

## 1. Introduction

Large area/high volume coatings on glass have been developed for a variety of products like plate glass for architectural and automotive glazing, hot and cold end coatings for container glass or for other articles from glass, like lamps. Depending on the effect to be obtained and the material to be used for this, either gas phase, vacuum or wet coating techniques have been chosen or have been developed, but for most of these coatings, the wet coating technique is not the preferred method at present.

Whereas in the case of vacuum coating the whole equipment including the technology (which is rather costly) can be bought from the supplier, in the wet coating area no standard equipment is available for large scale applications, and the technological know-how has to be generated at the user's company. A similar situation is observed for the coating material, since coatings based on commercially available organic polymer materials are of interest only in a few cases. Wet coating materials more or less are not standardized, not easily available and therefore have also to be developed by the users. Both factors, the non-availability of standard equipment and the non-availability of appropriate coating materials, seem to be the main draw back, and therefore wet coating techniques have not yet gained the same significance for large area/high volume applications as e.g. magnetron sputtering. This is in opposition to the large potential connected to chemical material synthesis, which allows to generate highly functional coating materials with interesting properties for glass surfaces and, in addition to this, the equipment costs may be only a fraction of the cost of other techniques. To exploit the potential of others than dip coating technologies for large scale applications have to be developed too.

## 2. New opportunities with wet coatings on glass

As already mentioned in the introduction, standardized wet coating materials with well-described properties are not available on the market. This is, on the one hand, a serious draw back. Wet coating materials can be employed as transparent and non transparent materials. Non transparent materials mainly may be used for decoration purposes for example using printing techniques. Transparent materials in form of organic paints never gained significance in practical applications. This however does not represent the potential of wet coating materials in any way. The application potential results from the opportunity of synthesizing unique material properties and to combine it with cost-effective coating techniques. Interesting material properties are, as pointed out later, easy-to-clean properties antifogging properties, strength increasing properties on thin glasses, micro-patternability of coatings, photochromic or electrochromic properties, but also properties presently fabricated by other techniques, as far as they can be prepared cheaper. There are antireflective (AR) coatings, IR reflecting coatings, coloured coatings or conductive coatings.

This short description about the materials situation shows that there is an interesting potential for these coatings. One advantage of wet coating techniques is, that molecular structures developed by chemical synthesis can be used to develop new properties either when preserving these structures on the surface, or to develop new desired molecular structures by heat-treatment and subsequent chemical reaction on the surface. So, one can distinguish between two basic routes: the first route comprises a high temperature treatment after the coating step in order to get „glass-like" or „ceramic-like" materials on the glass surface and the second type of technique would include a low-temperature UV- or infrared type of curing, where the functional chemical structures developed in the liquid coating material, more or less are maintained during this post-treatment.

## 3. Coating technologies

As general prerequisites for obtaining wet chemical coatings with high optical qualities on glass, it can be stated that the coating step has to be carried out under cleanroom conditions, the coating liquid has to be filtered and the glass has to be cleaned properly. The special features of the different wet coating techniques will be summarized in the next chapters.

### **3.1. Dip coating techniques**

Dip coating techniques can be described as a process where the substrate to be coated is immersed in a liquid and then withdrawn with a well-defined withdrawal speed under controlled temperature and atmospheric conditions. The coating thickness is mainly defined by the withdrawal speed, by the solid content and the

viscosity of the liquid. If the withdrawal speed is chosen such that the shear rates keep the system in the Newtonian regime, the coating thickness can be calculated by the Landau-Levich equation [1] (eq 1).

$$h = 0.94 \cdot \frac{(\eta \cdot v)^{2/3}}{\gamma_{LV}^{1/6} (\rho \cdot g)^{1/2}} \quad (1),$$

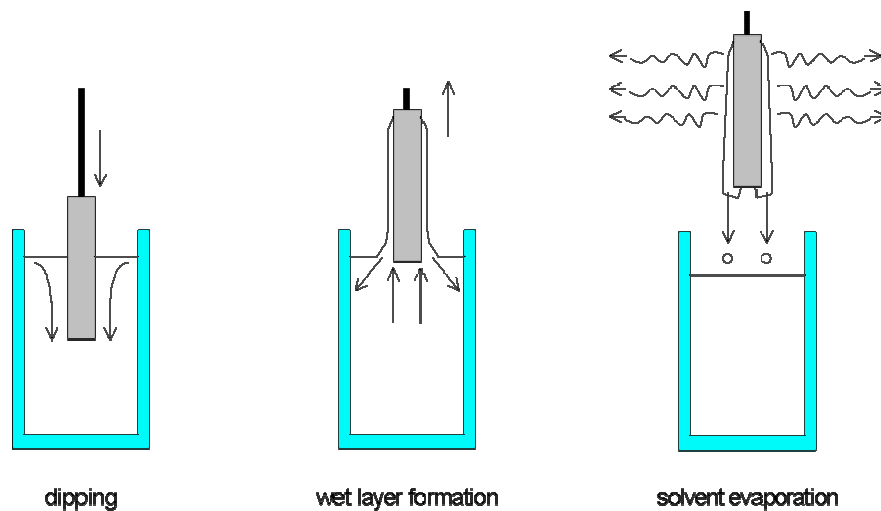
using:

