Evaluation of Superhydrophilic Polyelectrolyte Multilayered Films for Anti-fogging Applications

by

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B.S. Chemical Engineering & Materials Science and Engineering
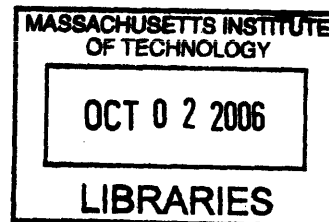University of California, Berkeley, 2003

Submitted to the Department of Materials Science and Engineering
in Partial Fulfillment of the Requirements for the Degree of

Master of Engineering in Materials Science and Engineering

at the

Massachusetts Institute of Technology

September 2006

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ABSTRACT

Polyelectrolyte multilayered (PEM) films created by an aqueous-based layer-by-layer assembly technique have been widely studied in the past decade. Owing to the simple, versatile and yet well-controlled nature of this technique, many potential applications of these thin films have also been proposed and explored. This thesis presents a recent work in fabricating nanoporous PEM films with superhydrophilic characteristics that demonstrate great promise for anti-fogging and anti-reflection glass coating applications. The automotive glass industry is then identified as a potential market for this technology, and competing anti-fogging technologies as well as relevant intellectual property are reviewed to further ascertain the commercial viability of this product. Finally a few possible business models for bringing this product to market are proposed and evaluated.

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ACKNOWLEDGEMENTS

To Professor Michael Rubner:
- For your patience in guiding me through my M.Eng thesis and for granting me this wonderful opportunity to explore the fascinating area of polyelectrolyte films.

To Professor Chee Cheong Wong:
- For the numerous interesting and insightful discussions that have truly helped me develop the ideas of this thesis.

To the SMA Office:
- For the generous support of the SMA fellowship award that has allowed me to pursue the M.Eng program at MIT.
- Particular thanks to the staff of the SMA-MIT office for your responsive and efficient administrative support, and for helping make my stay at MIT so comfortable and enjoyable!

To my fellow M.Eng colleagues:
- For your invaluable friendship and company this past year. It's been exciting going through the M.Eng program with you guys and I can't wait for our paths to cross again in the future!

To my dear Friends:
- I have learnt so much from each and every one of you and I am truly blessed to count you as my friends. Thanks for accompanying me through this journey of life and for making me who I am today.

Last but not least, to my beloved Parents and my lil' sister Belinda:
- For the selfless love that you are always so eager to give and for always being so encouraging and supportive in all that I do. Can't imagine what I would do without you – thanks for everything and I love you guys!

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1. INTRODUCTION

Polyelectrolyte multilayered films can be effectively deposited through a relatively simple process in which polyelectrolyte layers are sequentially adsorbed by alternating the substrate between exposures to solutions containing oppositely charged polyelectrolytes. This layer-by-layer technique was first demonstrated by Decher, *et al.* in the early 1990's and has since attracted much research attention for its versatility and excellent deposition control. To date, many different polyelectrolyte multilayer systems have been successfully fabricated on a host of substrates and various potential applications of polyelectrolyte multilayered films have been explored.

This work begins with an overview of the layer-by-layer assembly of polyelectrolyte multilayered films and some of the work that has been carried out in this research area. This is followed by the presentation of a recent work by the Rubner Group at the Massachusetts Institute of Technology in fabricating superhydrophilic polyelectrolyte multilayered films with exceptional anti-fogging and anti-reflection properties. In addition, various factors that influence the film deposition process and film properties will also be addressed.

In the next section, the anti-fogging capabilities of these superhydrophilic films are compared to other anti-fogging technologies in order to further determine the commercial viability of this product. An analysis of the intellectual property associated with various aspects of this technology will also be carried out to identify possible obstacles that may hinder the patent application process.

Next, the target market for the commercialization of the anti-fogging coating technology is identified, and some characteristics and recent trends of industries

associated with the choice market are presented and discussed. Finally three possible business models are proposed and evaluated to determine which is most suited to bringing the Rubner anti-fogging technology to market.

2.   POLYELECTROLYTE MULTILAYERED FILMS

2.1   Polyelectrolytes

Polyelectrolytes are polymers with electrolyte groups attached to their repeating units. When placed in water or any other ionizing solvent, these electrolyte groups dissociate, leaving the polymeric molecule charged along its chain. This dissociation of the polyelectrolyte is usually accompanied by the release of oppositely charged counter-ions that surround the dissociated polyelectrolyte in order to preserve charge neutrality.

The conformation of a polyelectrolyte is dependent on electrostatic interactions between the charged monomers along its molecular chain. For dissociated polyelectrolytes in weak ionic strength solutions, the electrostatic repulsion experienced by the similarly charged monomers causes the polyelectrolytes to adopt stretched and extended forms (Figure 1a). As the ionic strength of the solution is increased, the charge screening effect of the added ions suppresses the inter-monomeric repulsions and the polyelectrolytes become thicker and more coiled in shape (Figure 1b). However in the limit of high electrolyte concentrations, the polyelectrolyte solubility in the solvent decreases and polyelectrolyte precipitation may occur in a process known as "salting out". It has also been noted that higher valence ions result in greater charge screening and their effect is similar to that of increasing electrolyte concentration in solution[1].
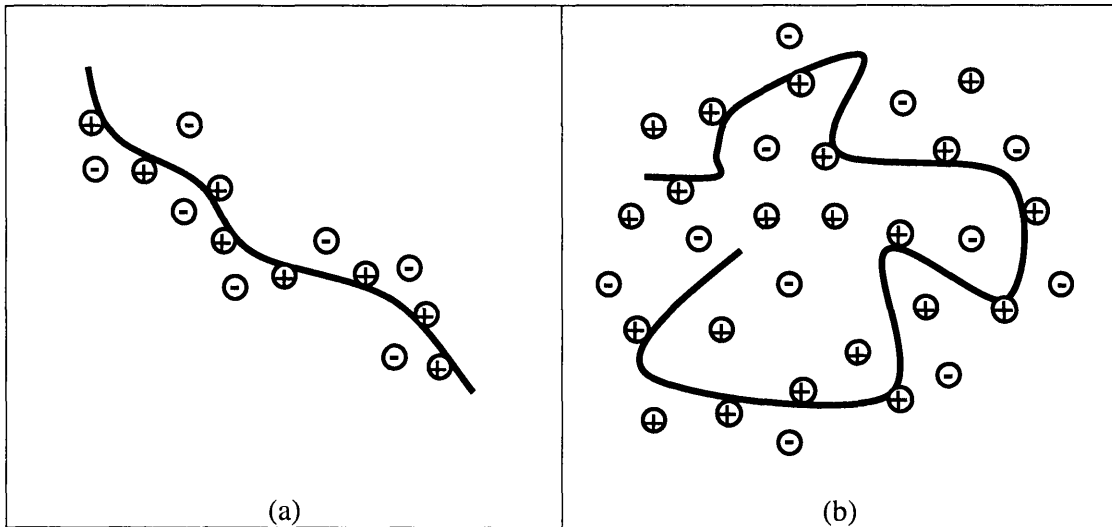
Figure 1: Schematic representations of a dissociated polyelectrolyte in (a) a weak ionic strength solution and (b) in a relatively stronger ionic strength solution.

Polyelectrolytes can be broadly characterized as "strong" and "weak" according to the extent of dissociation of their electrolyte groups in solution. Strong polyelectrolytes dissociate completely in solution and their degree of ionization is relatively independent of solution pH, while on the other hand, the extent of dissociation of weak polyelectrolytes is highly dependent on solution pH. Examples of strong polyelectrolytes include poly(diallyldimethylammonium chloride) (PDAC), poly(vinylsulfonic acid) (PVS) and poly(styrenesulfonate) (PSS), while two well-studied weak polyelectrolytes are poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH).

2.2 Layer-by-Layer Assembly of Polyelectrolyte Multilayered Films

The layer-by-layer (LbL) assembly of polyelectrolyte multilayered (PEM) films is a relatively simple process that is based on the principle of electrostatic attraction between oppositely charged polyelectrolyte layers and was first demonstrated by Decher in 1992[2]. In this assembly technique, the charged substrate is first dipped into an oppositely charged polyelectrolyte solution resulting in the adsorption of one layer of

polyelectrolyte onto the substrate surface. As the result of surface charge being overcompensated by the adsorbing polyelectrolyte, the surface charge of the film is reversed by the newly adsorbed layer, and this prepares the surface for subsequent absorption of the next layer of oppositely charged polyelectrolyte[3,4] (Figure 2). In addition, each newly adsorbed polyelectrolyte layer builds up an electrostatic barrier that prevents further absorption of like-charged molecules, resulting in a self-regulating and well-controlled single-layer deposition of polyelectrolytes with each dipping step[5].
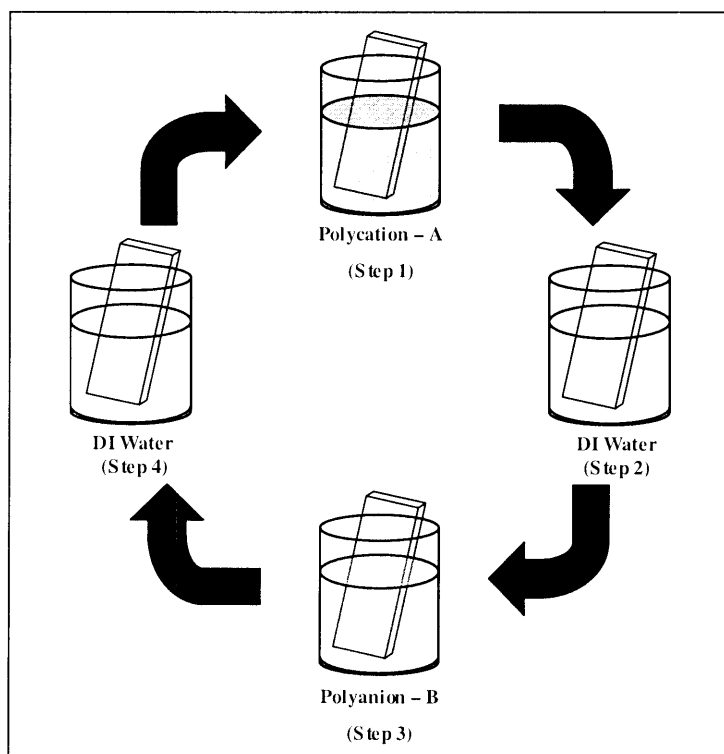
Figure 2: Schematic of the layer-by-layer assembly of polyelectrolyte multilayers. Each cycle (steps 1 through 4) result in the deposition of one polyelectrolyte bilayer. These cycles are repeated to obtain the desired number of layers in the multilayer film.

