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# INORGANIC COATINGS ON GLASS

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# FILMS BY SOL-GEL PROCESSES

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## Abstract

The sol-gel process is a method for the preparation of inorganic materials and organically modified ceramics by "soft" chemistry. The possibility of adjusting the rheology of intermediates leads to products for coating procedures. As coating techniques dip, spin-on, spray, roll, and others are possible. Different applications for glasses are possible: to improve the surface properties of glass (e.g. strength) and to generate special effects or functions (optical, chemical reactivity, sensitive, protective, and others). A general survey over coating problems is given and some special applications are discussed.

## 1. INTRODUCTION

In many cases, the surface plays an important role for the overall performance of materials. Appropriate coatings, for instance, can supply special properties to a component which the bulk material does not show. There are numerous examples. Many metals require corrosion protective coatings if applied under atmospheric conditions: steel, copper, brass, or aluminum. To improve surface hardness anti-abrasive coatings are applied on metals, on polymers (which is difficult in most cases), on wood, and on glass and ceramic materials, too. Other coatings can add special functions to components (e. g. immobilization of enzymes on solid surfaces; special adsorptive effects, special optical effects, colours, reflection behavior or special electrical effects like resistivity or conductivity). One can say that for many cases the properties of materials is mainly determined by their surface.

This is at least partially true for glasses, too. First, the mechanical strength is determined by the state of the glass surface. Second, optical properties (reflectivity, transparency, selective transmission or absorption for electromagnetic radiation) have to be adapted to special practical requirements. Third, chemical durability is necessary to be improved, if indispensable bulk properties result in low chemical durability glasses. Fourth, special surface reactivities must be created for special purposes, like coupling groupings for glass carrier based enzyme reactors or sensitive layers for integrated or fiber optic based sensors. This summary does not claim to be a complete one, but it illustrates the scope of the variety of possible coating applications on glass surfaces.

Different techniques are available for coating of glass. In most cases, due to the desired optical performance and the transparency of glass, these coatings necessarily must not reduce this performance. That means, high level coating techniques have to be applied and appropriate clean condition (vacuum, clean rooms) must be employed.

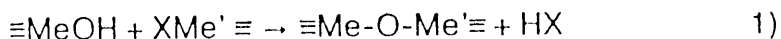
Two major groups of coating techniques are used: vacuum techniques and "wet" techniques. Vacuum techniques can use a variety of different deposition processes. Generally, the film formation is characterized by an isotropic growth of crystals or amorphous particles, and, in order to receive optically sufficient quality, particle or crystal size have to be controlled very thoroughly. Different types of materials can be deposited (metals, oxides, non-oxide inorganic compounds, and, with restrictions, organic materials). The wet processes include organic polymer films, metal deposition by electrolytic processes, and sol-gel techniques. They are characterized by the fact, that the coating material has to be prepared in a liquid form (solution, suspension) and (except electrolysis) that by an additional treatment, the coating after deposition has to be dried, hardened, densified, or phase transformed in order to create the desired properties.

## **2. BASIC FEATURES OF SOL-GEL FILM FORMATION**

### **2.1 Sol-Gel Techniques**

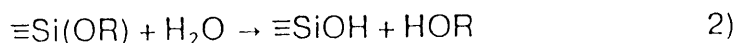
The sol-gel process describes the formation of an inorganic polymeric network by "soft", that means low temperature chemi-

stry (1). Precursors can be alkoxides (2), soluble oxides (3), salts, complexes (4), oligomeric (e. g. inorganic polyanions or polycations) or colloidal (e. g. colloidal silica) components. The network forming step is the condensation of hydroxides with other groupings 1)

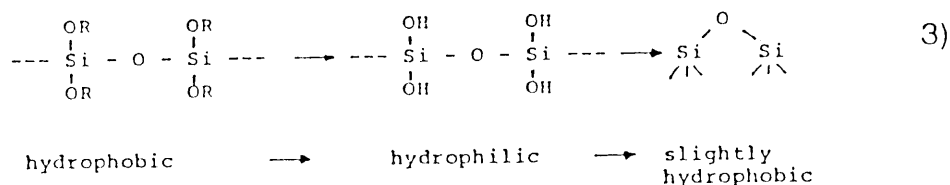


with X = e. g. OH, OR, NH<sub>2</sub>, halogen, acrylate.

The process goes through a colloidal (sol) phase and generally ends in a solid (at least diphasic gel) phase. Due to the three-dimensional crosslinking, the gels are brittle and porous. Drying results in stresses, which may lead to cracks, if no special measurements are applied (5). If alkoxides as starting materials are used, a hydrolysis process 2) takes place.