$h$  = coating thickness  $\eta$  = viscosity

$\gamma_{LV}$  = liquid-vapour surface tension  $\rho$  = density

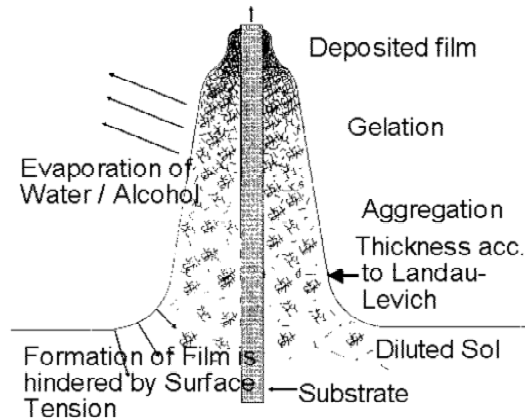
$g$  = gravity

As shown by James and Strawbridge [2] for an acid catalyzed silicate sol, thicknesses obtained experimentally fit very well to calculated ones. The interesting part of dip coating processes is that by choosing an appropriate viscosity the coating thickness can be varied with high precision from 20 nm up to 50  $\mu\text{m}$  while maintaining high optical quality. The schematics of a dip coating process are shown in figure 1.



**Fig. 1: Stages of the dip coating process: dipping of the substrate into the coating solution, wet layer formation by withdrawing the substrate and gelation of the layer by solvent evaporation**

If reactive systems are chosen for coatings, as it is the case in sol-gel type of coatings using alkoxides or pre-hydrolyzed systems - the so-called sols - the control of the atmosphere is indispensable. The atmosphere controls the evaporation of the solvent and the subsequent destabilization of the sols by solvent evaporation, leads to a gelation process and the formation of a transparent film due to the small particle size in the sols (nm range) [3]. This is schematically shown in figure 2.

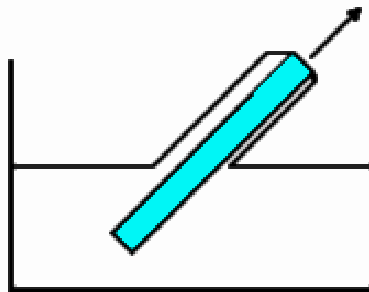


**Fig. 2: Gelation process during dip coating process, obtained by evaporation of the solvent and subsequent destabilization of the sol (after Brinker et al [3])**

In general, sol particles are stabilized by surface charges, and the stabilization condition follows the Stern's potential consideration [4]. According to Stern's theory the gelation process can be explained by the approaching of the charged particle to distances below the repulsion potential. Then the repulsion is changed to an attraction leading to a very fast gelation. This takes place at the gelation point as indicated in figure 2. The resulting gel then has to be densified by thermal treatment, and the densification temperature is depending on the composition. But due to the fact that gel particles are extremely small, the system shows a large excess energy and in

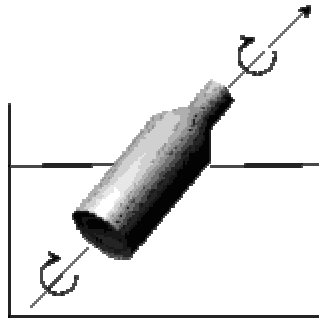
most cases a remarkably reduced densification temperature compared to bulk-systems is observed. However, it has to be taken into consideration that alkaline diffusion in conventional glasses like soda lime glasses starts at several hundred degrees centigrade and, as shown by Bange, alkaline ions diffuse into the coated layer during densification. In most cases, this is of no disadvantage, since the adhesion of these layers becomes perfect, but influences on the refractive index have to be taken into consideration for the calculations for optical systems. Dip coating processes are used for plate glass by Schott, based on developments of Schröder [5] and Dislich [6,7] for solar energy control systems (Calorex<sup>®</sup>) and anti-reflective coatings (Amiran<sup>®</sup>) on windows. The dip coating technique is also applied for optical coatings, e.g. on bulbs, for optical filters or dielectric mirrors by various SMEs and other companies, fabricating multilayer systems with up to 30 or 40 coatings with very high precision.

More recently, a angle-dependent dip coating process has been developed [5,8]. Control of layer thickness is important for optical coatings, and can be realized by Landau-Levich's equation with high precision. The coating thickness is dependant on the angle between the substrate and the liquid surface. Layer thickness can be calculated including the dipping angle and different layer thickness can be obtained on the top and bottom side of the substrate (figure 3).