The sample is also rinsed in deionized water after each polyelectrolyte adsorption step. This rinsing step acts primarily to remove any excess un-adsorbed material from the sample surface and also to avoid contaminating the polyelectrolyte solution in the

subsequent dipping step. Some researchers have also observed that the rinsing steps appear to stabilize the absorbed layer and even increase the amount of absorbed polyelectrolyte[6,7].

After being dipped into the second adsorption solution, the sample is again rinsed in water and these "dip and rinse" steps are repeated to achieve the deposition of the desired number of layers in the PEM film.

2.3   Factors Influencing LbL Assembly of PEM Films

The salt concentration of the adsorption solution used in the LbL assembly is the main factor that influences the film thickness and the structure of the PEM film deposited using strong polyelectrolyte systems. Early studies by Lvov and Decher have shown that the layer thickness of a PSS/PAH PEM increases with the square of the ionic strength of the adsorption solution[8], while others have reported a linear relationship between the layer thickness and salt concentration for PSS/PDAC polyelectrolyte systems[9,10].

As described earlier, fully-charged polyelectrolyte chains adopt a stretched structure in low ionic strength solutions and so strong polyelectrolyte systems typically result in deposited layers that are extremely thin (~5Å per layer). As the salt concentration of the adsorption solution is increased, the electrostatic interactions between the adsorbing polyelectrolyte and the film surface are decreased due to the screening effect of electrolytes. Consequently, more polyelectrolyte adsorption is required at the surface in order to compensate the surface charge and so the layer thickness increases[6]. Another reason for the layer thickness increase with more concentrated salt solution can be attributed to the coiled conformation of polyelectrolytes

in high ionic strength solutions[3] that results in thicker polyelectrolyte layers being deposited.

Another factor that can influence PEM thickness is the process temperature of the LbL assembly[11]. In a study by Büscher *et al.*, it was observed that the thickness of a PSS/PAH PEM film increases with adsorption temperature up to the limit of the precipitation temperature of the polyelectrolyte. As the adsorption temperature is raised, the polyelectrolyte-solvent interaction is enhanced and some of the polyelectrolyte-substrate bonds are broken. In order to maintain charge neutrality on the substrate surface, more polyelectrolyte is adsorbed, resulting in thicker deposited films. However as the number of strong electrostatic polyelectrolyte-surface bonds (per polyelectrolyte) is lessened, the adsorbed polyelectrolyte layers are less strongly bound to the surface. Consequently, the adsorbed polyelectrolyte layers take on a more loopy conformational state, and both thickness and surface roughness of the PEM film are increased.

When using weak polyelectrolyte systems for LbL assembly of PEM films, the pH of the adsorption solutions becomes important in determining the layer thickness, since the degree of ionization of weak polyeletrolytes is highly dependent on the solution pH. The effect of pH on the adsorption of two weak polyelectrolytes – PAA and PAH, has been widely studied and dramatic layer thickness changes have been observed to occur over a narrow pH range associated with the transition of the polyelectrolytes from fully-ionized to partially-ionized states[12].

This pH-dependent thickness behavior is best illustrated and explained in a recent study[13] by pairing PAA with strong polycations – PDAC or poly(4-vinylbenzyltrimethylammonium chloride) (PVTAC), and PAH with strong polyanions –

poly(vinylsulfonic acid, sodium salt) (PVS) or poly(sodium 4-styrenesulfonate) (SPS). With these weak-strong polyelectrolyte pairings, the pH-dependence of the degree of ionization of the weak polyelectrolytes can be isolated and more specifically analyzed, since the degree of ionization of the strong polyelectrolytes is unaffected by changes in solution pH. In the neutral pH range of 6.5 to 7.5, both PAA and PAH are in their fully-charged ionic states and consequently PEM films deposited in this regime are very thin (4-8Å per bilayer). However, the degree of ionization of these weak polyelectrolytes begins to decrease as pH is decreased (for PAA) or increased (for PAH) and this is accompanied by an appreciable increase in the average bilayer thickness when the weak polyelectrolytes transition from a fully ionized state to one that is 70-90% charged. It was proposed by a thermodynamic model[14,15] that in its partially ionized state, the entropic requirement of keeping the polyelectrolyte in a flat conformational state can no longer be compensated and the polyelectrolyte then takes on a more coiled shape. Consequently the coiled conformation of the adsorbed polyelectrolytes results in an increase in the thickness of the deposited layers.

While the control of layer thickness by salt concentration is limited by the "salting out" phenomenon of polyelectrolytes at high salt concentrations, the pH-dependent layer thickness behavior of weak polyelectrolyte systems allows film thicknesses to be manipulated in a well-controlled manner over a wider range of charge densities of the adsorbing polyelectrolytes. This advantage of better film thickness control has, in recent years, drawn increased attention and research efforts to the study of weak polyelectrolyte systems.

In addition to the factors highlighted above, the dielectric constant of the deposition solvent, the type of salt used, as well as the polyelectrolyte concentration and molecular weight have also been observed to affect PEM film growth characteristics[10], but to lesser extents.

2.4   Advantages of LbL Assembly of PEM Films

One of the most significant advantages of the LbL assembly is that PEM films can essentially be grown on any surface without any restrictions on substrate size nor shape[5]. The self-limiting nature of the adsorption of polyelectrolyte layers ensures a uniform film thickness over the entire coated surface. The precisely controlled layer-by-layer assembly also allows for a wide range of deposition materials to be used, and layer properties have been shown to be independent of the type of substrate used[16].

The growth of PEM via LbL assembly can be controlled by various process parameters with salt concentration and solution pH being the most important factors for strong and weak polyelectrolyte systems respectively. These characteristics, coupled with the controlled manner of LbL assembly, allow the fabrication of PEM films with a myriad of film properties and applications.

In addition, the LbL technique is low-cost, environmentally friendly and easy to scale-up[17]. The room temperature and pressure conditions eliminate the need for any expensive and elaborate vacuum systems, and the dipping process can be easily automated to facilitate commercial applications of PEM films.

2.5 Applications of PEM Films

Owing to the versatility of the LbL process, PEM films have been used in a wide host of applications where the distinctive and well-controlled film properties of PEM are exploited.

By controlling the PEM layer thickness and structure with solution pH, it has been possible to manipulate the dielectric constant and refractive indices of PEM films by varying the degree of porosity in these structures. This property has been employed in fabricating anti-reflection coatings[18] and Bragg mirrors[19]. The porous nature of the PEM films also allows them to be promising candidates for selectively permeable membranes[20,21] as well as for drug delivery functions[22].

By incorporating nanoparticles into the LbL assembly process, the properties of PEM film can be further expanded to reflect the unique optical, magnetic and electrical properties of the nanoparticles[17]. This aspect of nanocomposite multilayers, exploited in conjunction with various templating and patterning techniques[23,24,25], presents huge potential in electronics, photonics and information storage applications. The constantly growing list of PEM applications include conducting layers, light-emitting thin films, electrocatalysis, enzyme-active films, hydrophobic and hydrophilic coatings[10].

3. SUPERHYDROPHILIC PEM FILMS WITH ANTI-FOGGING PROPERTIES

The formation of water droplets on glass surfaces, often known as "fogging", is a common phenomenon that occurs when water vapor in warm, moist air condenses to create tiny water droplets on cooler surfaces. The hemi-spherical geometry of these miniscule water droplets causes light incident on the "fogged" surface to be scattered in

all directions, resulting in reduced visibility and distortion of images viewed through the otherwise transparent surface.

The loss of visibility that accompanies fogging is especially detrimental for car windshields and work safety goggles, as both safety and efficiency are greatly compromised. Hence, anti-fogging technology is important in maintaining the integrity and functionality of glass surfaces.

Recently, the Rubner Research Group at the Massachusetts Institute of Technology (MIT) has successfully utilized the LbL technique to fabricate nanocomposite PEM's with alternating layers of silica nanoparticles and PAH[26]. By optimizing the process parameters of the LbL assembly to give these nanocomposite films a high degree of porosity, these films have been demonstrated to display superior anti-fogging properties attributed to their superhydrophilic characteristics. The following section describes the experimental work done by this research group.

3.1   Film Fabrication

The anti-fogging thin film coatings fabricated by the Rubner group consist of a multi-layered structure of alternating layers of silica (SiO_2) nanoparticles and a polycation – poly(allylamine hydrochloride) (PAH), which are deposited using an automated layer-by-layer dipping process. In this process, the substrate is first dipped into a solution containing either the polyelectrolyte or nanoparticles for 15 minutes, and then rinsed in deionized water thrice before being dipped into the other adsorption solution. The inter-layer bonding in the multilayered film results from the electrostatic attraction between the oppositely charged layers and each dipping step results in the deposition of a monolayer of material. A few bilayers of PAH/SPS or PAH/PAA were first adsorbed

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onto the substrates before deposition of the SiO$_2$/PAH nanocomposite film. This process step of first depositing layers of polyelectrolytes with strong adsorption properties is commonly carried out to bind PEM films more strongly to the substrate[3]. After depositing the desired number of PAH/SiO$_2$ bilayers, the resultant film is then cured at 500°C for 4 hours in order to strengthen the coating.