Whereas Si(OR)<sub>4</sub> is a slow reacting ester, others react far quicker (B, Al, Ti, Zr, alkaline and earth alkaline compounds). During hydrolysis and condensation, surface tension and wetting behaviour may change due to the number of hydrophobic or hydrophilic grouping of the growing polymer 3)



Own contact angle measurements of a freshly prepared Na<sub>2</sub>O/B<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> sol shows a decrease and after some hours an increase of the contact angle to clean glass surfaces, underlining the hypothesis shown in 3). The structure of the oligomeric coating liquids can be controlled by different chemical means. The silica system has been investigated in detail by different authors (6-15) and the structural effect between acid and basic catalysis has been pointed out. Similar structural investigations of multi-component or quick reacting systems have not been carried out due to experimental difficulties. A lot of data on alkoxide complexes is available from work done by Bradley and Mehrotra (16) but they did not investigate the condensation processes and structures of the resulting polymers. The chemistry of these reactions is

still not very well-known. For the preparation of coating liquids, the condensation has to be stopped at a well defined level in order to establish an adequate viscosity.

The following influencing parameters are important for synthesis and property control:

solvent	(hydrolysis and reaction rate, structure, rheology, film formation)
catalyst	(reaction rates, structure, H <sup>+</sup> , OH <sup>-</sup> : equilibrium, stability of complexes)
cations/anions	(reaction rates, structures, complexes)
additives	(film formation, drying behaviour, densification behavior)
flow agents	(film formation)
composition	(rates, rheology, film form, densification, crystallization)
all mentioned parameters	(drying, crack formation, densification, adhesion, final properties).

These parameters have to be optimized for each single system. In many cases, the systems can be stabilized by addition of acids, which can prevent gelation due to the zeta potential of the system (e. g. alumina). The disadvantage of the parameter variety is overcompensated by the possibility of proper tailoring especially with respect to multicomponent systems. Exact stoichiometric control of composition with an almost unlimited number of components can be obtained. Special advantages result from the fact that low concentration components can be distributed homogeneously. Sol-gel coatings result in smooth, dense films, if applied correctly.

## 2.2. Film formation

As already pointed out in the introduction, the sol-gel process with a purely inorganic network leads to brittle gels which are not dense. If time dose not play any role, very slow condensation processes can lead to rather densified materials, as shown by the history of the Libyan desert glasses (fully dense SiO<sub>2</sub> sol-gel glasses at T ≤ 135 °C; t = several million years) by Ebelmen (17) who after some months gelation and drying received SiO<sub>2</sub> · H<sub>2</sub>O with

$\rho = 1.86 \text{ g/cm}^2$  which is rather high for room temperature drying. During drying, stresses can appear since interfacial forces can end up in localized tensions and, as a result, cracking occurs (figures 1, 2, and 3) (18). The capillary pressure  $p$  depends on the surface tension  $\gamma$  and the pore diameter (figure 1).

$\sigma_z$  defines the height to which a liquid can rise against gravity.

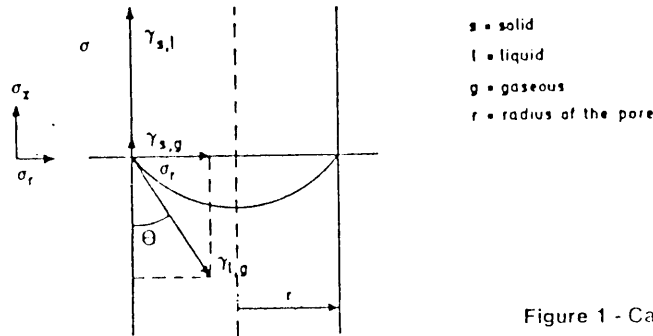


Figure 1 - Capillary forces in pores.

$$\sigma_r = \frac{2}{r} \cdot \gamma_{l,g} \cdot \sin\theta; \quad p = \frac{2\gamma}{r}$$

$$\sigma_z = \frac{2}{r} (\gamma_{s,g} + \gamma_{s,l} - \gamma_{l,g} \cdot \cos\theta)$$

$\sigma_r$  causes local tensions in the form of a ring around a pore (figure 2) and tries to narrow the pore. As long as the material can follow the tension, a plastic deformation and crackfree shrinking can take place. Since, in general, in gels neither pore shape nor pore diameters are constant, a tension zone will be formed during the drying process moving slowly through the material (figure 3)

