Decoration of crystal glassware via hybrid sol-gel coatings - Décoration d'objets en cristal avec des revêtements sol-gel hybrides

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Les techniques utilisées pour la coloration des revêtements sol-gel hybrides sont rappelées. Puis l'article présente les résultats de l'étude de revêtements colorés obtenus par dissolution de colorants organiques du commerce ou, pour les revêtements opaques, par dispersion de pigments classiques organiques ou inorganiques. Les revêtements obtenus permettent également de réduire la solubilité du plomb des objets en cristal.

The most important property of glass is its luminous transmittance, which is the basis for applying plane glass in windows of buildings and vehicles, as front cover of displays and traffic signs. Glass is also highly accepted as a clean, impermeable and recyclable container material to distribute, store and consume beverages and other nutrition products. Especially fascinating are coloured glasses in windows of historical buildings like cathedrals and other medieval sites. Today`s commercial architecture seems to discover glass facades again to demonstrate "glasnost" and support advertising purposes.
This has become possible by revolutionary developments in applying physically deposited thin coatings onto glass surfaces in order to change the light and heat transmissivity, thereby achieving very low g-values [1]. The modification of plane glass surfaces by wet chemical techniques to produce antireflective properties has also been commercialized on a larger scale [2]. Contrary, the colouration of glasses is still based on very traditional, laborious and costly means, especially in the crystal glass industry.

1. State of the art

The technical processes leading to coloured glasses are well known and predominantly involve the incorporation of transition metal cations into the oxidic network by adding the respective metal oxides to the batch for melting the glass. The most important elements imposing colour onto the final product are Cu, Ti, V, Cr, Mn, Fe, Co and Ni leading to blue, light purple, green, light yellow, brown and grey bulk material. The second way of tuning the colour of glasses is the so-called colloidal colouration. It is achieved by adding metal salts of Au, Ag or Cu, which are reduced to the metallic state during melting and segregate from the glass matrix while cooling. Similar phase segregation processes take place after the addition of CdS or CdSe to the glass batch, which is used to obtain intense yellow, orange and red colouration. It is obvious that these compounds present toxicological problems during production and recycling of these glasses.
The sol-gel process is also well known in the glass industry, e. g. for the production of thin inorganic coatings to obtain antireflective properties [2]. Hybrid sol-gel coatings have found long-term industrial use for the mechanical protection of polymeric lenses in the opthalmic business [3-4]. The high abrasion resistance of these Heteropoly-(organo)siloxanes is due to the fact that the small inorganic moieties (clusters or colloidal particles) growing during hydrolysis and condensation of liquid silicon or metal alkoxides are crosslinked by organic polymerization reactions in the presence of appropriate organo(alkoxy)silanes. Thus an intricate network or nanocomposite is formed after the curing step (thermally or photochemically) of films derived from the colloidal solutions by conventional techniques (e. g. spraying, s. figure 1).
The scheme of figure 1 also displays representative alkoxides and the practical means to