3.1.1 Effect of Solution pH

Solution pH affects the charge densities of both the PAH molecules and silica

nanoparticles, and this in turn affects the structure of the deposited film layers as

discussed in the earlier sections. Equation (1) below shows the hydrolysis reaction of

silanol groups found on the SiO$_2$ nanoparticle surface, while equation (2) shows that for

neutral PAH. Increasing solution pH drives the reaction represented by equation (1) to the

right, and the proportion of ionized silanol groups increases, resulting in an increase in

the surface charge density of the nanoparticles[27]. On the other hand, an increase in

solution pH drives equation (2) to the left, resulting in fewer protonated amine groups

and a decrease in the charge density of the PAH polyelectrolytes[13]. However, it has been

observed that decreases in the ionization of PAH occur only when solution pH increases

beyond 7.0[12].

$$\equiv \text{Si-OH} + \text{H}_2\text{O} \leftrightarrow \equiv \text{Si-O}^- + \text{H}_3\text{O}^+ \tag{1}$$

$$\begin{array}{ccc}
\text{--}(\text{CH}_2\text{--CH})\text{--} + \text{H}_2\text{O} \leftrightarrow & \text{--}(\text{CH}_2\text{--CH})\text{--} + \text{OH}^- \\
\quad\;\; | & \quad\;\; | \\
\quad\;\; \text{CH}_2 & \quad\;\; \text{CH}_2 \\
\quad\;\; | & \quad\;\; | \\
\quad\;\; \text{NH}_2 & \quad\;\; \text{NH}_3^+
\end{array} \tag{2}$$
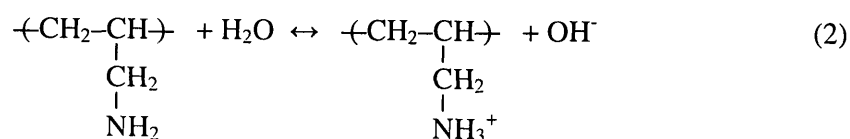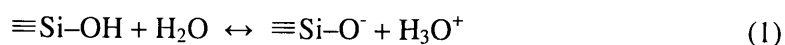
At pH values below 4.0, it was experimentally observed that the deposited nanoparticle layer appeared sparse and the superhydrophilic properties of such films were unstable and degraded with time. This was attributed to weak electrostatic attraction between the deposited layers due to the low surface charge densities of the silica nanoparticles at low solution pH. In addition, the charge densities of silica nanoparticles were found to be highly responsive to pH changes for values between 4.0 and 7.5, and the resultant films deposited in this pH range were highly unstable. This is consistent with literature which state that colloidal silica is generally stable only in the pH range of 8-10[27] (Figure 3). Hence, the optimal solution pH was determined to be in the range of 7.5 to 9.0.
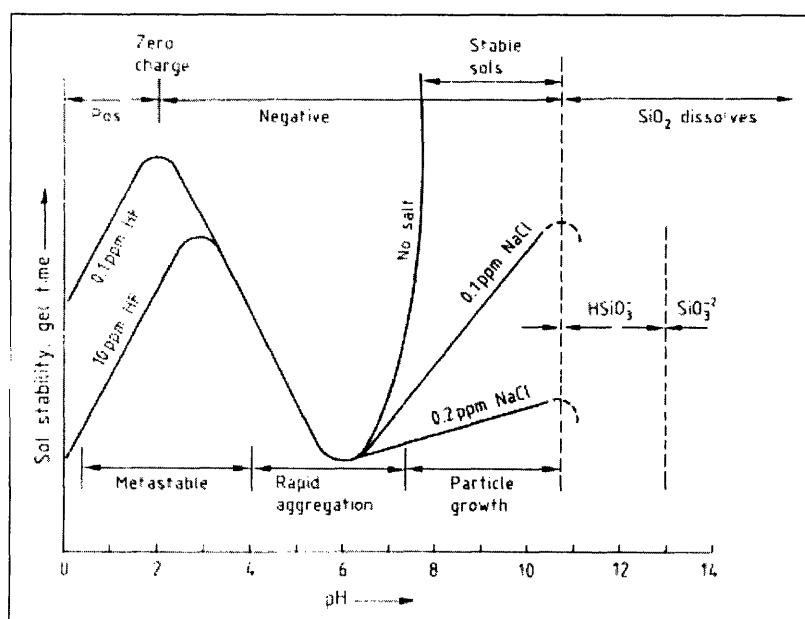

Figure 3[27]: Effect of pH on stability of colloidal silica-water systems.

3.1.2 Effect of Nanoparticle Size

The effect of nanoparticle size on the properties of the deposited film was investigated using SiO_2 suspensions with 3 different sized nanoparticles (7nm, 12nm and

22nm diameter). Using the larger 12nm and 22nm SiO_2 particles, the film transparency deteriorated once 8 PAH/SiO_2 bilayers were deposited. Furthermore, these films did not exhibit any superhydrophilic properties, and so it was apparent that these larger-sized silica suspensions could not be used. As for the 7nm-diameter SiO_2 nanoparticles, the transparency of the deposited film was maintained for up to 24 bilayers, and hence 7nm was selected as the optimal SiO_2 nanoparticle size.

3.1.3 Effect of SiO_2 Suspension Concentration

Finally the effect of varying the concentration of the SiO_2 suspension was studied. Using SiO_2 nanoparticles of the optimal diameter of 7nm, various SiO_2 nanoparticle solutions with concentrations ranging from 0.005 weight% to 0.1 weight% were prepared and used for this analysis.

It was observed that films fabricated from the low concentration solutions exhibited low surface coverage, while films fabricated from the highly concentrated solutions were too closely packed and no longer exhibited any superhydrophilic properties due to the loss of nanoporosity. It was experimentally determined that 0.3 wt% was the ideal suspension concentration as high quality PEM films were obtained with this concentration. Additionally, films deposited with this SiO_2 suspension concentration had very low refractive indices (about 1.25 for a 14-bilayered film) and the incremental film thickness was approximately constant as more bilayers were deposited. This latter feature is useful in allowing the thickness of the PEM to be accurately controlled by the number of deposition steps.

3.1.4 Film Curing Process

As previously mentioned, the final deposited film was heat-treated at $500^{\circ}C$ for 4 hours in order to improve the strength of the film. During this calcination process, the silica nanoparticles become joined together by siloxane bonds that form through the dehydroylation process of silanol groups found on the nanoparticle surface[28] (Equation 3). The formation of these strong siloxane bridges, which are less polar and more stable than silanol groups, gives the film better mechanical properties. Moreover, it should be noted that this dehydroylation process is reversible at temperatures below $500^{\circ}C$, and the siloxane bridges can be completely converted back into hydroxyl groups by contacting the silica nanoparticles with water vapor at room temperature[28]. Hence a process temperature of at least $500^{\circ}C$ had to be chosen to ensure the formation of stable siloxane bridges.

$$\equiv Si–OH + HO\text{-}Si \equiv \ \leftrightarrow \ \equiv Si–O–Si \equiv + H_2O \tag{3}$$
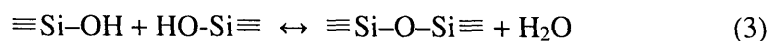
The high temperature employed during the curing process also results in the removal of the polyelectrolyte (which has a relatively low decomposition/vaporization temperature) from the film. Since the polyelectrolyte has a high refractive index, this removal process lowers the overall refractive index of the deposited film and improves its anti-reflection properties. This vaporization of polyelectrolyte also increases the porosity of the film and this is a crucial criterion for superhydrophilicity (*to be discussed later*). Unfortunately, the high temperature employed during this curing process also places a restriction on the possible types of substrates that can be coated, and plastics with low melting points are not suitable candidates for this anti-fogging coating process.

3.2 Superhydrophilic Anti-fogging Properties

The anti-fogging characteristic of the nanocomposite films deposited is essentially due to its superhydrophilicity that causes any water condensing on the glass substrate to immediately wet the substrate surface, and to form a thin sheet of water that does not scatter light and hence eliminating the fogging phenomenon.

For a film to be classified as superhydrophilic, it ought to wet with water at a contact angle of less than $5°$, in a time of 0.5 seconds or less. Video contact angle measurements taken for an 18-bilayered PAH/SiO_2 film demonstrated that the first and second drops of water (drop volume of $0.5\mu L$) onto a coated surface wets in 0.167 and 0.03 seconds respectively. In addition, it was also observed that while almost all deposited films displayed exceptional wettability, a minimum of 14 bilayers were required for the display of superhydrophilicity.

A simple experiment was carried out in order to demonstrate the anti-fogging properties of the multilayered thin films deposited – two glass slides, one coated with the multilayer superhydrophilic thin film and the other left uncoated, were placed in a $-18°C$ refrigerator for some time. When both slides were taken out of the refrigerator, it was observed that the coated slide remained transparent and unfogged, while water condensate readily formed on the uncoated slide. The coating was also noticed to keep water on a wet surface as a continuous sheet instead dewetting to form little water droplets. This property of the film means that good visibility can be maintained for a coated glass surface, even when the nanopores of the PEM film become saturated with water molecules.

The superhydrophilic nature of the multilayered PAH/SiO$_2$ films was attributed to 3 key factors. Firstly, the silanol groups found on the surfaces of the SiO$_2$ nanoparticles are highly hydrophilic[27], and so the deposited SiO$_2$ nanofilms readily attract water molecules. Next, some previous investigations have shown that superhydrophilicity can also be induced through surface roughness[29,30,31]. From atomic force microscopy (AFM) images taken of the fabricated PAH/SiO$_2$ multilayered films, it was clearly observed that these films did possess high surface roughness. However on further analysis, it was concluded that the surface roughness of the films was not the main reason for its superhydrophilicity as films with greater surface roughness were not always found to be more superhydrophilic.