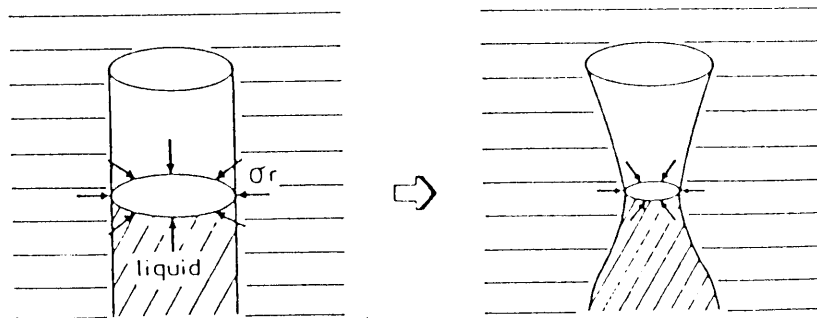


Figure 2 - Effect of interfacial tension on pore deformation.

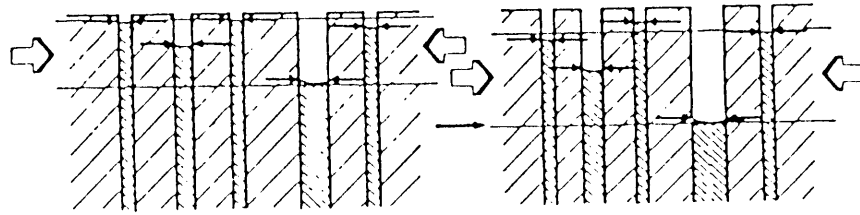


Figure 3 - Development of tension zone during drying

The tension depends on the pore radius and the interaction between the liquid and the pore wall. For a glass surface (good wetting, contact angle  $10^\circ$ ) and an assumed pore radius  $r = 5 \cdot 10^{-9}$  m,  $\sigma_r = 5.05$  MPa. For  $r = 10 \cdot 10^{-9}$  m,  $\sigma_r = 2.57$  MPa. Since the mechanical strength in gels in general is far lower, cracking takes place, if the coatings are thicker than several micrometers. With thin coatings, unidirectional densification behavior is observed (figure 4). This is probably due to a different structure of the gels. Brinker (19) developed a hypothesis which postulates a densification mechanisms during the drawing process of a dip coating procedure (figure 5) caused by shear stresses. As a matter of fact, the room temperature dried gel coatings show far less porosity than bulk materials obtained from the same sols. It is understandable, that the densifying and drainage zone is of limited thickness and the effect decreases with increasing film thickness and viscosity.

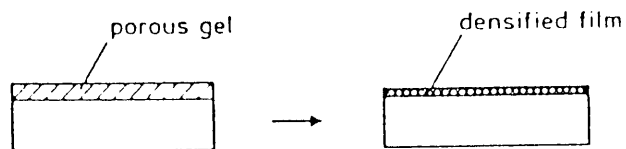


Figure 4 - Densification behavior of thin films.

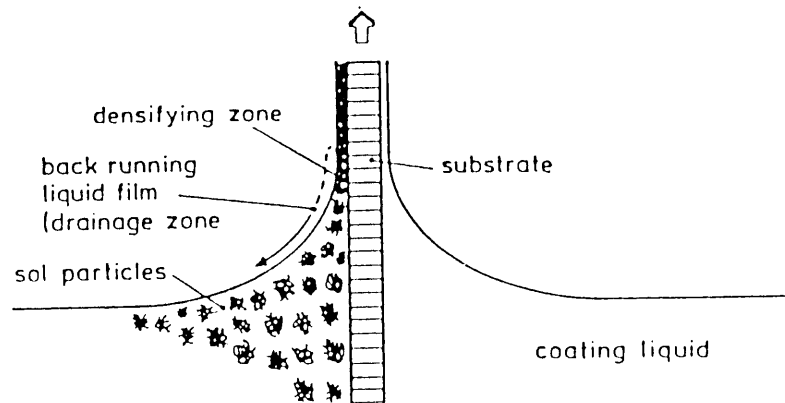


Figure 5 - Densifying process during dip coating.

The sol-gel process allows to prepare coating liquids with desired viscosities and to apply these liquids by use of common coating techniques. The following techniques can be used: spray coating, roll coating, dip coating, spin-on coating, and modifications of each. With spray coating and roll coating it is difficult to receive smooth surfaces with optical qualities; the use of additives and an optimized combination of solvent is necessary. Spin-on and dip coating generally result in high surface quality but rheological data have to be controlled very thoroughly, too.