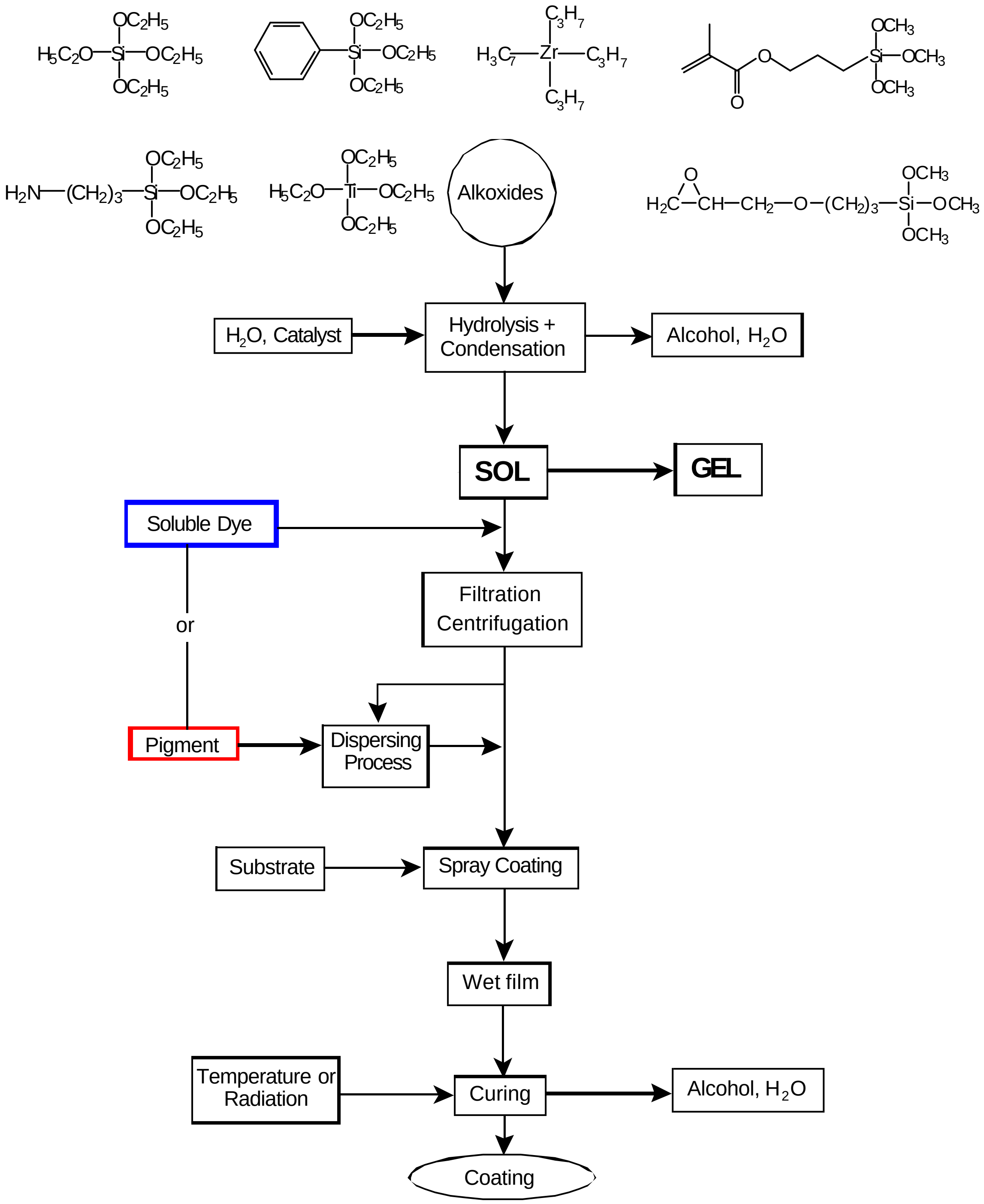

Figure 1. Flow chart illustrating the sol-gel processing of coloured hybrid coatings from silicon, (organo)silicon and metal alkoxides

introduce colour into the hybrid material. One possibility is to dissolve organic dyes in the solvents present in the sol after the hydrolysis of the alkoxides (alcohols of low molecular weight, like methanol, ethanol, n-propanol, n-butanol). This results in coloured transparent coatings, whereas pigments have to be subjected to a dispersing process to assure proper wetting and integration of the pigment particles into the hybrid matrix. Besides spraying, other methods like dip-, spin- or flow coating as well as roll or curtain coating methods can be applied. The curing step depends on the organic substituents present in the organo(alkoxy)silanes and is performed in relation to the thermal stability of the substrate, on glass surfaces thermal treatment at higher temperatures (up to 200 °C) is possible, whereby the thermal stability of the organic dyes or pigments has to be taken into account. Under these conditions, the time necessary to cure the coatings is rather short (a few minutes, s. [5]). The structure and the corresponding properties of hybrid sol-gel derived materials have been extensively investigated and reviewed throughout the last decade [6-9].

2. Development of hybrid sol-gel coatings for the decoration of crystal glassware

On glass surfaces a mixture comprising phenyl-tri(methoxy)silane, 3-glycidoxypropyl-tri(methoxy)-silane, 3-aminopropyl-tri(ethoxy)silane and aluminium-tri(2-butoxide) proved to meet the basic requirements of good adhesion, high abrasion resistance, variable colourability and sufficient shelf life. Within a few development steps, the proper choice of the inorganic and organic network forming constituents as well as copolymerizable additives resulted in a formulation [10] exhibiting also high resistance against alkaline media in commercial dish washing procedures. The properties of the respective sols and coatings produced from this formulation are summarized in table 1.

Property		**Method/Standard**
Viscosity	10,5 … 12,0 mm ^{2}/s (Clear-coat)	Capillary Viscometer
Solids Content	42-45 % (Clear-coat)	DIN 52316-A
Density	1.002 kg/m^3 (Clear-coat)	Pyknometer
Flash Point	301 K	DIN-ISO 3676
Spraying Conditions	Spray nozzle diameter 0,2 … 1,4 mm Pressure 1,5 … 3 bar	
Curing Conditions	433 K/2 h … 473 K/600 s	
Layer Thickness	8 … 12 µm	Profilometer
Adhesion	B 5-4	ASTM D 3359
Microhardness	Ca. 220 – 280 Mpa	Fischerscope H 100
Abrasion Resistance	1,3 … 2,3 % (Clear-coat, depending on epoxide content)	ASTM D 1044 (100 rev.)
Refractive Index	1,503 … 1,534 (Clear-coat, depending on epoxide content)	Abbé-Refractometer