Finally, it was proposed that the nanoporous nature of the deposited films was the most critical contributor to their display of superhydrophilicity. From AFM images of the deposited film, it was evident that the films possessed a porous structure that resulted from the randomized packing of SiO$_2$ nanoparticles in the film. The film structure can be visualized as consisting of a system of tiny pores that are linked, resembling the geometric structure of a sponge. Hence water that is attracted by the SiO$_2$ nanoparticles to the film surface can penetrate and be "soaked" up by the entire nanoporous film. This in turn accounts for the fast wetting process and the superhydrophilic characteristics observed. Furthermore, the sizes of these pores are smaller than the wavelength of light and so incident light is not scattered by them.

3.3 Anti-reflection Properties

In addition to exhibiting anti-fogging properties, the fabricated films were also shown to offer anti-reflection properties. As these silica films are nanoporous structures

comprised of SiO_2 and air-filled pores, their refractive indices lie in between that of silica (n≈1.455) and air (n=1). Since more porous structures contained a higher air-to-silica ratio. it is also possible to lower the film refractive index by increasing the level of porosity in the film. It was noticed that the refractive indices of all of the films deposited lay in the low range of 1.245 – 1.270 which makes them good candidates for anti-reflection coatings. Moreover, as each bilayer has a thickness of about 11-18nm, it was possible to carefully control the overall deposited film thickness to coincide with the quarter-wavelength of the incident light, so as to maximize the anti-reflection effects of the coating. It was experimentally shown that PEM-coated glass substrates exhibited transmittance levels well above that for uncoated glass (92%) throughout the entire visible wavelength spectrum, and the maximum transmittance achieved was a remarkable 99.8%!

4. COMPETITIVE ANALYSIS

From the discussions in the preceding sections, it has been clearly demonstrated that the Rubner group has been successful in fabricating superhydrophilic PAH/SiO_2 multilayered films with superior anti-fogging and anti-reflection properties. This next section compares this novel anti-fogging coating to other anti-fogging technologies that are currently commercially available.

4.1 Anti-fogging Sprays

Anti-fogging sprays represent the most common anti-fog solution, and they are widely used for eyeglasses and various types of goggles (ski, scuba diving, paintball, etc.). These sprays are often made of surfactants that promote the wetting behavior of water on

the applied surface, therefore causing water condensing on the surface to form continuous sheets that will not scatter light[32].

While these sprays are economical, easy to apply and can be used on plastic surfaces, their effects are non-permanent and frequent re-applications are necessary. In addition, these sprays are not practical for coating large glass surfaces (such as car windshields and building windows) and it is also extremely difficult to coat surfaces uniformly.

4.2   Titanium Dioxide Anti-fogging Glass Coatings

While the photocatalytic properties of titanium dioxide (TiO_2) have been studied for the past three decades, the photo-induced superhydrophilic property of TiO_2 was only discovered by researchers working at the laboratories at TOTO Ltd in 1995[33,34].

It has been proposed[34,35] that anatase-type TiO_2 which has a band energy of about 3.2eV can be excited by UV irradiation tot create electron-hole pairs. These electron-hole pairs have high redox properties and in particular, the strong oxidative power of the positive holes causes the O^{2-} anions from TiO_2 to be released as oxygen atoms. This process creates oxygen vacancies that readily attract water molecules to form Ti-OH bonds at the film surface. The superhydrophilicity of the TiO_2 film results from the presence of the hydrophilic hydroxyl groups found on the film surface.

While this technology has since been commercialized by various glass manufacturers, the requirement of UV irradiation still remains a major drawback. TiO_2 films rapidly lose their superhydrophilicity within hours of being isolated from a UV source, and hence, regular "UV-charging" of the TiO_2 films is required in order to maintain anti-fogging. Recognizing that the scarcity of sunlight during the typical

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fogging scenarios of cold weather and night, this fundamental disadvantage of the technology greatly reduces its attractiveness for use in car windshields where adequate night visibility is a key safety concern.

4.3   Anti-fogging Systems for Automobiles

As stated in previous discussions, the loss of visibility due to the fogging phenomenon is of particular concern to motorists due to the compromise of road safety. Currently, the solutions for demisting glass in automobiles include the wiper and front air vent systems for the front windshields, as well as heated wire filaments for the rear windshield. Basically these systems act to heat the windshield to that water vapor does not condense onto the warmed glass surfaces.

While these systems are now commonly included as "stock equipment" in most automobiles and have been proven successful in removing fog and condensate from the windshields, they remain essentially passive systems. What this means is that the anti-fogging effects of these systems need to be executed by the driver of the automobile and more often, these systems act to clear the windshields of existing condensate, rather than to prevent the fogging phenomenon from occurring in the first place. In addition, their operation relies on various electrical and mechanical systems of the vehicle, and these are subject to failure and require maintenance.

4.4   XeroCoat Pty. Ltd.

In 2004, a couple of physicists, Drs Michael Harvey and Paul Meredith from the University of Queensland (UQ) in Australia, developed a unique coating technology that boasts of exceptional anti-reflection and anti-fogging characteristics (much like the

Rubner technology). The pair obtained government funding of AUS $121,000 from the Queensland Sustainable Energy Innovation Fund, and a company, XeroCoat was subsequently founded with the help of UniQuest Pty. Ltd., a subsidiary of UQ whose aim is to aid in the commercializing technologies developed by the university[36].

The initial focus for application of this technology (as implicated by the grant) was in providing anti-reflection coating to solar panels in order to increase the efficiency of these photovoltaic devices. However, the developers of this technology have also recognized the huge potential in applying this technology to a host of other applications such as spectacle lenses, goggles, windows, computer and television screens and mirrors.

Since its founding, the company has been the recipient of various national science awards and government grants. Most notably in April 2006, a consortium of investors (namely Uniseed, inQbator, Allen & Buckeridge and teQstart Investment Fund) has agreed to provide funding to the company for further development of its coating technology[37]. Armed with sufficient capital funding, the company expects to proceed with further commercialization of the technology and to explore other potential applications of technology.

4.4.1   XeroCoat Technology

While the silica film coatings produced by XeroCoat are similar to those of the Rubner group in terms of function and their underlying principle of porosity-induced superhydrophilicity, the methods of producing these films are very different. The XeroCoat films are deposited via a sol-gel technique performed at room temperature and atmospheric pressure[38]. A silica precursor solution, formed by dissolving a silicic acid tetramethyl ester homopolymer mixture in an alcohol-based solvent, is first applied to the

substrate either by a dipping or spin coating technique. The coated substrate is then placed in an isolated ammonia-rich environment until the solvent is extracted and the film solidifies. The curing process takes place via two intermediary steps as shown by equations (4) and (5) below. In the first step, the silica precursor is hydrolyzed by the water vapor present in the enclosed environment to form $Si(OH)_4$ which subsequently undergoes a condensation process that is catalyzed by the ammonia in the curing environment.

$$Si(OR)_4 + 4H_2O \leftrightarrow Si(OH)_4 + 4ROH \tag{4}$$

$$Si(OH)_4 \leftrightarrow SiO_2 + 2H_2O \tag{5}$$
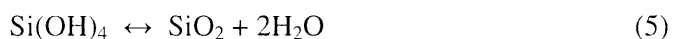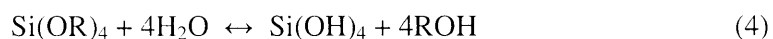
In this technique, the pore density is controlled by the alcohol content in the silica precursor mixture, while the pore sizes are dependent on the type of alcohol used in the solvent. Also, the film thickness can be manipulated either by the composition of the precursor mixture, or by the process parameters of the coating process.

Films deposited by this technique have been shown to possess remarkably low refractive indices in the range of 1.1 to 1.56 and this in turn gives them high optical transparency and anti-reflectivity. Using a simple pencil scratch test, these films were also found to have hardness greater than 7H-type pencil lead (typically hard coatings are regarded as those with hardness greater than 3H). In addition, the films did not desorb when rinsed in water, alcohols and common acids and alkai, and good anti-fogging properties were also demonstrated.

It is obvious that the XeroCoat technology is extremely competitive to the Rubner technology, and that it possesses the distinct advantage of being able to coat plastic materials since the film curing process occurs at room temperature. However there are

still some advantages that the Rubner technology has over XeroCoat, as accorded by the different film assembly principles employed by the two technologies. Firstly, while both deposition techniques utilize the dipping method in order to apply the coating, it is recognized that films with uniformed thicknesses are more easily attained with the Rubner technology. This is due to the fact that the LbL assembly is driven by the electrostatic attraction and so the film uniformity is not as dependent on the process parameters of each dipping step. Furthermore, the thickness of LbL assembled films can be more easily controlled by varying the number of dipping deposition steps, while the thickness of the sol-gel films is influenced by the withdrawal speed of the substrate from the dipping solution which is more difficult to control. Another persistent issue with sol-gel techniques is the shrinkage experienced by deposited films during solvent extraction (due to the evaporation of solvent) which can lead to cracks in the film[39].

In addition, multilayered films can be easily fabricated using the LbL technique by simply using suitable solutions containing the desired chemical species (provided that each successive adsorption solution is oppositely charged from the prior one), and this fact allows films with multiple functions and applications to be made. On the other hand, depositing multilayered films using sol-gel techniques is typically a more tedious process as intermediate curing steps are required after the deposition of each layer to prevent the desorption of the previously deposited layer during subsequent deposition steps[40].

4.5   Comparison of Technologies

As compared to anti-fogging sprays, the Rubner technology offers a permanent anti-fogging solution, as well as an efficient method to coat large surfaces evenly. It is also clear that while the superhydrophilic TiO_2 technology has already been successfully

commercialized and adopted by glass manufacturers, its fundamental drawback of requiring UV exposure for the activation of its superhydrophilicity still limits its widespread application. The Rubner technology clearly presents an all-day anti-fogging solution that is independent of any external catalyst. In addition, applying the technology to automobile windshields enables an active anti-fogging solution that keeps windshields fog-free without the need of operating any mechanical or electrical systems.