With dip coating the film thickness depends strongly on viscosity. For low viscosities ( $N_c \ll 10^{-4}$ ), Landau and Levich (20) had been able to estimate the coating thickness as 4)

$$\Delta s = K \cdot N_c^{1/6} \left( \frac{\eta \cdot v}{\rho \cdot g} \right)^{1/2}, \quad N_c = \frac{\eta \cdot v}{c} \quad 4)$$

$\Delta s$  = film thickness;  $\rho$  = density of the coating solution;  $g$  = gravitational constant;  $\delta$  = surface tension;  $v$  = lifting speed;  $\eta$  = viscosity (mPa·s);  $k$  = constant;  $N_c$  = capillary number.

In figure 6 calculations according to 3) are compared with viscosity measurements. The system is a sodium borosilicate glass with 80 % SiO<sub>2</sub>, 15 % B<sub>2</sub>O<sub>3</sub> and 5 % Na<sub>2</sub>O (wt.-%).  $K$  was determined as 0.055. The agreement is very good.



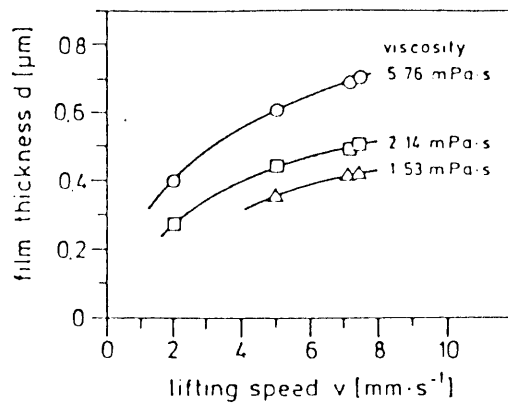
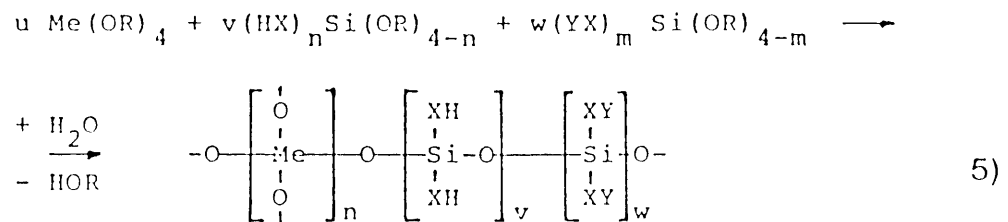


Figure 6 - Comparison between calculated (full lines) and measured (symbols) film thicknesses for a Na<sub>2</sub>O/B<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> sol-gel coating [21].

The sol-gel process, in addition to the preparation of pure inorganic coatings enables the introduction of organics into inorganic networks according to 5),



X z. B. -CH<sub>2</sub>-, -C<sub>6</sub>H<sub>4</sub>-

Y z. B. -NH<sub>2</sub>, -CHO, -COOH, Vinyl, Epoxy, Methacrylat

and modified glass structures can be synthesized (figure 7).

Due to the decreased network connectivity, these modified glasses (ORMOCERs = **organically modified ceramics**) show an increased relaxation behavior and can be densified to thicker layers without cracking (18,22).

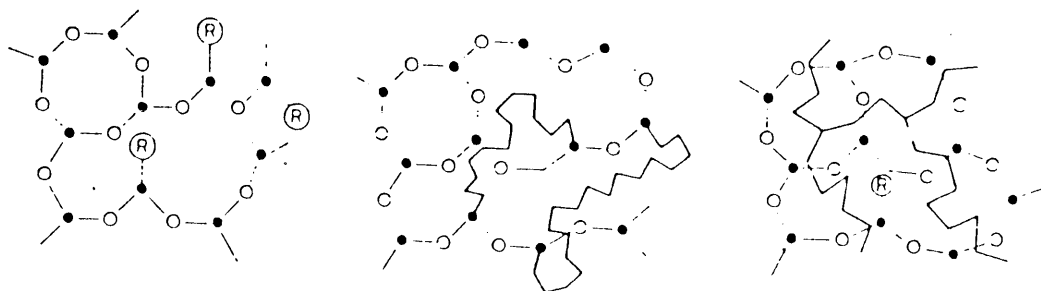


Figure 7 - Organically modified glass structures; O = Si; o = O (fourth bond of Si beneath or above drawing plane a) organic network modifiers; b) organic network formers; c) interpenetrating network with organic network former.