**Fig. 3: Schematic of angle dependent dip coating**

The calculations show also that the number of layers can be reduced drastically to obtain similar optical properties as to be obtained with layers of one and the same thickness. Dip coating processes have also been developed for curved surfaces like eye-glass lenses, mainly to employ scratch resistant coatings for plastic substrates. For bottles, a variation of the dip coating process has been developed by revolving the bottle during the withdrawal process as one can see from figure 4.



**Fig.:4 Coating of bottles by dip coating and revolving**

Variations of dip coating processes are employed for fibre coatings in optical fibre industry, where the fibres are drawn through a coating liquid (mainly polymers) to protect the surface from mechanical impacts. Last not least, it should be mentioned that a very "old" coating process in the lead-crystal industry to fabricate coloured beakers or wine glasses has been used since centuries. It's the so-called "flash process" where a hot piece of an uncoloured glass is dipped into a coloured glass melt of the same basic composition and then blown to the final shape.

The drawbacks of large scale dip coating is the difficult handling of large panes and the stability of the dipcoating baths under atmospheric conditions. The development of easy to handle materials and techniques is necessary.

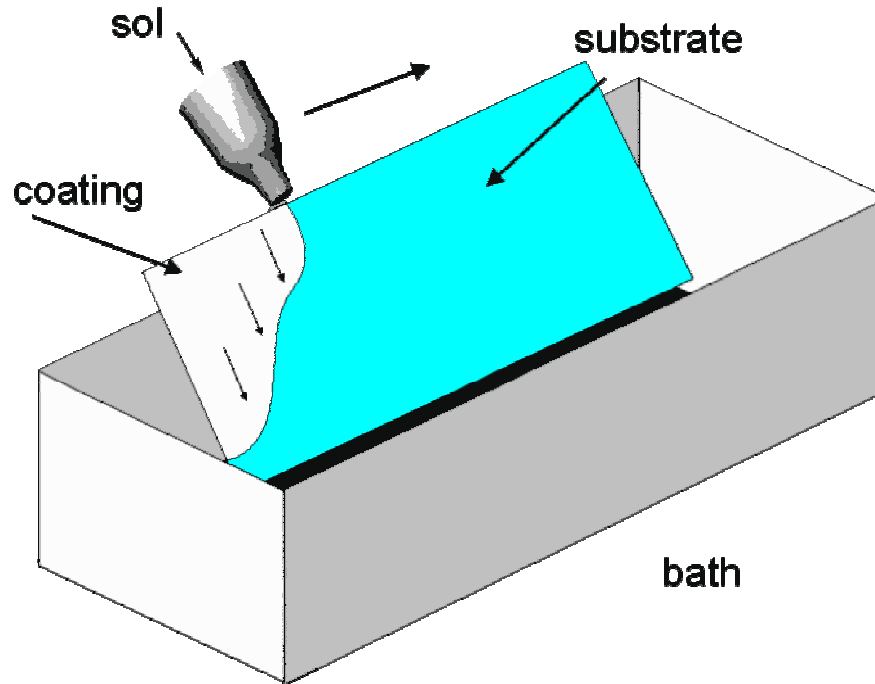
### **3.2. Spray coating techniques**

Spray coating techniques are widely used in industry for organic lacquers. For coating irregularly shaped glass forms like pressed glass parts, lamps or container glass (cold end coating) it is also feasible. Philips has developed a combined spin and spray process for functional sol-gel coatings on TV screens [9], however, for the preparation of optical coatings (thickness variation < 5 %) on large area glass surfaces, it is not used on industrial level. It has been shown very recently [10] that glass like coatings (coloured coatings and electrochromic  $WO_3$  coatings) with thickness in the range between 100 nm and 220 nm and a thickness accuracy of about 5 - 10 % could be prepared on flat glass (0.5 m x 0.5 m) using an automatic flat spraying equipment (type HGS, Venjakob) in combination with HVLP (high volume, low pressure) nozzles on pilot plant level, after the coating sols originally developed for dip coating were modified by the addition of solvents with increased boiling point. The preparation of optical coatings by spraying offers several advantages compared to the dip coating technique, since the so far realized processing speed of 1 m/min is already 10 times faster, the waste of coating sols is much smaller, coating sols with rather short pot lives can be used and the coating step is suitable for establishing an in-line process.

Processes similar to spray coating, where very fine droplets are produced (atomizers) like the pyrosol-process, in general lead to very homogeneous coatings on hard substrates, but the coating material does not hit the surface in form of liquid droplets but more or less in form of dried small particles in the nanometer range. Due to the high reactivity of these particles when reaching the hot surface, a continuous glass film can be formed.

### **3.3. Flow coating processes**

In the flow coating process the liquid coating system is more or less poured over the substrate to be coated as shown schematically in figure 5.