Although the XeroCoat technology has the clear advantage of being able to coat plastic surfaces, both the XeroCoat and Rubner technologies have comparable performances for glass surfaces. Moreover, the versatility of the LbL assembly process in fabricating multilayered films gives the Rubner technology greater opportunity to incorporate other chemical properties into their anti-fogging, anti-reflection coatings.

Furthermore, the LbL assembly technique is a cost-effective process that is carried out in ambient environment conditions without the need of expensive vacuum systems. The assembly process can also be easily automated and scaled-up, and it is both environmentally and energy friendly.

By exploiting the technology's strength in being cost-effective for large-scale coating operations, as well as by recognizing its limitation of film application to only high temperature resistant materials, the automotive glass industry was identified as a potential target market for commercialization of the anti-fogging technology. Although the construction glass industry represents a larger market than the automotive glass industry, this choice was made because of the high relevance and benefits of anti-fogging technology to motorists, in terms of increased visibility and road safety. In addition, it should be appreciated that the automobile industry is more consumer-oriented where

product differentiation and innovation are highly regarded by an automobile manufacturer in achieving competitive advantages. Hence, it is believed that the anti-fogging technology will be more well-received by the automotive glass industry than the construction glass industry.

5.   INTELLECTUAL PROPERTY

Intellectual property is broadly defined as intangible assets which result from creation of intellectual activity in areas of industrial, scientific, literary and artistic fields[44,45,46]. Intellectual property is granted many of the same rights as "real" property and can thus be treated as an asset that can be traded, licensed or even given away for free. Patents, copyrights, trademarks, and trade secrets are some key forms of intellectual property[47]. A patent describes an "invention" and creates a legal situation in which the legal rights of making, using or selling the invention is given exclusively to the inventor for a limited period of time (generally 20 years). An "invention" refers to a solution to any specific problem in the field of technology and may relate to either a product or process[44].

Intellectual property is crucial to a business for a number of reasons. Firstly, intellectual property offers a good source of revenue, either through the sale or licensing of the intellectual property. Secondly, intellectual property gives credibility to a technology, which in turn will convince investors of the robustness of the business and also give consumers confidence in the product or service that they are purchasing. Finally, the exclusive rights awarded by intellectual property set up barriers for potential entrants into the market and limit the competition that the business will face.

In this section, various patents associated with the LbL assembly of superhydrophilic PEM films are presented and analyzed in order to ascertain the patentability of this technology which will be an important consideration when exploring various commercialization routes for the technology.

5.1 LbL Assembly of PEM Films

There are currently numerous patents in existence that incorporate the use of the LbL technique for depositing PEM films. However, most of these patents are focused on the applications related to the deposited PEM films, rather than on the LbL assembly technique itself. The most prominent patent on the LbL technique is that which was filed by Gero Decher and Jong-Dal Hong in 1993[48] titled "One- or multi-layered layer elements applied to supports and their production" (US 5,208,111). The primary claim of this patent is a "layered element applied to a support, comprising a modified support having an even surface" and "one or more layers made of organic materials" with each subsequent layer having an opposite charge from the previous one. This patent also proceeds to claim the process of preparing such a layered element in the primary claim. While this patent consists fairly broad claims on the nature of the polyelectrolyte used, it fails to cover the possibility of creating a composite PEM film with layers of inorganic materials (such as SiO_2 which is used in the Rubner technology). In addition, neither the use of solution pH to control layer thickness and porosity, nor any specific applications of such "layered elements" were mentioned in this patent. Finally, the fact that many other patents related to the LbL assembly technique have since been published suggests that it is still possible to file patents in this research area without infringing this particular patent.

5.2   Superhydrophilic Anti-fogging Films

As was mentioned earlier, the LbL assembly technique has been used to fabricate PEM films with various applications and Decher's patent has been cited in 38 other patents to date. None of these patents specifically refer to the fabrication of superhydrophilic surfaces for anti-fogging applications although the formation of hydrophilic surfaces was mentioned in a number of these patents. Of these, three are owned by Swiss pharmaceutical company Novartis AG (Basel, CH)[49,50,51] while another three are owned by Massachusetts-based company Advanced Surface Technology, Inc (AST)[52,53,54]. The three patents owned by Novartis explicitly mention the use of hydrophilic surfaces to increase the degree of lubrication of biomedical devices (specifically contact lenses) while the AST-owned patents specify the use of the hydrophilic coatings for articles in an aqueous environment. Moreover in all of the above patents, the hydrophilicity of the surface was attributed to the presence of hydrophilic functional groups present on the top-most polymer layer, and not the nanoporosity of the thin film structure.

Another patent that is related to the fabrication of hydrophilic coatings is U.S Patent 5,688,855 titled "Thin film hydrophilic coating"[55]. This patent was granted in 1997 and is owned by S.K.Y. Polymers, Inc (Rocky Hill, NJ). The primary claim of this patent is "a hydrophilic coating composition for hydrophobic substrates" made up of a mixture of a "hydrogel-forming polymeric component" and a "polymeric water-soluble component" in a "common solvent". The patent is rather detailed in listing various possible polymeric components but again the possible use of inorganic materials is not mentioned. In addition, the hydrophilic coating is deposited using a sol-gel technique and

not the LbL technique. Finally, the hydrophilic nature of the coating is credited to the presence of "long, hydrophilic terminal blocks" present in the hydrogel-forming component and no mention is made to porosity of the film.

Patent searches were also conducted to identify intellectual property in the research areas of anti-fogging technology and superhydrophilicity-induced anti-fogging. It was discovered that most anti-fogging technology patents were related to anti-fogging sprays and similar chemical applications, while those filed for superhydrophilicity-induced anti-fogging technologies were typically related to TiO_2 photocatalytic films. The proposed mechanism of superhydrophilicity in TiO_2 films was presented earlier, and it is evident that the basis for the superhydrophilic nature of films fabricated by the Rubner group is very different from that in TiO_2 technology. Hence, it is unlikely that these TiO_2-related patents will affect the patentability of the Rubner technology.

5.3   XeroCoat Patent Application

A provisional patent application (PCT/AU2004/001622) entitled "Silica films and method of production thereof" was filed in Australia by Drs. Michael Harvey and Paul Meredith on November 22, 2004[38]. The patent claims "a method of forming a silica film coated on a substrate" using a sol-gel technique of depositing a "silica precursor formulation" and then curing it in "an ammoniacal environment". The patent goes on to highlight various characteristics of the silica films fabricated and various possible applications of the technology, including anti-fogging, are mentioned. This patent also acknowledges that the superhydrophilicity of the films is a result of their nanoporous structure and ways of manipulating the degree of porosity in the film are described.

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As brought up in an earlier section, even though these silica films are similar to those fabricated by the Rubner group in terms of structure and film properties, the means by which these films are deposited are very different. In addition, the porosity of the deposited silica film is controlled by the alcohol content and type in both the solvent and curing solutions, which is unlike the Rubner technology where different deposition parameters, such as nanoparticle size and concentration, are involved. Hence it is concluded that as a whole, this patent application does not appear to have much effect on preventing the Rubner technology from being patented.

6.   FLAT GLASS MANUFACTURING

The float glass process is the manufacturing process by which almost 90% of the world's flat glass is produced[41]. This section gives an overview of this glass manufacturing process and presents some of the common glass coating techniques used in industrial processes. This background information will provide an understanding of how the Rubner anti-fogging technology might be implemented in glass manufacturing and also identify some key aspects in which the technology might need to be modified to adapt to the automotive glass industry.

6.1   Float Glass Process[41,42,43]

This process was developed by Sir Alastair Pilkington in 1959 and has since been adopted as the industry standard for flat glass manufacturing. In the first step of this process, a mixture of raw materials known as the batch is melted in a furnace at about $1600^\circ C$. While the composition of the batch mixture can be modified to impart particular properties to the glass, it is typically made up of sand (silica), soda ash (sodium oxide),

limestone (calcium oxide) and dolomite (magnesium oxide). Sand is the main component of the batch, while soda ash is added to lower the melting temperature of the mixture, and lime and dolomite act to improve the physical properties of the glass. Sometimes, broken glass known as cullet is also recycled into the batch. After undergoing various refining and homogenizing processes, the molten glass mixture leaves the furnace at a temperature of about 1100°C and is poured onto a molten tin bath, known as the float bath.

Because the density of molten glass is less than that of molten tin, the glass mixture flows over the surface of the tin melt and conforms to give smooth flat surfaces. The float bath is typically about 200 feet long and it is maintained in a N_2 and H_2 rich environment to prevent the tin from oxidizing. Top rollers are also present to move the molten glass over the tin surface, and the glass thickness can be controlled by the rotating speed of these rollers. The molten glass exits the float bath at about 600°C in the form of a glass ribbon that is sufficiently hardened such that the glass surface is resistant to markings and distortions.

This glass ribbon is then moved by conveyor rollers through a chamber known as a lehr, where it is gradually cooled in a well-controlled manner. The cooled ribbon leaving the lehr is just above room temperature and it is then sent for inspection and cut into desired sizes. The cut glass is powder-coated to prevent scratches to its surfaces during transport, and is finally sorted, packed and either shipped to customers or sent for further downstream fabrication.

A typical float plant runs continuously over its lifetime of 11-15 years, with production rates of between 300-600 tons per day (approximately 37,500 to 75,000 m^2, assuming an average of 125m^2/ton).

6.2 Automotive Glass Processing[43]

In order to obtain finished automotive glass products for use in automobile assembly lines, flat glass slabs from the float glass process described above are required to undergo additional downstream processing steps.

First, the glass is cut into the exact shape desired and the edges of the glass are smoothened. This is followed by drilling of any holes or notches into the glass that might be required for the attachment of hinges or frames. The piece of glass is then cleaned before various printing steps, such as the embossing of trademarks or rear windshield defogging wires, are performed in a clean-room environment.