### 3. EXAMPLES

#### 3.1 Glass Strengthening

The poor strength of glass is an unfortunate combination of its brittleness and the lack of surface perfectness. Crack or flaws are growing under certain load due to the lack of the ability of plastic deformation and stress energy dissipation. The homogeneity leads to a steady crack growth along the direction governed by tension; the crack cannot be deflected by microstructures like in ceramic materials. Surface compressive stress, e. g. by ion exchange, leads to a remarkable increase of strength as well as thermo-shock treatment, since the effect of flaws is reduced. Another concept could be to heal the flaws, e. g. by sol-gel coating. A series of systematic investigations has been carried out with different sol-gel coatings (21). The variation of the thermal expansion coefficient leads to coatings with tensile stress, no stress and compressive stress on the glass surface after densification. As coatings,  $\text{Na}_2\text{O}/\text{SiO}_2$  and  $\text{Na}_2\text{O}/\text{B}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SiO}_2$  systems were used. In figures 8 and 9, the results of these coatings on glass rods is shown. Figure 8 shows the effect of non-compressive coatings, leading up to a 70 % strength increase by flaw healing only. Figure 9 shows compressive strain coatings leading to strength increases of almost 300 % after multiple coating. This means that flaw healing and compressive stress are increasing strength. Since procedures are not yet optimized, there is still more potential. Sol-gel coatings can be used as an easy way to increase strength.

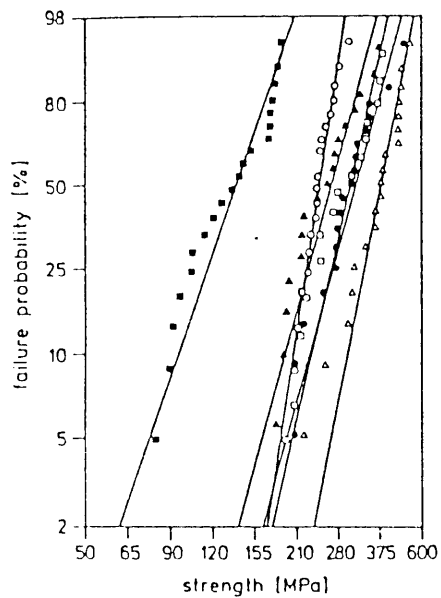


Figure 8 - Strength distribution of sodium alumoborosilicate coated glass rods;

- : not annealed uncoated glass rods,  $\sigma_0 = 165.9$  MPa,  $m = 4.1$
- : one-step coating,  $d = 0.4$   $\mu\text{m}$ , thermal treatment a,  $\sigma_0 = 291.1$  MPa,  $m = 9.1$
- ▲: 3 x coating,  $d = 1.5$   $\mu\text{m}$ , thermal treatment d, final coating - thermal treatment a,  $\sigma_0 = 327.6$  MPa,  $m = 5.1$
- : 6<sup>o</sup>x coating,  $d = 2.9$   $\mu\text{m}$ , thermal treatment d, final coating - thermal treatment a,  $\sigma_0 = 374.4$  MPa,  $m = 6.1$
- : 8<sup>o</sup>x coating,  $d = 4$   $\mu\text{m}$ , thermal treatment d, final coating - thermal treatment a,  $\sigma_0 = 393.7$  MPa,  $m = 5.1$
- △: 11<sup>o</sup> x coating,  $d = 5.7$   $\mu\text{m}$ , thermal treatment d, final coating - thermal treatment a,  $\sigma_0 = 465.5$  MPa,  $m = 7.1$ .

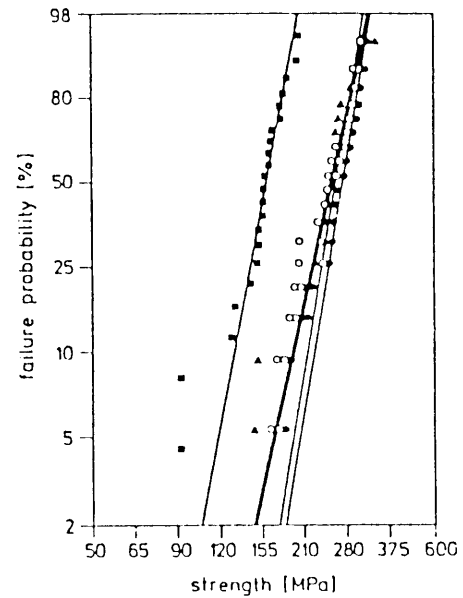


Figure 9 - Strength distribution of sodium silicate coated glass rods;

