Advanced coatings offer glazing a clear future

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The glass industry has for many years been trying to solve a problem which affects almost every building in the world. How do you maintain the fundamental characteristics of glass, such as optical clarity and external aesthetics without constant maintenance? Whether the building is for commercial or residential use the one constant requirement is for regular cleaning to be undertaken to ensure the glass maintains its optimum appearance.

The challenge for the glass industry is increased as a result of architects finding ever more resourceful and novel uses for glass. The use of glass in atria and overhead glazing can sometimes result in complex areas, which can make maintenance more difficult.

The glass industry has, for many years, worked hard to meet the ever more stringent solar control, aesthetic appeal and structural requirements. Key to meeting these requirements has been the development of coating technology within the glass industry.

Full scale commercialization of large area vacuum deposited coatings as a semi-continuous process took place during the sixties with the exploitation of a range of coating technologies by various glass manufacturers (pyrolytic spray (*PPG*), thermal evaporation (*Saint-Gobain*) and electron beam evaporation (*LOF* - now *Pilkington*), in batch or in-line systems. However, the key technological

Pilkington has led the world's flat glass manufacturers with the launch of the first self-cleaning glass, Pilkington Activ™. Kevin Sanderson and Jose M. Gallego, senior members of the development team for the product, review the coatings technology used to achieve this remarkable product.

development took place during the seventies with the development and commercialization of the planar magnetron (*Airco Temescal*), invented earlier by JS Chapin (Sputtering Source and Apparatus, US Patent 4166018 1974). The throughput and automation capability, as well as scalability of the sputtering process, enabled the field of coatings to grow quickly to the considerable size of today. Today, many of the world's glass companies have access to both vacuum deposition techniques as well as a range of on-line coating systems, where the coating is deposited as the glass is manufactured. On line processes are normally based on spray pyrolysis, chemical vapour deposition or powder spray processes. Coatings based on this technology have now been available for over two decades.

Since those early days, in-line sputtering has changed considerably and has become the most widely used coating technology for large area deposition on glass. Its features and flexibility not only have facilitated the present market size but also the variety of products on offer. Notwithstanding the progress made, the number of materials and coating designs that have been exploited so far has been limited and consequently there is great scope for both technical and commercial growth in this field.

Architectural applications currently constitute by far the largest market for coated products. Both the market and technology have grown steadily over the last two decades. Given its strategic value to the glass manufacturing industry as well as many specialists coating manufacturers and glass processing outlets it is promising to continue developing both from a commercial and a technical point of view.

The first large coater with the capability to handle jumbo size glass plates (6 metres x 3.21 metres) was installed in 1981 by Pilkington in Germany. Product availability and specification have increased over the years from simple stacks of dielectric-metal-dielectric targeted to basic low emittance (energy saving) coatings to enhanced performance designs consisting of as many as ten layers for both low emittance as well as solar control products. It is likely that the changes will continue for the foreseeable future as the competing players search for new functionality, better optical and thermal performance.

The market for large area coatings in this particular field of application has been driven primarily by energy saving reasons due in part to the greater awareness of the effect of CO_2 emission on global warming.

Given the strategic value of the technology, many changes and improvements have taken place over recent years in addition to a substantial increase in capacity. More and more of the newly developed plants are capable of handling the large jumbo plates. The com-

Fig. 1 - Modern architectural coater with an annual capacity of 4-5 million square metres of high performance energy saving product

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plexity, flexibility and capabilities of these plants are also increasing.

The original magnetron electrode has come a long way since its invention in the late sixties. The reliability and homogeneity in coating thickness have improved considerably as a result of better engineering, improvements in the materials and stability of the magnets as well as by the design of the vacuum plants. Dual magnetrons were recently introduced and were to an extent developed for avoiding the deleterious effect of arcing and improve electrical performance. They have enabled difficult but technically strategic materials, such as titanium oxide, to be deposited routinely for long periods of time. This, in turn, has allowed the design of high performance coating stacks with a handful of materials and a small number of layers. Extension of these devices for depositing mixtures of elements and compounds as well as the possibility of multiple assemblies brings new technological and product opportunities.