Next, the glass undergoes either one of these two common glass shaping and strengthening methods – tempering or laminating. Tempered glass is more often used for the rear and side automobile windows and is formed by subjecting the glass to a series of controlled heating cycles where high temperatures above 640°C are reached. As the glass is heated to high temperatures, it begins to soften and can then be shaped and curved accordingly. Laminated glass consists of a polyvinylbutyral (PVB) polymer layer that is placed between two thin glass sheets. The polymer layer acts to hold the windshield in place in the event of damage, and laminated glass is typically used for front automobile windshields. After the two thin glass pieces are shaped at temperatures of about 620°C, the actual lamination process occurs by placing the PVB layer between the two glass

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pieces and applying pressure of about 10 to 15 kg/cm^2 at 140°C in order to fuse the layers together.

In addition to the steps outlined above, the glazed automotive glass pieces may undergo more post-processing steps to add further value to the finished glass products. These post-processing steps include encapsulation to provide enhanced protection and bonding of the glazing to the glass, and the attachment of various hardware components (e.g. hinges and clips) to create integrated automotive glass systems.

6.3   Glass Coating Techniques

Coatings are most commonly applied to float glass via either the chemical vapor deposition (CVD) or sputtering techniques. Both of these techniques originate from semiconductor processing and are employed for on-line deposition of coatings during the float bath stage of the glass manufacturing process. The success of these techniques has been largely driven by their abilities to be well-integrated into the float glass process and to cope with the high float-line speeds (typically about 1ft/s). Currently, the on-line CVD technique is used by Pilkington in the fabrication of both their anti-reflective and self-cleaning glass products[43].

In addition, various off-line coating techniques can be used for the deposition of specialty coatings on glass[40]. These coatings are often based on sol-gel technology and are applied using spin coating, dip coating or spraying methods. Of these three methods, dip coating and spraying have proven to be more effective for large applications and are hence favored for commercial applications. While the key advantage of the dip coating technique is that the thickness of the coating can be well controlled by manipulating the sol viscosity and the withdrawal speed, it is nevertheless a batch process associated with

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relatively long process times. On the other hand, the spraying method offers high production rates and can be adapted for on-line processing, although the quality of the deposited coating may be marginally compromised. Hence, it is evident that the choice of deposition technique will be largely influenced by the type of coating, its dimensions, as well as the processing rate required.

6.4   Adapting the Rubner Technology to the Automotive Glass Industry

From the overview of the glass manufacturing process in the above sections, it is recognized that the Rubner anti-fogging coatings will have to be applied as a post-processing step, since these nanoporous films have to be present as the topmost layer on the glass surface in order for them to execute their superhydrophilic capabilities. Even as this fact comes as a relief (since the technology does not have to meet the challenges set forth by the fast float-line speeds), it is evident that the present dipping technique employed for the LbL assembly is still much too slow to cope with overall glass production and coating demands. As it has been shown that a minimum of 14 PAH/SiO$_2$ bilayers is required for superhydrophilic films to be achieved, this would translate to a total coating process time of approximately 13 hours (including film curing) by employing the current fabrication scheme outline in an earlier section[26].

In order to shorten the coating time of the Rubner technology, it might first be necessary to identify aspects of the deposition process that may not yet be optimized for time. For example, the duration of dipping steps might be studied to ascertain if shorter dipping times can be employed as well as what compromises may be made to film properties fabricated with shorter dipping time (since it is probable that for commercial applications, the film properties may not need to be as exceptional as those demonstrated

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for research purposes). Also, other polyelectrolyte-silica systems can be evaluated to identify if another nanocomposite combination can be used to produce superhydrophilic films with fewer bilayers. In addition, it is likely that the technology has to be modified to adopt the spraying method (or some other continuous flow method) for the coating deposition, as this will significantly improve the process rate. Another possibility that can be explored is in depositing the coating via a modified liquid phase epitaxy (LPE) system where the glass substrate in moved through different zones containing the various adsorption solutions. This method also allows for a well-controlled flow process, and it is currently widely used in the semiconductor industry for the fabrication of light-emitting diodes.

Another important issue that has to be considered is that of contamination of the film during the automobile assembly process, and how contamination may affect the anti-fogging properties of the coating. As the superhydrophilicity of the film is critical upon its nanoporosity, contaminants such as oil and dirt may clog up the pores and inhibit the water-penetration and wetting mechanisms, and the film may lose its anti-fogging characteristics. This aspect of the technology must certainly be studied in greater detail, but it is probable that suitable cleaning methods and de-greasing solutions will have to be developed. It may also be interesting to take advantage of the versatility of the LbL assembly process in fabricating complex multilayered films, and to incorporate layers comprising chemical species that are capable of decomposing oils into smaller molecules (a property similar to that of photocatalytic TiO_2) for easy removal from the film's nanoporous structure. Another possible solution is the incorporation of oleophobic groups

to the film structure. The presence of these functional groups will act to repel oil from the film to prevent contamination and clogging of the nanopores.

While only two key concerns of applying the Rubner technology to the automotive glass industry are highlighted in the previous discussions, it is important to realize that these issues, as well as others that may have been overlooked, will need to be adequately addressed in order to establish the compatibility of this technology with the targeted industry.

7. MARKET ANALYSIS

As discussed in an early section, the automotive glass industry was selected as a target market for the commercialization of the superhydrophilic SiO_2 films. This choice was made by both considering the importance of anti-fogging technologies in enhancing the visibility and road safety of motorists, as well as by exploiting the advantages of the LbL technique for cost-efficient large-scale applications.

However, it is also necessary to realize that commercialization decisions must be made with careful consideration of the market forces that affect the target industry and that commercial success is often driven by the ability to maneuver these forces. Hence, an overview and some recent trends in various relevant markets (namely, the flat-glass, automotive glass and automotive industries) will be presented in the following section. In addition, a rough estimate of the potential market size of the anti-fogging technology for automotive glass applications will also be offered.

7.1   Flat Glass Industry

In 2004, the global flat glass market was approximately 38 million tons, of which 4 million tons was used in automotive glass applications[56]. Using current price levels, this production translates to EUR 15 billion and 44 billion in primary and secondary processing respectively. The overall industry has also experienced a healthy growth rate that averaged 3.9% per annum for the past 20 years, though this rate varies across products and market geographies. In this respect, higher growth rates have been observed for value-added glass over basic glass products, and emerging markets, particularly China, have experienced faster growth as well. The activity and growth of this industry is further illustrated by its worldwide industry capacity utilization rate of 90% in 2004.

The global flat glass industry is also a rather consolidated one, both in terms of key players and global demand distribution. It is dominated by four key players – Asahi Glass Co. of Japan, Pilkington of the United Kingdom, Guardian Industries of the United States and Saint-Gobain of France, that together account for 61% of global flat glass production [57]. This trend of consolidation has been influenced by the increasing customer demands that favor glass manufacturers who are able to provide comprehensive services with greater economies of scale. In addition, the impact of emerging markets has also biased large glass manufacturers with a global network of plants. While the markets of North America, Western Europe and China currently total almost 75% of global flat glass demand (Figure 4), it is important to note that in China's glass demand has risen dramatically from one-fifth of total global demand in the early 1990's to the current one-third.
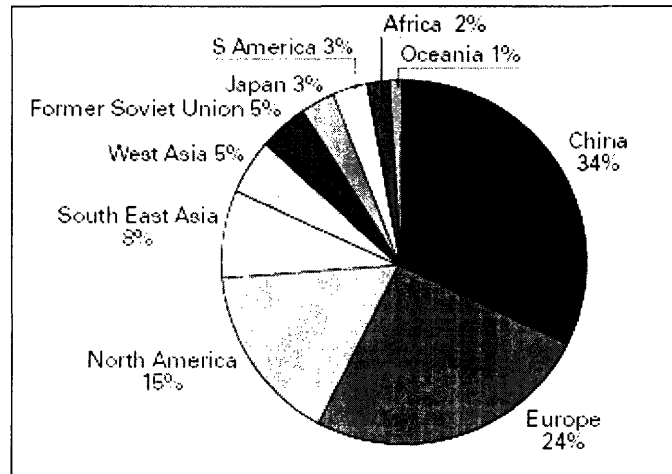
Figure 4: Geographical distribution of global demand for flat glass in 2004[56].

In terms of cost, the flat glass industry is a highly capital intensive one. Typical float glass plants cost EUR 100–150 million to build, and are expected to run continuously 365 days each year. It has also been estimated that a minimum plant capacity utilization of 70% is required before the operations can be profitable[56]. Hence, float glass manufacturers tend to have designated production lines for each of its products so as to minimize any process changeover time that might result from recalibration and optimization of a new process.

Transportation costs are significant in the flat glass industry and are estimated to take up about 10% of total cost. The high cost of transporting glass is due to the fragile nature of the glass sheets, which necessitates specialized labor and equipment, not only for the physical transporting but for the loading, unloading and storage of glass as well. Typically, the land transportation distance of flat glass is limited to around 200 km with 600 km being estimated as the economic limit[56]. Therefore, it is not uncommon to find glass manufacturing plants being located close to their immediate customers in order to minimize these costs.