- : uncoated glass rods, thermal treatment a,  $\sigma_0 = 190.8$  MPa,  $m = 7.1$
- : 75  $\text{SiO}_2/25\text{Na}_2\text{O}$ , coating thickness 0.35  $\mu\text{m}$ , thermal treatment a,  $\sigma_0 = 308.3$  MPa,  $m = 6.1$
- ▲: 80  $\text{SiO}_2/20\text{Na}_2\text{O}$ , coating thickness 0.35  $\mu\text{m}$ , thermal treatment a,  $\sigma_0 = 308.3$  MPa,  $m = 6.1$
- : 85  $\text{SiO}_2/15\text{Na}_2\text{O}$ , coating thickness 0.35  $\mu\text{m}$ , thermal treatment a,  $\sigma_0 = 315.2$  MPa,  $m = 8.1$
- : 90  $\text{SiO}_2/10\text{Na}_2\text{O}$ , coating thickness 0.35  $\mu\text{m}$ , thermal treatment a,  $\sigma_0 = 331.0$  MPa,  $m = 8.1$ .

### 3.2. Decorative Coatings

Thin non-fully densified coatings can have good optical appearance, if there are no cracks and if the pore size is small ( $< 100$  nm). Coatings of this type can be obtained at  $T < 300$  °C and exhibit good mechanical properties. It is possible to introduce organic dyes into gels (23) and one can receive intensive colours

with gel coatings of only 0.2 to 0.5  $\mu\text{m}$  thickness. As coating materials  $\text{SiO}_2$ ,  $\text{Na}_2\text{O}/\text{B}_2\text{O}_3/\text{SiO}_2$ ,  $\text{H}_2\text{O}/\text{TiO}_2/\text{SiO}_2$  and  $\text{TiO}_2/\text{SiO}_2$  systems were used, alcohol soluble dyes were added and the coatings dried at 250 to 300  $^\circ\text{C}$  (according to the thermal stability of the dyes). The hydrolytic stability was tested in boiling water, hot  $\text{NaOH}$  (5 %) and a mixture of boiling  $\text{CH}_3\text{COOH}/\text{C}_2\text{H}_5\text{OH}$ . The best results were obtained from  $\text{TiO}_2/\text{SiO}_2 = 10:90$  (molar ratio). Figure 10 shows the absorbance of ORASOL<sup>®</sup> blue before and after treatment.

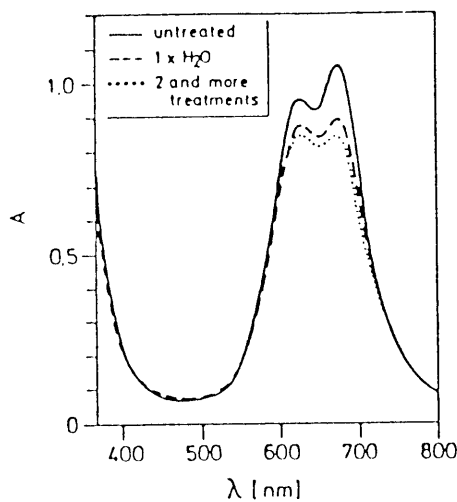


Figure 10a - ORASOL BLUE CN  $\text{SiO}_2:\text{TiO}_2 = 90:10$  system before and after  $\text{H}_2\text{O}$  leaching.