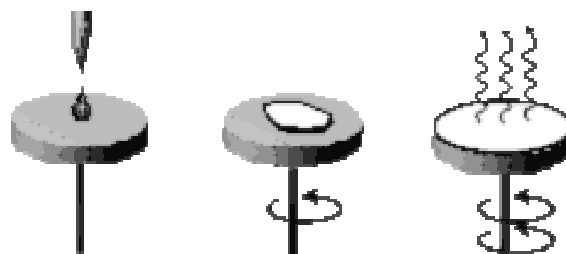
**Fig 5: Scheme of the flow-coating process**

The coating thickness depends on the angle of inclination of the substrate, the coating liquid viscosity and the solvent evaporation rate. Flow coating processes at present are used for outfitting of automotive glazing from polycarbonate with hard coating but also can be used for float glass to employ functional coatings. The advantage of the flow-coating process is that non-planar large substrates can be coated rather easily. As a variation of this process, the spinning of the substrate after coating may be helpful in order to obtain more homogenous coatings.

If no spinning process is employed, the coating thickness increases from the top to the bottom of the substrate.

### ***3.4. Spin coating process***

In the spin coating process, the substrate spins around an axis which should be perpendicular to the coating area. The spin-on process has been developed for the so-called spin-on glasses in microelectronics and substrates with a rotational symmetry, e.g. optical lenses or eye glass lenses. The schematics are shown in figure 6.



**Fig. 6: Stages of the spin coating process: deposition of the sol, spin up, spin off and gelation by solvent evaporation**

Fully automated spin coating processes have been introduced in the ophthalmic glass industry under clean room conditions and fully automated handling. The coating thickness vary between several hundreds of nanometers and up to 10 micrometers. Even with non-planar substrates very homogeneous coating thickness can be obtained. The quality of the coating depends on the rheological parameters of the coating liquid, and it has to be mentioned, that one should operate in the Newtonian regime. Another important parameter is the Reynolds number of the surrounding atmosphere. If the rotation velocity is in a range, that the atmospheric friction leads to high Reynolds numbers (turbulences), disturbances in the optical quality are observed. Meyerhofer [11] described the dependence of the final thickness of a spin coated layer on the processing and materials parameters like angular velocity, viscosity and solvent evaporation rate by the semi-empirical formula shown in equation 2.

$$h = (1 - \rho_A / \rho_{A0}) \cdot \left( \frac{3\eta \cdot m}{2\rho_{A0} \cdot \omega^2} \right)^{1/3} \quad (2)$$

with

$\rho_A$  = mass of volatile solvent per unit volume

$\rho_{A0}$  = initial value of  $\rho_A$   $h$  = final thickness

$\eta$  = viscosity  $\omega$  = angular speed

$m$  = evaporation rate of the solvent

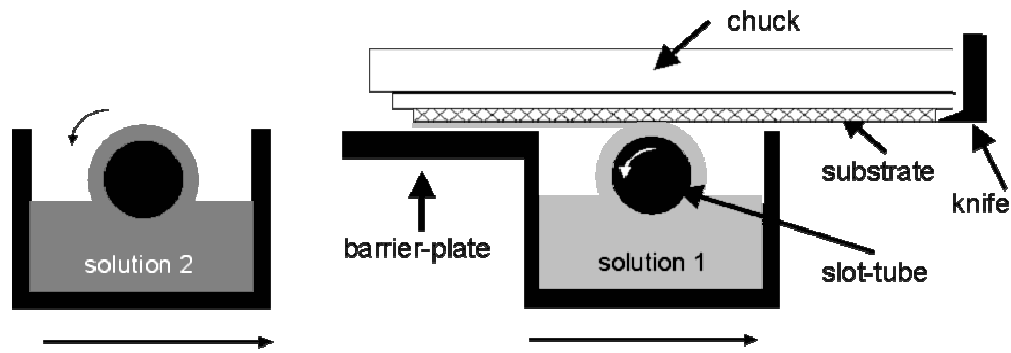
Since  $m$  has to be determined empirically any way, the more simple formula, given in eq. 3 may be used:

$$h = A \cdot \omega^{-B} \quad (3)$$

where  $A$  and  $B$  are constants to be determined empirically. Lai, Chen and Weill [12-14] independently determined thickness of films obtained by spin coating, using different angular speeds, and their results could be fitted very well with equation (3).  $B$  was determined to be in the interval between 0.4 and 0.7, which is in rather good agreement with eq. (2), where the exponent for  $\omega$  is 0.67.