7.2   Automotive Glass Industry

The automotive glass industry used about 4 million tons of flat glass in 2004. Like the flat glass industry, the automotive glass industry is also a consolidated one where three of the key flat glass manufacturers, namely Asahi, Pilkington and Saint-Gobain, account for about 76% of global automotive glazing requirements. Two routes to market exist within the automotive glass industry – Original Equipment (OE) products that are supplied directly to automobile manufacturers and Automotive Glass Replacement (AGR) products which are supplied to the after-sales market. By volume, the OE market demand outweighs that of AGR by five times (83% for OE vs. 17% for AGR). Hence, it is not surprising that the market demand for automotive glass is directly dependent on the performance of the automotive industry (*which will be presented in the next section*) and it is estimated to have been growing at an average rate of 2.7% per annum since 1991[56] (Figure 5).
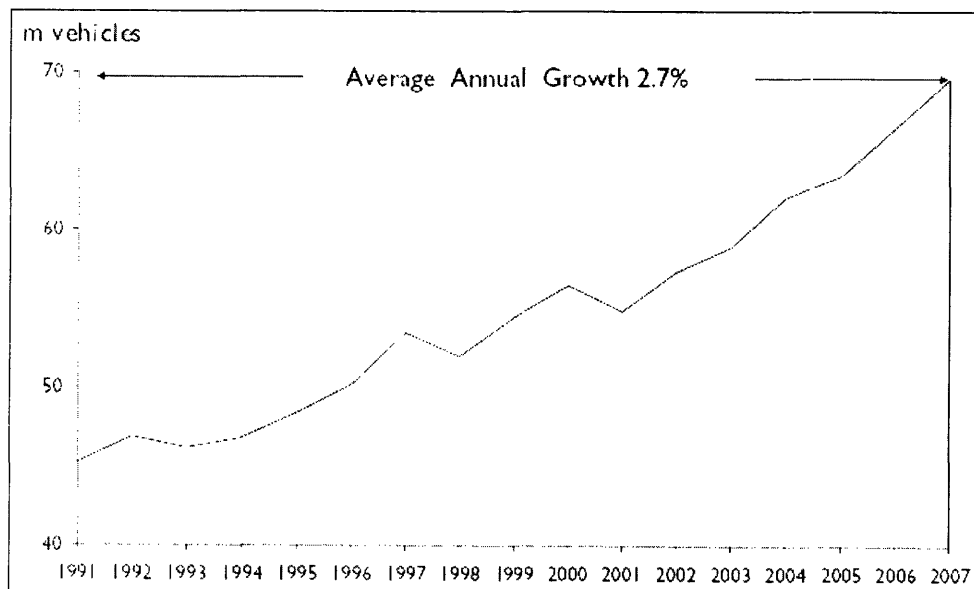

Figure 5: Global Automobile Production from 1991 to 2007 (*data after 2004 is projected*) [56]

In addition to the direct impact of global automotive production, the design trends of current automobiles have also influenced automotive glass demand. The Pilkington Group estimates that 20% more glass is being used in European cars now as compared to 20 years ago, while the average glazed windshield area has increased by 60%[56]. The popularity of new vehicle types such as minivans and sports utility vehicles (SUVs) have also contributed extensively to the increase in automotive glass demand due to the larger glass requirements of these larger vehicular builds.

Long-term growth in global demand for AGR products is estimated to be about 2.6% per annum and is determined by the automotive glass replacement rate that is in turn affected by various factors. An analysis conducted by business consultancy Frost & Sullivan of New York has revealed that glass replacement rates are noticeably higher in regions that experience harsh weather conditions (such as Colorado and Illinois) than those with milder weather (such as California). The study also showed that factors such as number of miles driven, road conditions, climate, income levels, vehicular crime rates, insurance policies and national legislation can also affect the glass replacement rates[57].

To illustrate the possible impact of national legislation on automotive glass demand, a recent development in the U.S is presented. In the U.S, the Federal Motor Vehicle Safety Standard (FMVSS) 103 specifies requirements for windshield defrosting and defogging systems (i.e. front air-vent system), and mandates that each vehicle must have a front windshield defrosting and defogging system[58] in order to assure good visibility and safety. While rear window defrosting units (comprised of heated electrical wires that are embedded in the rear windshield) are currently non-mandatory, a study has recently been commissioned by the National Highway Traffic Safety Administration

(NHTSA) to investigate the benefits that may accompany the implementation of rear window defogging systems in all vehicles[59]. If the study leads to further regulation to make the installation of rear window defrosting systems mandatory, this will no doubt increase the demand for AGR products and also signify greater market opportunities for anti-fogging technology.

7.3   Automotive Industry

The global automotive production in 2004 was 62 million, of which production in Western Europe, North America and Japan totaled 42.3 million or nearly 70%. In addition, the 20-year average growth rate of this industry is about 2.7% per annum. As discussed earlier, the automotive glass industry is directly impacted by the performance of the automotive industry. As will be apparent shortly, recent trends and developments in the automotive industry, particularly in its supply chain management, have affected the business climate of the automotive glass industry tremendously.

One major trend in the automotive industry has been that the mergers and acquisitions of automobile manufacturers. There were about 100 independent automobile manufacturers in operation worldwide back in the early 1960's[60]. Today, these M&A activities have aggregated 6 major automobile manufacturing groups (DaimlerChrysler, GM, Ford, Renault-Nissan, Toyota and VW) with almost 80% of the global market. This trend has left the automotive glass industry with a smaller customer base which in turn means more competition between automotive glass manufacturers. In addition, these automobile giants are able to drive glass prices down by seeking economies of scale when negotiating contracts.

Developments in the automotive supply chain have also greatly affected in automotive glass industry. The automotive supply chain has been well-known for its "tiered" system, where "Tier 1" suppliers provide finished components which are used directly in the automobile assembly lines, "Tier 2" suppliers service the "Tier 1"s and "Tier 3" suppliers are those who sold raw materials to either of the above tiers. Recently, "tier one-half" suppliers have emerged in response to automotive manufacturers demanding more involvement from their suppliers. In this tier, suppliers are expected to deliver more complete and integrated modules to the automotive manufacturer. For example, instead of delivering just a rear glass windshield to the automotive manufacturers, automotive glass suppliers are now expected to deliver an integrated SUV tailgate complete with hinges, struts, wiper and latching mechanisms. In addition, automotive manufacturers are also working more closely with suppliers in product design and innovation, and hence large-scale suppliers with established in-house research and development capabilities are favored.

Another trend in the automotive supply chain is the adoption of a just-in-time (JIT) assembly process where supply chains are kept short and inventory of parts is kept at a minimum. The JIT process stipulates a steadily delivery of components (in smaller batches, but at higher frequency) to the assembly line and this has increased the transportation and logistics cost of suppliers appreciably. Automotive glass suppliers are especially affected since transportation costs in the industry are already very significant.

Finally, the effects of globalization and the rising demand of emerging markets have forced to the automotive industry (and in fact, all manufacturing-based industries) to expand its operations internationally and to acquire a global network. This trend is

evident by the fact that while 83% of the global automotive demand was met by North American, Western European and Japanese automobile production back in 1991, this figure has since decreased to only 68% in 2004. In particular China, with automobile production of 4.6 million in 2004, has been experiencing an average growth rate of 15.1% per annum since 1991(as compared to the global growth rate of 2.7%)! Correspondingly, automobile manufacturers are looking for suppliers with strong global presence to support their globalization efforts in pursuing new markets. This requirement by their customers has been critical in driving the strategic alliance efforts of the automotive glass industry, as this allows glass manufacturers to share the financial risks involved with entering foreign markets.

From the preceding discussions, it is clear that these recent developments in the automotive industry have placed great pressure on the automotive glass industry as a whole. In addition, these trends bias large international glass manufacturers with strong research and financial capabilities, and huge barriers for potential entrants into the automotive glass industry are also created.

7.4   Estimating Market Size for Anti-fogging Automotive Glass

In order to further justify the attractiveness of marketing the anti-fogging technology to the automotive glass sector, an estimation of the market size was performed. The first step of this analysis was to determine the value of anti-fogging technology to the consumer. This was estimated using the present cost of installing a defrosting system to the rear windshield of an automobile, which in turn was assumed to be the price difference between front and rear replacement windshields. By surveying the costs of front and rear windshields for some 30 different car models, the cost of a

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defrosting system was established to be about US$98 per windshield. Multiplying this figure with the world annual production of 62 million[56] automobiles gives an impressive market size of US$6.08 billion.

It is also important to note that this figure is an underestimation of the value of the anti-fogging automotive glass, as it only accounts for one windshield per automobile (in practice, both front and rear windshields, as well as door windows and side mirrors, are also likely candidates for being replaced by anti-fogging glass). In addition, the implicit cost savings of switching away from the electric defrosting systems (such as lower power consumption and eliminating the need for repair of broken heating filaments) have also been excluded from this analysis. While this method of estimating the size of the anti-fogging automotive glass market is not entirely rigorous, it does however provide strong justifications for the attractive market opportunities this niche market presents.

8.   BUSINESS MODELS

Figure 6 displays a simplified schematic of a proposed process flow for anti-fogging automotive glass from flat-glass manufacturer to automobile manufacturer (OE products) or an after-market retailer (AGR products). Flat-glass manufacturers can either provide anti-fogging glass directly to the automobile manufacturers or retailers, or they can outsource the anti-fogging coating operations to an external coating company. In either case, it is likely that an equipment vendor, who will provide the tools required to perform the coating functions, will also be involved in the process flow.
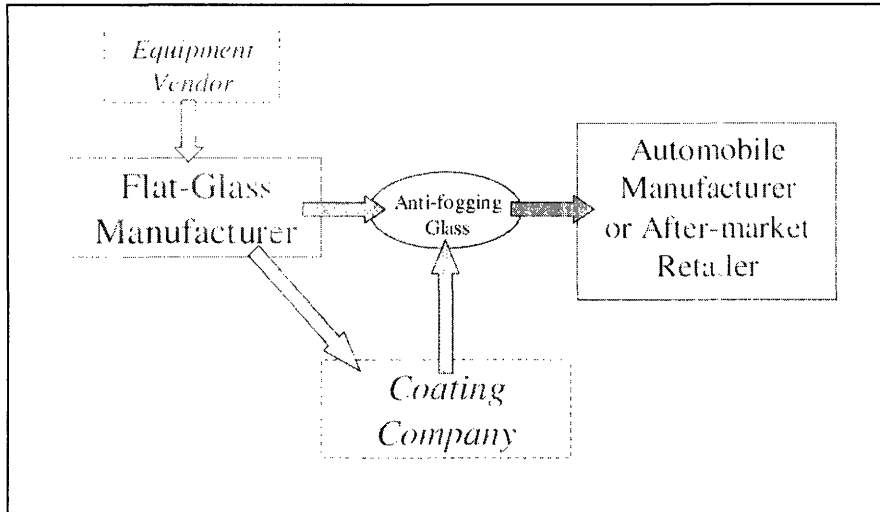
Figure 6: Schematic diagram showing a simplified process flow for anti-fogging automotive glass.