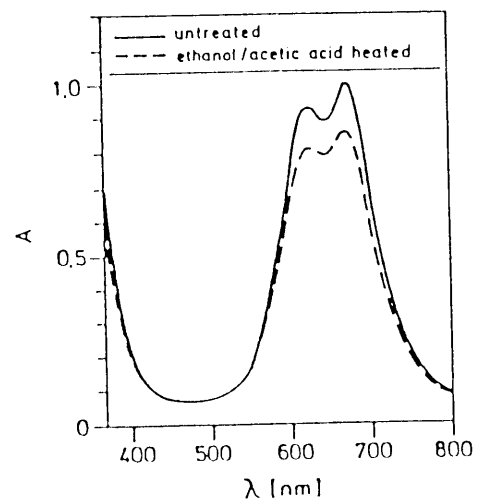


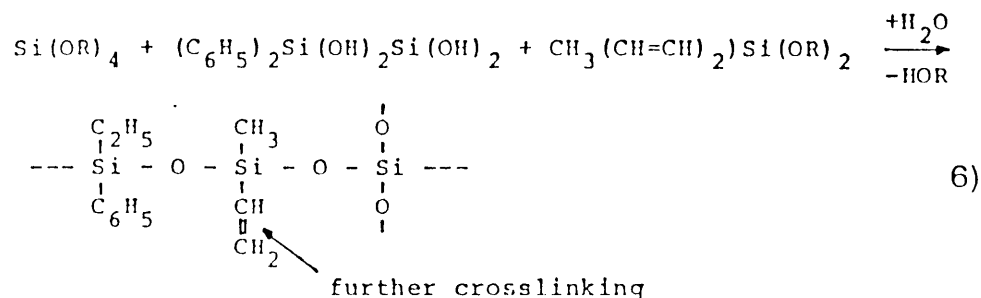
Figure 10b - ORASOL BLUE CN  $\text{SiO}_2:\text{TiO}_2 = 90:10$  system before and after ethanol/acetic acid leaching.

This shows a convenient possibility for preparing intensively coloured glass surfaces. The principle, of course, can be extended to other organics like acids, bases, complexes, polymers, and sensitive compounds. A large variety of coatings can be prepared, not much has been developed up to now.

### 3.3. Organically Modified Coatings

The introduction of organics allows to synthesize coatings with special functions. Protective coatings for medieval glasses have

been developed (24) which are based on a sol-gel synthesis from  $\text{Si}(\text{OR})_4$ ,  $\text{C}_6\text{H}_5$ ,  $\text{Si}(\text{OH})_2$  and  $\text{CH}_3(\text{CH}=\text{CH}_2)\text{Si}(\text{OR})_2$ , and (optional)  $\text{Ti}(\text{OR})_4$  as precursor 6).



This system (25) shows an excellent adhesion on glass surfaces and with mica or glass flakes (figure 11) a perfect corrosion protection on sensitive glasses.

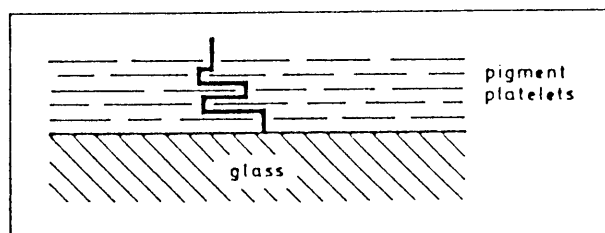


Figure 11 - Scheme of the structure of an ORMOCER protective coating with diffusion barriers: the thick line shows the diffusion path expansion

The system can be cured by vinyl polymerisation. The full protection system is shown in figure 12.

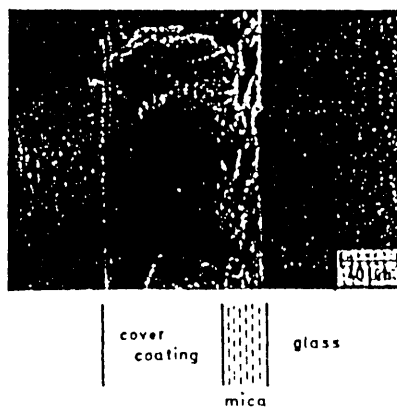


Figure 12 - Compact protective system (two layers).

Protective coatings can also be based on variations of the above system: Si can be partially substituted by Al. Thus, hard protective coatings can be synthesized, which are hard (25), transparent (optical quality) and can be used for protection of glasses (mechanical and chemical). A similar system has been developed for the protection of plastic eye glass lenses (CR 39) (25).

Functional coatings have been prepared for the inner side of glass tubes. These coatings are synthesized from two or three components  $\text{Si}(\text{OR})_4$ ,  $(\text{CH}_3)_2\text{Si}(\text{OR})_2$ , and  $\text{R}'\text{Si}(\text{OR})_3$ . R' is an organofunctional group as aldehyde, hydroxy, amino, anilino, and others (26). These coatings which show the chemical functions of the groupings on the surface have a good adhesion to glasses and can be used for immobilization of enzymes or other biological materials. Thus, a radioimmunoassay has been developed (figure 13) (26).

The incorporation of special functions was used for the development of a  $\text{SO}_2$  sensor on  $\text{SiO}_2$  glass. The glass substrate is covered with an interdigitated capacitor structure and the sol-gel coating contains reversible  $\text{SO}_2$  acceptor ligands (27) (see figure 14).

