-strength film.

3. Making Super Hydrophilic Film

To make the super hydrophilic film, we apply a water-based coating liquid to a substrate and harden it with heat. The coating liquid contains a high-hydrophilic polymer developed by our functional polymer design technology. The procedure consists of the three steps below (Fig. 5).

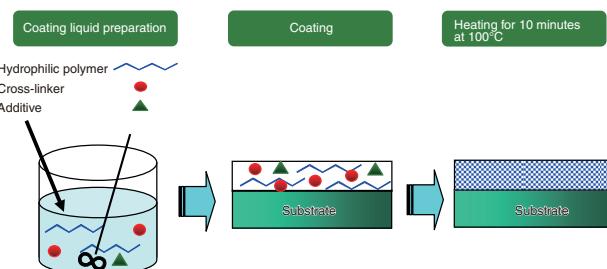


Fig. 5 Production method of super-hydrophilic layer.

(1) Preparing coating liquid

Mix the hydrophilic polymer, cross-linker and additive and agitate the solution for two hours at room temperature. That produces a sol precursor of an organic-inorganic hybrid.

(2) Film making

The coating liquid can be applied to various substrates in various thicknesses. The thickness ranges from several tens of nanometers to several micrometers utilizing our precise coating technique.

(3) Hardening

Heating and drying for 10 minutes at 100°C accelerates the hardening and results in a nanocomposite of the organic-inorganic-hybrid super hydrophilic film.

4. Features

We have found that our super hydrophilic film has greater hydrophilicity than other companies’ hydrophilic films using organic materials, such as photocatalyst and polyacrylic acid. We will explain its significant features as below with the experiment data.

(1) Sustainability of surface hydrophilicity

Photocatalysts exhibit hydrophilicity in sunlight but they cannot keep the hydrophilicity in the dark. Our super hydrophilic film, different in mechanism from a photocatalyst (TiO_2), keeps the super hydrophilicity

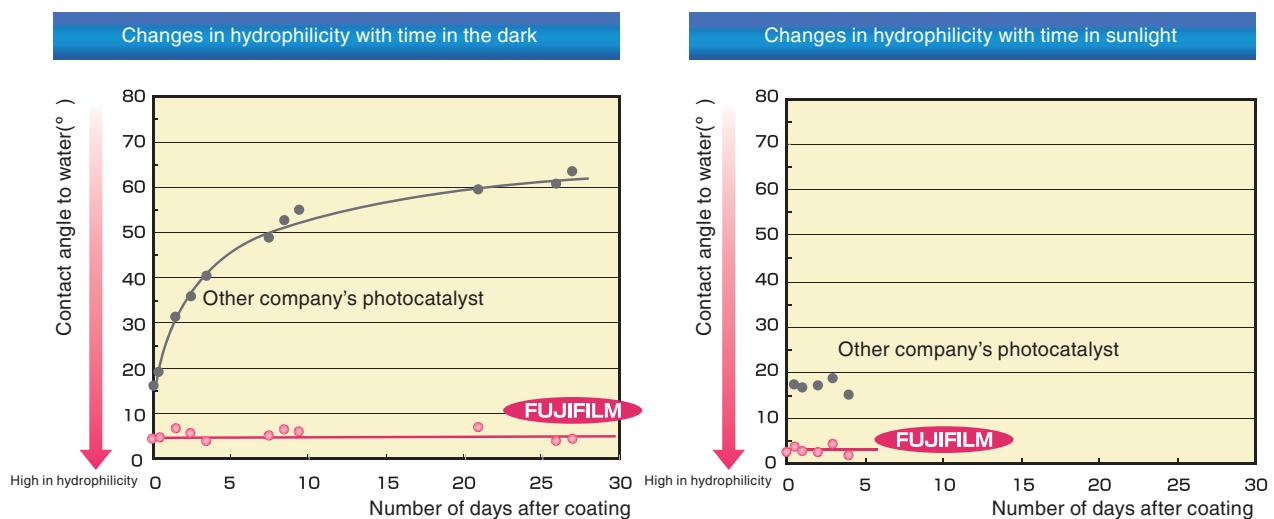


Fig. 6 Change of hydrophilicity under a dark room condition.



Fig. 7 Super-hydrophilic effect.

in the dark for at least one month (Fig. 6). And, the contact angle of our film does not exceed 10 degrees. Our film will be suitable for indoor applications, which are difficult for photocatalysts.