### **3.5. Capillary coating**

Spray and spin coating processes are characterized by the fact that the coating material cannot be brought all onto the substrate. So, in spray coating processes more than 100 % overspray is obtained, and similar amounts are wasted with spin coating. Dip and flow coating processes mainly depend on the shelf life of the coating material and in optical dip coating only 10 to 20 percent of the coating liquid actually can be used for fabrication of coatings. To overcome these problems, the so-called capillary or laminar flow coating process has been developed by Floch [15,16] and CONVAC Co. [17], which combines the high optical quality of the dip coating process with the advantage that all the coating liquid can be exploited. In figure 7 the capillary coating process is shown schematically.



**Fig. 7: Schematics of the capillary coating process, Floch [15]**

The tubular dispense unit is moved under the substrate surface without physical contact. A spontaneous meniscus is created between the top of the slot tube (or porous cylinder) and the substrate surface, and achieving laminar deposition conditions a coating is deposited with high uniformity. Experimental investigations with  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  coatings showed, that the coating thickness can be controlled by the deposition rate  $v_d$  following equation 4:

$$h = k \cdot v_d^a \quad (4)$$

with  $v_d$  = deposition rate,  $a$  = exponent and  $k$  = empirical factor, depending on the viscosity.

For the exponent  $a$ , values of 0.65 ( $\text{SiO}_2$ ) and 0.73 ( $\text{Al}_2\text{O}_3$ ) have been obtained, which is in good agreement with the exponent in the Landau-Levich-equation (eq. 1) of 0.67, which describes the thickness for dip coating under laminar conditions.

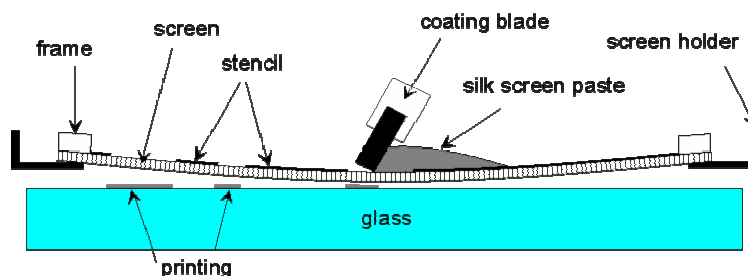
Coating thickness down to 15  $\mu\text{m}$  in high optical qualities are obtained and multilayer coatings for dielectric mirrors in confinement fusion experiments with high power lasers can be fabricated by using two dispense lines one after the other, as one can see from fig. 7.

### 3.6. Roll coating

Roll coating processes on plate glass are not state-of-the-art techniques. But pilot plant investigations have shown that optical qualities are obtainable [18]. It is of importance that in order to avoid structures in the surface cutted roles have to be used, and coating thickness and viscosity of the liquid have to be adapted very thoroughly. Using cutted roles, the amount of liquid transported onto the glass surface is defined by the voids cutted out of the role. After the deposition, the parts have to coagulate and to form a homogeneous film. For this reason, the wetting behaviour of the glass against the liquid has to be perfect and the drying speed has to be adapted to the film forming velocity. Therefore, temperature and atmosphere have to be controlled perfectly.

### 3.7. Printing technique

The most common printing technique for glass decors is the silk screen printing process [19,20]. In figure 8 the schematics of the silk screen printing process are shown.



**Fig. 8: Silk screen printing process**

This state-of-the-art-technology is widely used (automotive industry, decorative glasses e.g. in dashboards and windows of kitchen stoves). Coating materials based on organic polymers, to be cured at low temperatures or UV curing as well as enamel coatings with ceramic paints and appropriate low melting glass frits are used. Enamel like coatings are densified near the  $T_g$  of the glass substrate or, in combination with a thermal strengthening process or with a bending process, at appropriate higher temperatures. Typical film thickness are in the range from several 10 to several 100  $\mu\text{m}$ . Therefore the coefficients of thermal expansion of enamel have to be matched to that of the substrate glass.

Beside silk screen printing, continuous [21] and discontinuous [22] ink jet printing of sol-gel ceramic and organic-inorganic hybrid coating materials have been applied to ceramic and glass surfaces to obtain decorative coatings and micro-optical elements (micro lenses and micro lens arrays).

### **3.8. Chemical coating**

Chemical coatings should be understood as a process where a chemical reaction, e.g. the reduction of a metal is involved. The most common process is the fabrication of mirrors where the glass surface acts as a nucleating agent for the reduction of  $\text{Ag}^+$  to  $\text{Ag}^0$  in presence of reducing agent. The vast majority of all mirrors still are fabricated using this process. Another technology, which is suitable as an example for precipitating copper layers on glass, is the currently metalization process with commercially available liquids after seeding of the glass surface.