Based on the simplified schematic shown in Figure 6, three possible business models for commercializing the anti-fogging technology are proposed, discussed and evaluated in the following sections.

8.1   Service Business Model

In this business model, the technologist keeps ownership of the original intellectual property and sets up a business that provides anti-fogging coating services to the flat-glass manufacturers. With this business model, the technologist retains absolute control of his technology and sets his own pricing for the product. While this model can present the highest possible profit margin for the technologist (since profit and market share do not need to be shared), there are also high risks and barriers associated with such a model.

Firstly as was discussed before, the flat glass industry is highly capital intensive and the estimated cost of a typical automotive glazing plant is between EUR 50 to 70 million[56]. When considering the increasing demands of the automotive manufacturers

for suppliers to undertake product development activities, it can be expected that even more capital will be required to establish capable in-house research facilities.

The considerable transportation costs, as well as the implementation of the JIT assembly process, will necessitate that the coating plant be in close proximity to both the glass and the automobile manufacturers. This means that the market size serviced by each coating plant will be limited geographically to cover only a few assembly plants (a typical automobile assembly plant has an annual capacity of 50,000 to 300,000) and the business of the coating plant will be contracted to only a small number of glass and automobile manufacturers located in its proximity. This creates an overdependence of the business on its customers and may lead to a disadvantageous position when negotiating the pricing of the coating service.

The consolidation trends of both automotive glass and automobile industries also present critical barriers to the execution of this business model. The most obvious impact would be that consolidation would bring about a smaller customer base to the coating business, and this would affect the pricing of coating services. Moreover, with automobile manufacturers seeking suppliers with greater economies of scale and strong global networks, it will be extremely challenging for a new coating business to enter into the market.

Also as noted earlier, 76% of the global automotive glazing requirements is currently met by 3 key players. Since these large glass manufacturers are already performing most of their glazing and coating processes in-house, it might be difficult to convince them to outsource solely the anti-fogging coating operations to another company. In addition, with these glass manufacturers taking on the responsibilities of

"tier one-half" suppliers, the outsourcing operations would entail unnecessary transportation and logistics costs to be incurred, since the anti-fog glass would still need to be returned to the glass manufacturer after coating for further assembly into more integrated components (i.e. an SUV tailgate) before being delivered to the automotive assembly plants. Furthermore, this arrangement is especially difficult to manage logistically when taking into account the demands of the lean supply chain of the automotive industry as well as the implementation of the JIT process.

A final disadvantage of this business model is that the business' success will be directly dependent on market demand and response to the new anti-fogging technology. If this feature of anti-fogging glass is not well-received by automobile manufacturers and consumers, or if interest in the anti-fogging glass is not sustained, the anti-fogging coating service will become redundant to the automotive glass industry and the company will lose its business. One way to promote the interest and demand of a novel product is often through effective wide-spread marketing efforts. However, assuming limited business funds of a start-up company, it is unlikely that large sums of capital will be available for extensive product marketing efforts.

8.2   Equipment Vending Model

In this next proposed business model, the technologist packages the anti-fogging technology with the necessary processing equipment and software and in essence, assumes the role of an equipment vendor. Profits are realized in this model through the sale of the equipment, as well as through service contracts for the maintenance of the equipment. This business model has the advantages of allowing the technologist to maintain autonomy and ownership over the intellectual property, as well as control over

the financial aspects (e.g. determination of price, profit margin, etc.) of the business. Also, high initial cash flow is accorded to the business through the sale of equipment.

However, this business model requires the technologist to step beyond the realms of the business' core competency (i.e. the anti-fogging coating technology) and to acquire new skills in the areas of mechanical/equipment design and operation, as well as software development. Also, considering that automotive glass manufacturing plants are globally located, this business model still necessitates the presence of an international sales and maintenance team which might be difficult to manage both financially and administratively. Furthermore, by shifting the target entrant market to that of glass coating equipment, this business model no longer capitalizes on automotive industry's large consumer base and the technologist is unable to reap the benefits that are associated with the high sales volume presented by the automotive glass sector.

8.3   Licensing/IP Model

With this business model, the technologist licenses the anti-fogging technology to two possible target groups of customers – the major flat glass manufacturers with the capabilities to perform in-house coating operations; and the equipment vendors who can utilize the technology to provide glass manufacturers with the necessary anti-fog coating apparatus. Controlled rights to the intellectual property are given to these licensees for a limited period as determined by the terms of the license agreement.

Revenue is attained through royalty fees that the licensor collects based on the sales or revenue of the product that is enabled by the intellectual property. Royalty rates can be determined in a variety of ways based on the nature of the intellectual property and the industry it is related to. One common method employed to calculate royalty rates

is the "25% Rule"[46]. In this approach the expected profits for the product where the intellectual property will be applied to, accrued over the duration of the licensing period, is first estimated. This figure is then divided by expected net sales to give the profit rate. The royalty rate is then computed as 25% of the profit rate and is applied to the net sales of the product over the licensing period. Some other commonly used methods by which royalty rates are calculated include basing on industry norms or benchmarking, and the "5% of Sales Rule". It is clear that royalty rates can vary significantly when different methods are employed and it is therefore important to adopt a method that is carefully suited to the technology and industry so as to value the intellectual property most accurately.

Principal advantages of this model are that capital investment requirements are relatively low and that the technologist gets to retain some rights and control over his intellectual property. However, this latter advantage also implies that the licensing agreement must be very thoughtfully drafted so that the licensee does not acquire more rights than the licensor intends to grant. Understandably, one major risk that the licensor faces is that the licensee can potentially take advantage of the knowledge gained through the license to improve upon the intellectual property and end up as a competitor. Hence, it is necessary to realize that the licensor has to take constant measures to improve upon the original intellectual property and to actively expand its intellectual portfolio. The licensing model is most often exploited by universities and research organizations with extensive research capabilities but limited capital funds. Essentially, this model marries the licensee's manufacturing expertise and financial resources with the licensor's

technical expertise, and the success of this coupling has been demonstrated in numerous case studies.

The licensing model has been adopted by Japanese company, TOTO Ltd. for commercialization of its superhydrophilic, photo-catalytic TiO_2 coatings known as Hydrotect™[61]. TOTO Frontier Research, a subsidiary of the company, was set up to be responsible for the continual research of this product, as well as its intellectual property and commercialization. In the TOTO business model, the licensee is charged a royalty fee based either on the sales volume or the revenue of the product, and is then given access to 70 patents regarding this particular technology, subject to exclusions and limitations set forth by the licensing agreement.

Since its institution, TOTO Ltd. has filed more than 1000 patents applications and 270 patents have already been granted. Currently, the company has entered into license agreements with almost 50 companies worldwide. In particular, the superhydrophilic TiO_2 technology has been licensed to major glass manufacturers, PPG Industries Inc., Asahi Glass Co. Ltd and Nippon Sheet Glass Co. Ltd., for use in various self-cleaning glass products.

From the example of TOTO Ltd., it is evident that this business model is well-suited to the flat-glass industry, particularly due to large market size and the dominance of the four key global industry leaders. By licensing the technology to the major glass manufacturers, the technologist can leverage on the huge sales volumes of these companies, which will translate to a healthy cash flow in the form of royalties. In addition, the market scope can be broadened to include other glass products (e.g. construction glass) if the glass manufacturers decide to extend the use of the anti-fogging

technology to their other products. Also, the market reach can be further broaden to capture foreign and emerging markets that are serviced by these large glass manufacturers. On the other hand, servicing a global market would not have been possible with the other two business models without the use of huge amounts of capital investment.

While it is apparent from the preceding discussions that the Licensing Model is best suited for commercialization of the Rubner technology, it is also important to realize that ownership and maintenance of a valuable IP portfolio is vital to the success of this model. Hence, the business should focus on the research and development of its technologies, as well as the expansion of its IP portfolio. Basically, it can be viewed that the technologist is now providing a service to the licensee in the form of R&D, and its competitive advantage and partnership with the licensee can only be sustained through continual improvement of its technology and intellectual property. As identified in the earlier sections, adapting the Rubner technology to the automotive industry remains a priority and challenge, and the various issues to be tackled (particularly in decreasing the process time required for fabricating the superhydrophilic films and in developing film cleaning and de-greasing solutions) present good opportunities for the expansion of the technology's IP portfolio. In addition, it will be useful to perform further prior art searches and analyses on IP related to glass coating and cleaning techniques in order to define the scope of patentable areas surrounding the technology. This will also aid to identify the focus areas for future developmental efforts of the technology.

9. CONCLUSIONS

The work of the Rubner group in successfully fabricating superhydrophilic nanoporous films with remarkable anti-fogging properties has been clearly demonstrated. A comparison of this technology with current anti-fogging technologies has revealed clear advantages, and the XeroCoat technology was identified as a keen competitor to the Rubner technology especially since their technology allows plastics to be coated as well. However, it was noted that both technologies are comparable in terms of glass coating applications, and that the versatility of the LbL assembly process employed by the Rubner technology gives it more potential for product innovation and development. Furthermore, the ease of scalability and cost-efficient large-scale production of the fabrication process were noted and these findings clearly support the strong commercial viability of this product.

The automotive glass market was identified as the initial target market for commercialization of this technology, and an overview of the glass manufacturing process highlighted the fact that various aspects of the technology still need to be developed before it can prove suitable for automotive glass applications.

The analyses of the relevant industries revealed the attractiveness of the automotive glass industry as well as some challenges that would affect the decision-making processes involved in commercializing the technology. Finally, three business models – Service, Equipment Vending and Licensing Models, were proposed and evaluated. Assuming that this technology can be successfully patented, and by considering recent trends and developments observed in the automotive glass industry, the licensing model appeared to be the most suitable and promising business model for commercializing the Rubner anti-fogging technology.

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