(2) Anti-fog quality and ease of cleaning

Fogging on glass or mirror is generally caused by very small water droplets on the surface. The droplets form acute angles to the surface. They reflect and diffuse light and the surface looks as if it is fogged. Our super hydrophilic film has high anti-fog quality. It does not fog even when water vapor of a humidifier is directly blown on the film (Fig. 7). The film also has high easy-cleaning quality. Oil and grease are easily washed off the film with water (Fig. 7). We infer that this is because the hydrophilic group is oriented toward the outermost surface of the film and that a uniform water layer is easily formed on the surface.

(3) Coating film strength

Another feature of our film is the high coating film strength. Our film is harder than other companies' organic hydrophilic polymers (Fig. 8). We presume that

the strength comes from the elaborate molecular bridge structure of the nanocomposite.

Hydrophilic effect in the dark and coating film strength

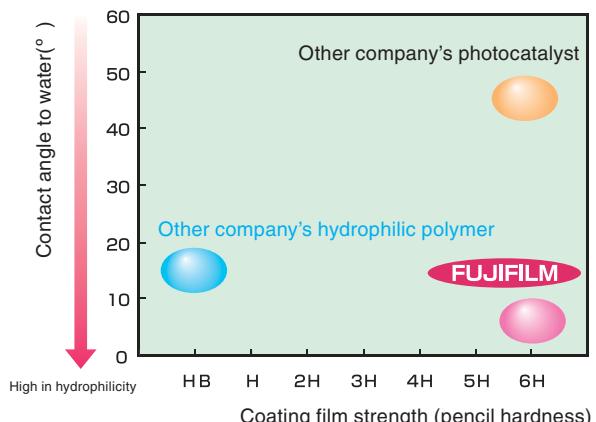


Fig. 8 Comparison with other hydrophilic products.

Unlike photocatalyst, our film does not decompose the substrate. That means our film can be used for a wide variety of substrate materials, such as glass, resin and metal,

although it needs a primer layer suitable for the substrate material (Table 1).

Table 1 Typical physical properties applied to various substrates.

Substrate	Contact angle to water		Hydrophilic properties			
	Untreated	Treated	Pensile hardness		Adhesion	Scratch resistance
			Untreated	Treated		
Glass plate	14°	≤5°	≥9H	6H	Good (no peeled off)	Good (no scratch)
Tile	14°	≤5°	≥9H	6H	Ditto	Ditto
Polycarbonate plate	89°	≤5°	≤6B	≤6B	Ditto	Ditto
Acrylic plate	67°	≤5°	B	HB	Ditto	Ditto
PET film	67°	≤5°	≤6B	H	Ditto	Ditto
SUS plate	99°	≤5°	2B	B	Ditto	Ditto

◊ Adhesion: 180-degree peel test using adhesive tape

◊ Scratch resistance: Rub the surface back and forth with a wet cloth 1,000 times and perform visual check. Load of 500 g at 5,000 mm/min.

5. Applications

Table 2 shows the functions and possible application fields of our super hydrophilic film.

Table 2 List of properties and corresponding anticipated applications for super-hydrophilic layer.

Functions	Applications (examples)
Anti-fog	Mirror, window, showcase and lens
Self-cleaning / easy-cleaning	Washbasin, sink, exterior wall and car body
Quick dry	Bathroom floor, sanitary ware and glass dishes
Cooling	Warehouse roof and asphalt
Draining / water distribution	Fuel battery and air-conditioner aluminum fan
Water absorptive	Fiber and filter
Resistant to snow and ice accretion	High-voltage power line and road safety mirror
Biocompatible	Contact lens and catheter
Antistatic	Display monitor and plastic component
Enhancement in coating material performances	Enhancement in wettability and ease of coating

6. Conclusion

We have developed a super hydrophilic film with a strong molecular bridge structure. We have made the film using delicate hydrophilicity/hydrophobicity control of the film surface and making the most of the functional polymer design/synthesis technology honed in the development and manufacturing of graphic materials and nanocomposite technology. It provides super hydrophilicity based on its mechanism different from that of photocatalyst. One of the features is the coating film strength higher than other hydrophilic polymers. To launch the super hydrophilic film, we need further study tailored to the requirements of individual applications. We are planning to start technological development for those requirements.

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