Some of the difficulties during the early days of this industry were connected to durability issues. Changes have been brought about in part by substantial process improvements and also by the fact that companies processing the product have developed the right handling skills as well as equipped themselves with superior processing equipment.

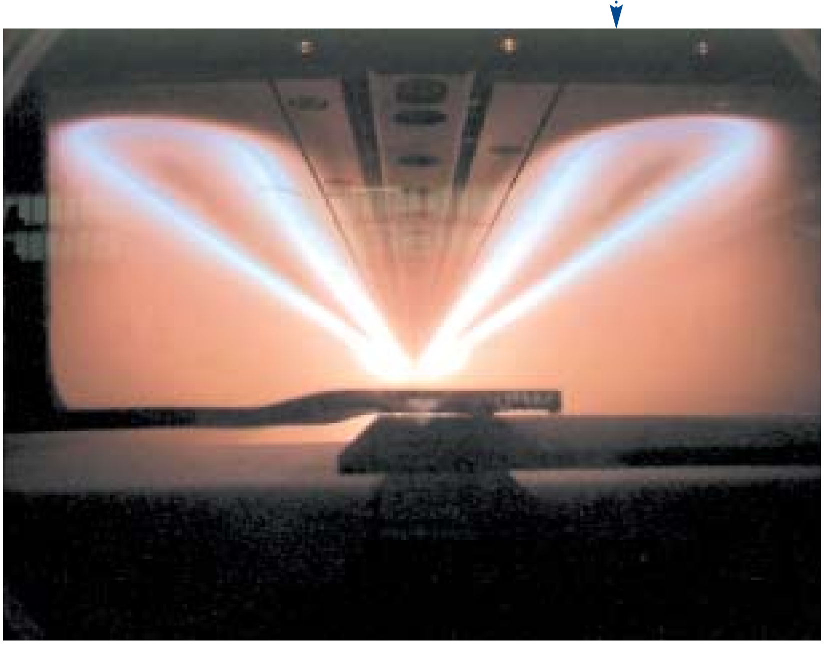

Fig. 2 - Twin cathode assembly

TABLE 1

TABLE 1	1980	2002
Day light transmission [%]	80	88
Emissivity [%]	8-10	4-5
(*) Resistance to corrosion [days]	5-10	25-30
(**) Resistance to scratches [Newtons]	0.1-0.2	5-10

Relative performance of energy-saving coatings between 1980 and 2000. (*) at 40°C and 90% humidity, (**) using the Van Laar test

The products have undergone substantial changes and improvements in performance over the last 20 years. Table 1 gives a snapshot of product (low emittance) performance in four critical areas, namely daylight transmission, emissivity, resistance to corrosion and resistance to scratches.

The performance summarized in Table 1 has enabled the initial U-values of 3.0 W/m^2K to come down to 1.0 with the help of Argon filling and the use of double silver stack designs. This, in turn, has made possible considerable savings in energy with the negligible cost associated with providing one pane with a coating. Until recently, however, the maintenance issue has not been addressed. In the last two years the glass industry has tried to respond to this challenge with the introduction of a range of coatings designed to reduce the amount of maintenance that glass requires.

The coatings are all designed to address the issues of what makes a piece of glass look dirty and unacceptable to the owner/occupier of the building. When glass is exposed to the environment it is subject to dust, city pollution, rain and wind. As a result, over time dirt builds up on the surface of the glass and reduces the visual appeal of the glass. Everybody is likely to have observed the typical droplet and rivulets pattern that dirty glass exhibits. Added to this, there is the loss of clarity when it rains as a result of the rain droplets causing distortion on windows.