### **3.9. Drying and curing techniques**

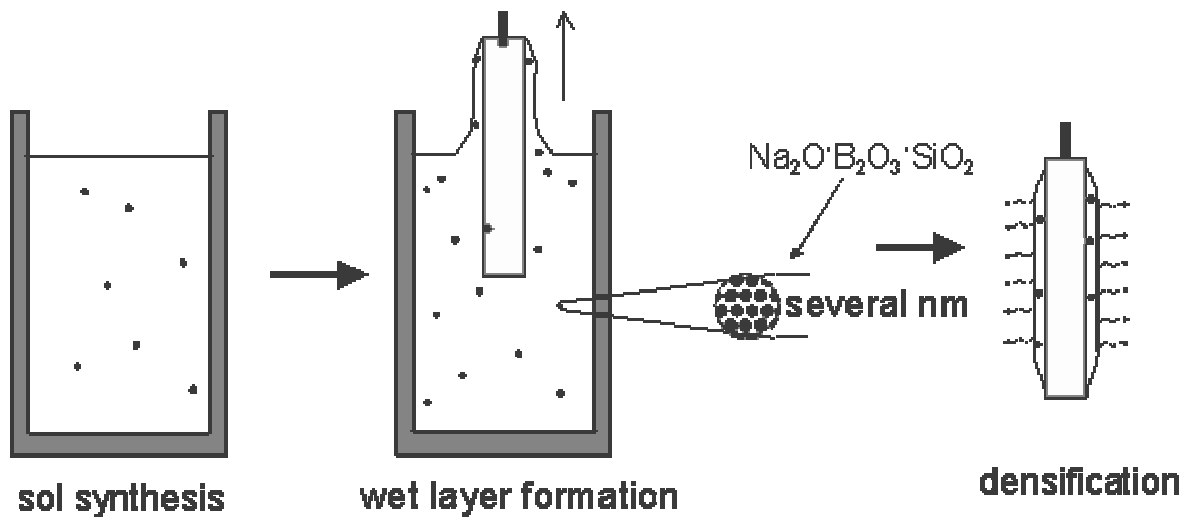
Drying and curing techniques are important for obtaining the appropriate coating properties. Depending on the type of the coating material high temperature curing and low temperature curing can be distinguished. If high chemical durability are required, the coating temperature mainly is chosen just below  $T_g$  of the glass in order to maintain the shape. Glass frits or sol-gel systems then are converted to ceramic- or glass-like coatings. If special functions have to be obtained, the control of the atmosphere may be of importance (e.g. in the case of electronically conductive coatings where the oxidation state is important for the electrical performance. Organic polymer or organic-inorganic hybrid coating materials can be cured by a low temperature IR treatment or UV-curing. For some special applications, the development of electron beam curing seems to be of interest.

## **4. Coating materials**

### **4.1. Oxide layers**

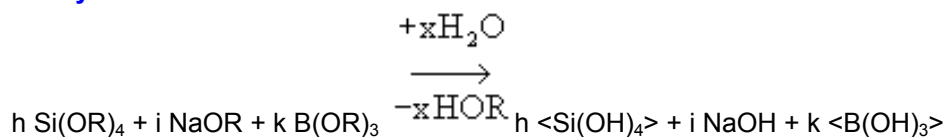
Oxides as coatings are the most investigated coating systems. All the work of Dislich [6,7] has shown that a large variety of systems can be prepared in form of sols, following the alkoxide synthesis route. For this reason, the alkoxide process for the fabrication of sols is shown schematically in figure 9 for a sodium borosilicate glass coating as an example.