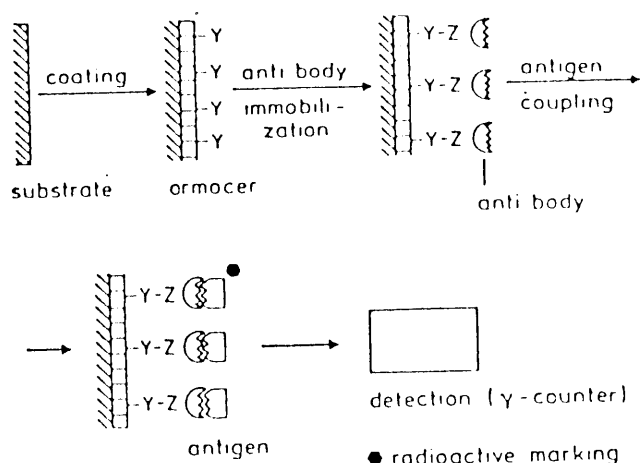


Figure 13 - Scheme of a radioimmunoassay with ORMOCER.

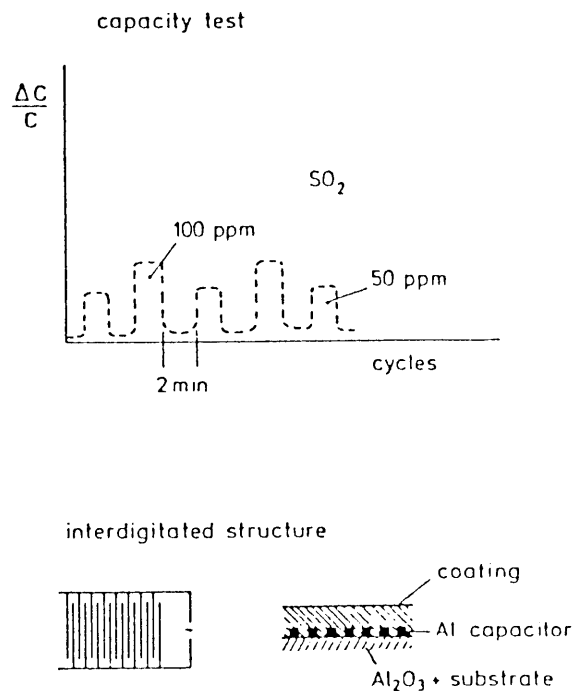


Figure 14 - Detection of  $\text{SO}_2$  and principle of a interdigitated capacitor with an ORMOCER coating.

According to the  $\text{SO}_2$  concentration change, the sensor shows a change of capacity. Coatings like these seem to be useful on integrated optic or fiber optic sensor, too.

#### 4. CONCLUSION AND OUTLOOK

Sol-gel techniques for coating coatings  $\leq 1 \mu\text{m}$  can be applied very easily onto glass surfaces since an unidirectional shrinkage occurs. The possibility of establishing an appropriate rheology for the coating and the possibility of preparing homogeneous multicomponent systems with exact stoichiometrics are the main advantages. The sol-gel process allows the preparation of different types of materials as films:

- glasses
- ceramic materials
- ORMOCERs.

For glasses coatings can have very different functions like improving of mechanical properties (strength, abrasion). Therefore, sol-gel coatings can be used (flaw healing, compressive stress) with remarkable results. The potential is still not exploited, especially with respect to other coating techniques (spray, curtain, powder, electrostatic, aerosol, and others) and densifying techniques (e. g. IR radiation, LASER etc.). Especially densification techniques which include controlled heat transfer to the glass surface (which is possible by rapid laser irradiation) can be used for high Tg coatings ( $\text{SiO}_2$ ,  $\text{SiO}_2/\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2/\text{TiO}_2$ ).

In our own experiments, laser densification of  $\text{TiO}_2/\text{SiO}_2$  and  $\text{Na}_2\text{O}/\text{B}_2\text{O}_3/\text{SiO}_2$  coatings on glass surfaces (plate glass) after optimization resulted in optical transparent surface layers which increase strength in the ranges indicated in chapter 3, too. Surface temperature control by a surface pyrometric device is indispensable. Thus, depending on the surface temperature, surface crystallization could be achieved, too. These are results of preliminary investigation so far.

The field of sol-gel application for optical coatings is very wide (e.g. antireflective coatings, antilaser damage coatings, coloured coatings). Interesting is the field of coatings with special functions. As indicated in only a few examples, there is a tremendous potential for sol-gel derived coating specialities, e.g. incorporation of organic molecules, ions, complexes and others, which add properties to glass surfaces not able to be achieved by other techniques (optical, sensitive, coupling, electrical, and other properties). Therefore, the sol-gel process is a unique tool which can help to develop new "high-tech" applications for the "old" material glass.



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