The solution to this problem has been the introduction of a range of coatings based on a material called titanium dioxide. Titanium dioxide is a widely used material that is usually a white powdery material and finds everyday use in such items as toothpaste, paints and also sun tan creams. Glass substrates containing a coating of titanium dioxide are designed to offer a dual action cleaning process which will reduce the amount of maintenance a piece of glass will require. The two properties that the coating provides are related to the fact that titanium dioxide is a wide band n-type semiconductor with a band gap of approximately 3.2eV. When exposed to UV radiation the two effects generated are:

HYDROPHILIC EFFECT

When exposed to sunlight the coating absorbs a portion of the ultra violet light and becomes hydrophilic. Hydrophilic or water loving effectively means that when rain falls onto the surface of the glass it rapidly spreads out. As more droplets fall and spread out on the surface, they rapidly coalesce to form a sheet of water. This effect has two benefits. Firstly, there is far less distortion, which means that for the first time on rainy days you can still look out of your window and admire the view without the world outside being strangely distorted. This effect is shown in the photo below. However, this sheeting action of the water has a second major benefit. As the water sheets down the glass it is ideal for washing off some of the dirt that has fallen onto the surface of the glass. As an additional benefit, however, the hydrophilic behaviour also allows the glass to dry without leaving the traditional droplet marks of float glass. The chemistry behind this effect is still under investigation by a range of techniques.

At present, the effect is understood to be related to a change in the nature of the titanium surface. When exposed to UV radiation it is believed that there is a change in the oxidation state of the titanium at the surface. The titanium oxidation state changes from 4+ to 3+ as a result of oxygen vacancies being created at two coordinate bridging sites. These Ti3+ domains are believed to be favourable for dissociative water adsorption. This results in a hydroxyl-rich surface, which is hydrophilic. This effect is quantified by the change in contact angle1 at the surface. Typically glass has a very variable contact angle of between 25 and 60°. This results in the typical effect that is seen on normal glass where droplets and rivulets are formed. Hydrophilic surfaces typically have a very uniform contact angle of <20° the water spreads out as shown in Figure 3.

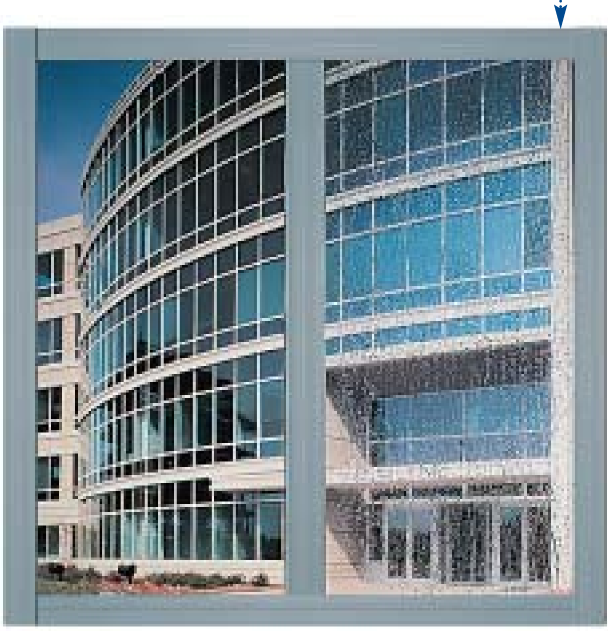

Fig. 3 Comparison of Pilkington Activ™ hydrophilic surface (left) and float glass (right) when exposed to rain

PHOTOCATALYTIC ACTIVITY

When exposed to sunlight the coating absorbs some of the ultra violet light and exhibits photocatalytic activity. When exposed to UV light the titanium dioxide which is a wide band n-type semiconductor with a band gap of approximately 3.2eV results in the formation of hydroxyl radicals and a form of active oxygen at the surface. The reactions that lead to the formation of these species are shown in Figure 4.

These two species which are very strong oxidizing agents are able to accelerate the decomposition of organic material that is on the surface of the glass. As this is a truly catalytic process, the coating is not changed or used up in the process.

These species can then interact with organic dirt on the surface to accelerate their decom-

$$O_2 + e^- \text{--------------->} O_2^-$$

$$H_2O + h^+ \text{------------>} OH^*$$

Fig. 4 - The formation of active species at the surface of titanium dioxide

position. An example of this would be the destruction of stearic acid. This reaction is shown in Figure 5. It must be noted that whilst the breakdown products of this reaction are water vapour and carbon dioxide. There is actually no increase in the output of carbon dioxide into the atmosphere as a result of the use of titanium dioxide, because these would be the natural by-products of the natural breakdown of this material and the surface is simply accelerating this decomposition.

$$CH_3(CH_2)_{16}COOH + 26\,O_2 \xrightarrow[h\upsilon \geq 3.2\ ev]{TiO_2\ Film} 18\,CO_2 + 18\,H_2O$$

Fig. 5 - Equation showing the decomposition of stearic acid at a photocatalytic TiO_2 surface

These two functions each work independently to reduce the build up of dirt on the surface of the glass. However, it is the combination of these two actions that provides a reduced maintenance action in real life conditions. This is demonstrated in the Figure 6.