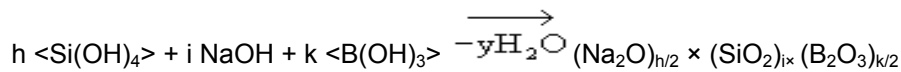


**Fig. 9: Sol synthesis and formation of sodium borosilicate coating on glass**

**Sol synthesis:**



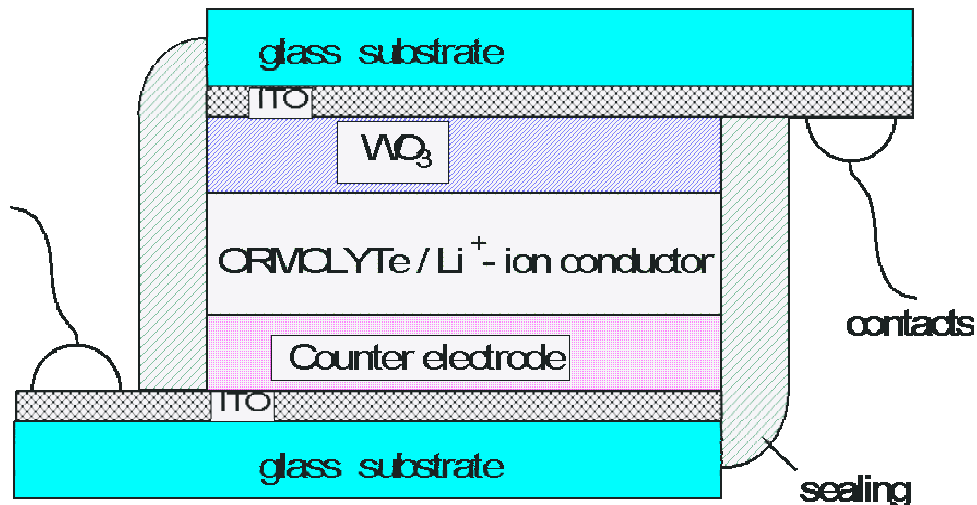
**Densification at 500 °C:**



As expressed in the reaction equation shown in figure 9, the sol is a "living system", where particles are formed, which are stabilized by a surface charge when using the appropriate pH. These particles in general tend to grow by Ostwald-ripening, and the characteristics of the sols are changed, as it has been investigated by Brinker and Scherer [23]. This means that the sols have a limited shelf life. If single-component sols are used, the shelf life can be increased by using low pH (addition of acids). This is valid for sols from SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub> or even Al<sub>2</sub>O<sub>3</sub>. Despite increased shelf lives, as already mentioned above, the yield of the coating liquid to be used for dip coating is below 20 percent.

Combinations of oxides with high and low reflective indexes (e.g. SiO<sub>2</sub> and TiO<sub>2</sub>) can be used for the production of optical coatings (reflective coatings, anti-reflective coatings, wide and narrow band filters or dielectric mirrors). Another interesting area for oxide coatings are electronically conductive coatings where sol-gel prepared ITO-systems show sheet resistances of below 10 Ohms per square [24]. SnO<sub>2</sub>-coatings can be prepared in high quality and with various dopants, but the sheet resistivities are in the range of about 80 to 70 Ohms per square only [25-27].

Electrochromic coatings using WO<sub>3</sub> or mixtures of WO<sub>3</sub> and MoO<sub>3</sub> as well as intercalation electrodes based on CeO<sub>2</sub> or TiO<sub>2</sub> or even Nb<sub>2</sub>O<sub>3</sub> [-] have been prepared. These types of coatings, which are at the break through for industrial production, normally are employed by dip coating processes with subsequent curing at appropriate temperatures. In figure 10 an electrochromic cell [31] is shown.



**Fig. 10: Construction of an electrochromic cell**

All kinds of conductive oxidic systems have been tried on a lab-scale for dip coating processes but haven't reached large area/high volume applications so far.

#### **4.2. Hydrophobic coatings**

Hydrophobic or water repellent or easy-to-clean coatings have been developed by wet chemical processes, since these coatings in general have to be multifunctional coatings. From Central Glass a process has been introduced [32] where sol-gel derived  $ZrO_2$  is deposited on plate glass by dip coating and treated at low temperatures to micro- or nanoporous layers. These layers then are impregnated by perfluorinated silanes. Embedded in the zirconia network, the perfluorinated sidechains show a high thermostability and "survive" the bending process. These coatings show a permanent hydrophobicity and dust repellence on car windshields. Another type of hydrophobic coatings has been developed by PPG [33,34]. These coatings are mainly based on organic polymers and can be employed by dip- or very special spray coating techniques.

Another type of hydrophobic fluorinated coating has been developed by Kasemann et. al. [18,35,36]. This coating is based on colloidal silica, surface modified by methyl groups and compounded with a sol, prepared from fluorinated organoalkoxy silanes. After employing on a glass surface, this coating undergoes a self-alignment, in which the fluorinated groups turn to the air side of the coating and the reactive silanes to the glass substrate to perform adhesion. The coating is stable for temperatures up to  $400^\circ C$ . A similar coating has been developed by Toyota [37].

#### **4.3. Hydrophilic coatings**

For automotive applications, coatings with a good wetting behaviour against water for outside uses as well as those with antifogging properties for inside applications are needed. Further requirements are good mechanical properties (scratch and abrasion resistance) and stability against wet climate conditions and UV radiation. Hydrophilic coating materials based on organic polymers exhibit several disadvantages. They show a poor mechanical stability (haze after 100 cycles Taber-Abraser test over 15 %) and the tendency to swell by incorporation of water. In order to overcome these disadvantages, functionalized inorganic-organic nanocomposites (Nanomers®), known for their good adhesion and excellent scratch resistance with hydrophilic compounds, have been developed recently [38].

First investigations with a hydroxyethylmethacrylate modified nanocomposite (DH about 10 % after 100 cycles Taber-Abraser test, contact angle below  $30^\circ$ ) showed the necessity to use diffusible and immobilized surfactants to guarantee a long term stability of the hydrophilic effect. Hot water exposition with this material led to swelling and a loss of mechanical stability. The introduction of additionally crosslinking aromatic diols increased both the abrasion resistance (DH about 5 % after 100 cycles Taber-Abraser test) and adhesion after

water exposition (75 °C) for 7 days after optimization of several parameters. The coatings had contact angles against water below 30 °, but were not sufficiently UV-stable, even after incorporation of UV-stabilizers.