Table 1. Properties and processing conditions of sols and coatings

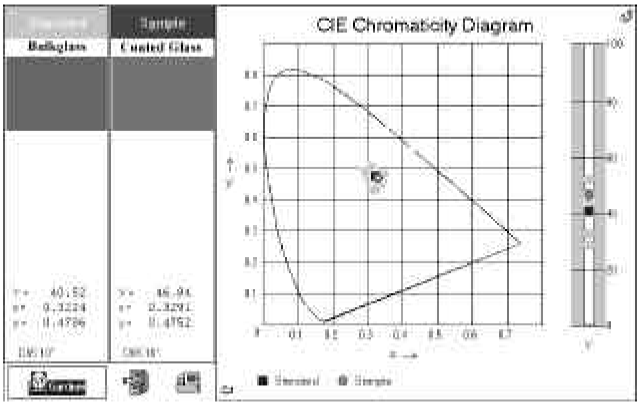

Fig. 2: Trial and error series of experiments performed to achieve the green colour of a bulk crystal glass (standard) by spray coating the surface of a colourless sample of the same type of glass

The colouration of the developed clear-coat system has been accomplished by dissolving commercially available organic dyes (e. g. Orasol®, Ciba-Geigy) or, alternatively, for opaque coatings by dispersing conventional organic or inorganic pigments (figure 1). The incorporation of the latter substances is realized with high speed dissolvers. The quality of the coated samples with respect to the colourimetric data of standard bulk coloured glasses is controlled through colour measuring devices (e. g. Coloursphere®, Byk Gardener). Figure 2 tinted standard green crystal glass. presents the results of a series of coating experiments with different dye containing sols to achieve the green colour of a mass tinted standard glass sample. After seven trials the colour of the coated glass sample closely matched the chosen mass. The hybrid sol-gel coatings due to their highly crosslinked nature and good adhesion to glass also show barrier effects against the diffusion of metal cations from the glass surface into liquids, which are in touch with the glasses. In the crystal glass industry this might be important for the reduction

of lead release of inner surfaces in the case of bowls or jars. Table 2 summarizes the lead release values of a crystal glass bowl coated inside in comparison to the data achieved without coating or by different pretreatments. It is evident from these experiments that the lowest values result from the hybrid sol-gel coating. The barrier effect of these layers against migration of lead ions resists even 100 cycles in the dishwashing machine. The alternative pretreatments show the initial release values after only a few cycles of dishwashing. Similar results have been achieved after colouration and pigmentation of the coatings.
The application of such coatings on glass ware containing foodstuff or beverages additionally requires that no migration of constituents of the layer itself occurs during use.

Pretreatment Lead Release (mg Pb/l)	None	Acid Polishing	Ammonium Sulphate	Silicone Resin	Hybrid Sol-Gel Coating
Initial Value	0,25	0,05	0,06	0,01	0,002
After 25 Cycles	0,26	0,24	0,09	0,25	0,003
After 50 Cycles	0,24	0,24	0,24	0,25	0,006
After 100 Cycles	0,25	0,24	0,25	0,25	0,02

Table 2. Lead release of original, pretreated and coated lead crystal glass surfaces (in accordance with DIN 51031)

The appropriate investigations have shown that with respect to German standards and to the US FDA regulations (§ 175.300) for resins there is no relevant migration into acidic (3 % acetic acid) or lipophilic (isooctane) solvents.
The coloured sols are applied by conventional spraying techniques onto crystal glass goblets by mounting the pieces horizontally underneath the spray nozzle and rotating them while spraying (figure 3).
Thereby the film obtained from the sol converts to a gel and the increasing viscosity prevents the film from developing inhomogeneities in the layer thickness. Afterwards, the gel is thermally cured to form the final coating.
This process has now been used by the crystal glass manufacturer Kristallglasfabrik Spiegelau GmbH since 1995 [11]. Figure 4 shows crystal glass objects coated in part as well as other glass products completely coated by transparent, coloured hybrid sol-gel layers. The successful marketing of these first products might lead to further interest in related industries.

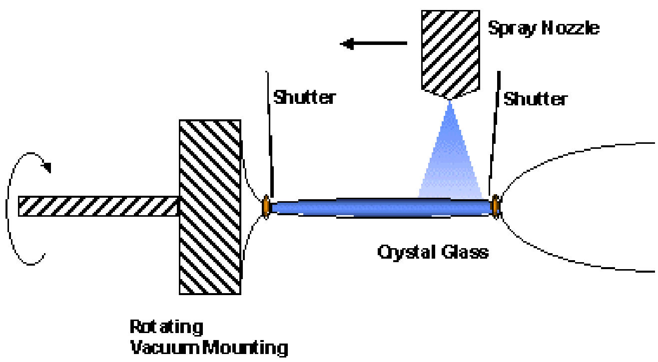

Figure 3. Decoration of crystal glass goblets via spraying of coloured hybrid sols

Figure 4. Glass ware demonstrating the still glassy appearance of crystal glass and other types of glasses after being spray coated with hybrid, sol-gel derived layers

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