Whilst the ability of titanium dioxide to show these key properties has been known since the first reports in the early 1960's[2], it has only been in recent years that products based on this type of technology have been commercialized. The first commercial products to utilize this fundamental property of TiO^2 were in Japan. The Asian Pacific region has over the last few years seen a vast number of products from ceramic tiles, sanitary ceramics, deodorization devices, water purification and self cleaning building materials being developed. Books reviewing the development of this technology are available and go into far more detail that this article can accommodate[2,3]. New developments using this technology are being announced all the time and it is clear that Asia has a leading role in the fundamental research associated with this technology. Indeed, worldwide, there are now many conferences specifically dedicated to the science and application of photocatalytic TiO_2.

The challenge for the glass industry, however, was to achieve a coating which, whilst demon-

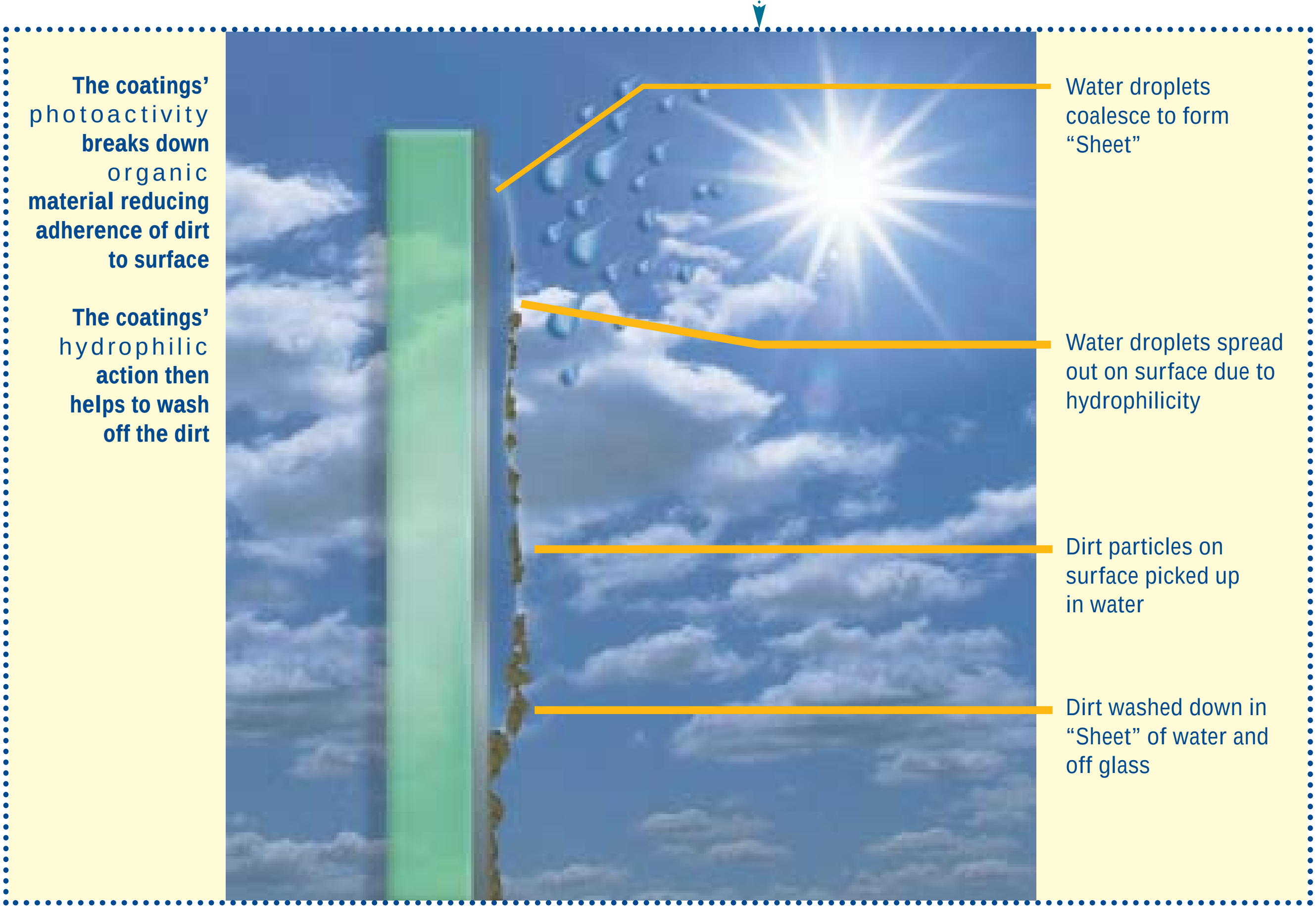

Fig. 6 - The hydrophilic and photoactive functions of the coating combine to reduce the window maintenance required

strating these actions and being able to perform for many years, maintains the optical clarity and appearance of normal glass. The way this has been achieved is to use coating technology. Pilkington use a process called Chemical Vapour Deposition to produce one such product called *Pilkington Activ*™.

Chemical vapour deposition involves forming a vapour of several chemical species, which is entrained in an inert carrier gas such as nitrogen. In the case of Pilkington, this vapour stream is then delivered to a coating system, which is located on the float line, where the glass is actually manufactured. The advantage of such a system is that the coating can be applied as the glass is still at an elevated temperature of approximately 600-700°C. The thermal decomposition of the precursors results in a hard, durable coating which has a similar appearance to normal float glass. The process results in a film of approximately 15 nanometres in thickness.

Alternative technologies for depositing this type of film include sol-gel, spray and sputtering technologies. Such technologies allow a wide range of substrate materials to be coated including aluminium, ceramic tiles and cloths. As the transparency of the final product is of less importance in some of these applications the properties of the films can be modified as appropriate.