In a following approach, an aliphatic cross-linked system based on a newly developed inorganic-organic compound called ACDS (amidocarboxydisilane) was synthesized. After hydrophilic modification, a coating system with the following properties resulted: DH about 3-4 % after 100 cycles Taber-Abraser test, contact angle against water below 30 °, UV-stability for more than 7 days in the unfiltered light of a Xenon lamp. By incorporation of a percolating and interpenetrating inorganic network with predispersed SiO<sub>2</sub> nanoparticles, the abrasion resistance was increased resulting in 16 % haze after 1000 cycles Taber-Abraser test with unchanged hydrophilic properties. The further development of this system finally lead to a waterbased and highly nano-silica filled epoxysilane system with an abrasion resistance with 8-10 % haze (1000 cycles Taber-Abraser test) and contact angles below 30 ° against water.

These materials allow the use as coatings for inside applications. For the application on the outer side of a windscreen however, a haze increase of maximum 2 % after 1000 cycles Taber-Abraser test is allowed. This objective seems to be reachable by optimization of the composition and curing conditions.

#### **4.4. Printing pastes**

Printing pastes have two main applications in glass industry: the colouring effect or to obtain conductive channels, e.g. for heated screens in cars. Conductive pastes as well as decorative pastes are a state-of-the-art material, commercialized by a variety of specialized companies.

Recently, it has been shown that in decorative enamel type silk screen printing pastes, consisting of an organic oil, organic binder, glass frit and ceramic pigments, the organic printing oil and the organic binder can be replaced by a lead boron zink silicate gel [39,40]. In this case, the rheological properties required for the printing process can be obtained by interparticulate interactions. The organic content of this printing paste is below 1 %, and, therefore no organic compounds have to be burnt off during the firing, since the "printing medium" is converted to glass.

#### **4.5. Special materials**

##### Colloidal colours

As shown by Mennig and co-workers, the metal colloid formation as already known from gold ruby glasses can be carried out in coating materials and even in very thin coatings below 1 µm very intensiv colours can be obtained [41,42]. Based on this technology, a coating technique for eye glasses or plate glass has been developed which are partially already used in industrial processes. A wide variety of colours can be obtained like red, blue, grey, green, yellow, brown, orange. The colour is developed during a nucleation and growth process of the colloids during the heat treatment. And this allows the control of the colour intensity by using only one type of colouring system. Different colours in one-step process can also be obtained using a mixed colloidal system or alloy nanoparticles. The sols are prepared by keeping the metal colloid forming element in a stable form in the liquid (e.g. with complex formers). After coating and drying, the temperature treatment can be carried out under various atmospheres which also influence the type and intensity of colours.

##### Photochromics

Photochromic colours can be obtained by using photochromic dyes and incorporate them into sol-gel type of organic-inorganic hybrid materials to be coated according to the methods mentioned above [43,44]. A Nanomer coating system, developed recently [45] allows the incorporation of different blue, violet, yellow and orange photochromes (oxazines, pyranes, fulgides) and neutral tinted mixtures thereof with fast switching kinetics (half darkening and half fading times < 10 s) and good scratch resistance by incorporation of SiO<sub>2</sub> nanoparticles. In case of a blue coloured spirooxazine dye lifetimes of up to 200 h in sun test could be obtained after incorporation of an appropriate stabilizer (partial UV absorber), which is sufficient for ophthalmic applications. For other dyes, the stability obtained so far, has still to be improved.

##### Glass Strength improvement

Compressive stress coatings can be obtained by densifying ceramic or glass coating systems, having a lower thermal coefficient of expansion than the substrate glass and at the same time can be densified below the T<sub>g</sub> of glass. So it has been shown that borosilicate sol-gel coatings after densification can improve the bending strength of float glass by the factor of 4. Inorganic-organic composite coatings also show that the strength of glass bottles can be improved substantially.

##### AR, filters, IR reflectors

Coating sols, consisting of high ( $\text{TiO}_2$ ) and low ( $\text{SiO}_2$ ) refractive index nanoparticles, surface modified with uv-polymerizable groups have been developed recently [46]. They allow the preparation of stacks of optical layers with refractive indices between 1.46 and 2.2 on glass by dip coating and subsequent UV curing. The stacks can be fired finally at 450 °C to obtain AR systems, colour filters or IR reflective layers. So far, stacks with up to 5 single layers have been fired without any defects on lab scale [47]. This can lead to decreased processing costs, since with state of the art  $\text{SiO}_2$ - and  $\text{TiO}_2$  coating sols, each layer has to be densified at 400 - 450 °C before the next one can be deposited.

Micropatterning with so-called moth-eye structures on top of plate glass can be used to develop angle-independent anti-reflective systems. But these systems are very sensitive to dirt. They currently are developed for solar collector systems.