Photocatalytic and hydrophilic technology is finding ever more uses. Coating technology has already allowed commercialization of a range of products utilizing this technology. The introduction of reduced maintenance glazing is just one of these. However, it demonstrates the glass industry's continuing commitment to respond to the home owners and architects requirements. The future for this technology appears at present to be limited only by our imagination to find beneficial applications for the technology. Whilst architectural applications currently dominate the market for coated glass, however, technical applications are becoming of increasing importance. One example of this could be to consider this technology being linked to other advances such as Pholtovoltaic devices. Table 2 shows the benefits that coating technology could provide to this growing area.

In the glass industry, however, we appear to have solved one issue for the architect, home-owner and building owners only to raise another. The latest question is now - What about the *inside* of our windows?

TABLE 2

FUNCTION	GAIN IN EFFICIENCY
Anti-reflection coating - single sided	*Up to 4% in added light transmission*
Anti-soil	*Up to 5% in losses due to dirt*
Rolled glass	*Up to 5% increased absorption*

Table 2
Benefits of providing photovoltaic panels with added features such as AR, anti-soil and patterning of the surface of the glass

REFERENCES

(1) *Definition of contact angle. The angle formed at a point on the line of contact of three phases, of which at least two are condensed phases, by the tangents to the curves obtained by intersecting a plane perpendicular to the line of contact with each of the three phases. One of the phases must be a liquid, another phase may be a solid or liquid and the third phase may be gas or liquid.*

(2) *An overview of semiconductor photocatalysis and references therein*
Andrew Mills and Stephen Le Hunte
Journal of Photochemistry and Photobiology A: Chemistry 108 (1997) 1-35

(3) *TiO2 Photocatalysis - Fundamentals and Applications*
Dr. Akira Fujishima, Dr. Kazuhito Hashimoto, Dr. Toshiya Watanabe (All professors at The University of Tokyo)
Book published by BKC Inc, 4-5-11 Kudan-minami, Chiyoda-ku, Tokyo 102-0074 Japan
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