

# Sol-gel coatings for the substitution of fluoride or lead containing white decorations on glass

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## Abstract

A SiO<sub>2</sub>-based sol was developed, which allows the deposition of thick (10 μm), crack free coatings on soda-lime glass. By homogeneous dispersion of TiO<sub>2</sub> particles (10 nm to 250 nm in radius) lead and fluorine free white paints are obtained, which can be applied by spray coating to as produced glass without any pretreatment. The coatings can be densified using rapid firing in a tunnel furnace at a temperature of about 560°C for about 30 min, which is typical for firing of enamels. After this densification step, the coatings show good adhesion on soda-lime glass (class 0 of cross hatch cut and tape test) and excellent chemical durability according to Kesternich-Tests.

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## 1. Introduction

The demand for decorated glass is increasing. For white decorations on glass either high fluoride containing (CaF<sub>2</sub>) glasses and controlled phase separation or enamels with TiO<sub>2</sub> pigments and large PbO (up to 80 wt%) containing frits are in use. Beside environmental problems, both types of materials have additional disadvantages either by volatilization of fluorine during the melting process or poor chemical durability against acid attack in case of high PbO content. Furthermore grey spots are obtained due to an uncontrolled reduction of Pb<sup>2+</sup> during firing [1].

Therefore the aim of this study was to develop a white lead-free sol-gel coating to be introduced into the production process of conventional enamels without significant changes.

## 2. Experimental approach

Sols were synthesized from methyltriethoxysilane (MTEOS, 40 ml) and tetraethoxysilane (TEOS, 12.0 ml). A colloidal silica sol (Bayer Levasil 300/30, 14.2 ml) was added to this mixture and afterwards hydrolysis and condensation was initiated using concentrated hydrochloric acid (0.36 ml). After cooling in an ice bath the sol was filtered to obtain a colorless and transparent coating material.

TiO<sub>2</sub> powder was used as a pigment on the one hand in a mixture of 4.0 g Merck 808 [2] and 2.0 g Degussa P25 [3], on the other hand 6.0 g Degussa P25 which was dispersed homogeneously in the as prepared sol by ultrasonic disintegration to obtain the corresponding spray coating sol.

On the one hand the decorated soda-lime glass substrates were heated in a muffle furnace to 280°C (heating rate 1 K/min) and kept at this temperature for 30 min. Afterwards temperature was increased with 0.5 K/min to 500°C and kept for 2 h. On the

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other hand decorated substrates were fired in a tunnel furnace using a conventional firing profile for enamels.

### 3. Results

White coatings on soda–lime glass have been obtained by the described preparation routes. The ratio of 250 nm TiO<sub>2</sub> to 10.5 nm TiO<sub>2</sub> of 2:1 lead to the best results with respect to the white appearance. The pigment to matrix ratio was optimized to 2:7 due to a minimum over all transmittance of about 34% and sufficient adhesion of the densified coating (mark 0 in cross hatch cut test).

It was found, that the rapid firing process, which was realized by firing at 560°C for 12 min in a preheated muffle furnace and by firing in a tunnel furnace, which is used for the firing of white enamels, did not lead to disadvantages with respect to optical appearance, adhesion or chemical durability, compared to the slow heating process with small heating rates. The adhesion of the rapidly fired white coatings was determined to be class 0 according to cross hatch cut and tape tests. The chemical durability was determined with Kesternich tests [4], using SO<sub>2</sub> gas atmosphere. No corrosion or changes in the optical appearance were served. Therefore the chemical durability of the developed decorations is much better than that of PbO-containing enamels.

### 4. Discussion

To obtain sufficient light scattering, high refractive index particles distributed in a low index matrix are suitable. To evaluate the appropriate particle size, calculations according to Eqs. (1) and (2) have been carried out [5,6]:

$$Q_s = 32\pi^4 c_p \frac{R^3}{\lambda^4} \left[ \frac{n_p^2 - n_m^2}{n_p^2 + 2n_m^2} \right] \quad (1)$$

where  $Q_s$  is the relative scattering cross-section,  $R$  is the radius of the particles,  $c_p$  is the the volume fraction of the particles,  $\lambda$  is the wave length,  $n_m$  is the refractive index of the matrix, and  $n_p$  is the refractive index of the particles.

The transmission can be calculated with respect to Lambert–Beer's law and is given by Eq. (2):

$$T = e^{-Q_s d}, \quad (2)$$

where  $d$  is the thickness of the matrix.

One can see that the dependence of the relative scattering cross-section upon the wavelength becomes evident for the transmittance especially for particles with radii smaller than the wavelength. From this calculation, TiO<sub>2</sub> with a particle radius of 250 nm seemed to be suitable. On the other hand, it was desirable to use low cost commercially available TiO<sub>2</sub>. To be able to vary the average particle size, it was decided to mix 250 nm TiO<sub>2</sub> with 10.5 nm TiO<sub>2</sub> and to evaluate the whiteness index.

To obtain a sufficient whiteness, coatings with high thickness have to be prepared. It is known [7–10] that sols prepared from MTEOS/TEOS allow the deposition of coatings with thicknesses of about 1.5 μm on glass after densification at 500°C. Methyl modified, particulate SiO<sub>2</sub> sols however allow the preparation of transparent and crack free coatings with thickness of 10 μm as shown in Refs. [11,12].

For this reason the SiO<sub>2</sub>-colloidal sol type was chosen as a matrix. At first investigations were carried out to vary the optical properties. Coatings were prepared containing TiO<sub>2</sub> particles with an average particle radius of about 10.5 nm (P25). Dip coatings has showed a slightly red color in the transmitted light. This effect can be explained by Eqs. (1) and (2) and the absorbance curves calculated from these equations.

The absorbance curves were calculated for three different wavelengths as a function of the particle size. The results are shown in Fig. 1.

and it can be seen that with 10.5 nm TiO<sub>2</sub> there is a transmittance of about 60% at a wavelength of 700 nm. This results in the slightly red color of the transmitted light obtained in the described experiment.

Mixtures of 250 nm TiO<sub>2</sub> particles (Merck) and 10.5 nm TiO<sub>2</sub> (Degussa) lead to a white appearance in reflected and transmitted light. The ratio of 250 nm TiO<sub>2</sub> to 10.5 nm TiO<sub>2</sub> of 2:1 lead to the best results with respect to the white appearance. For that no quantitative explanation can be given according to Eq. (1) due to the fact, that it is valid for very

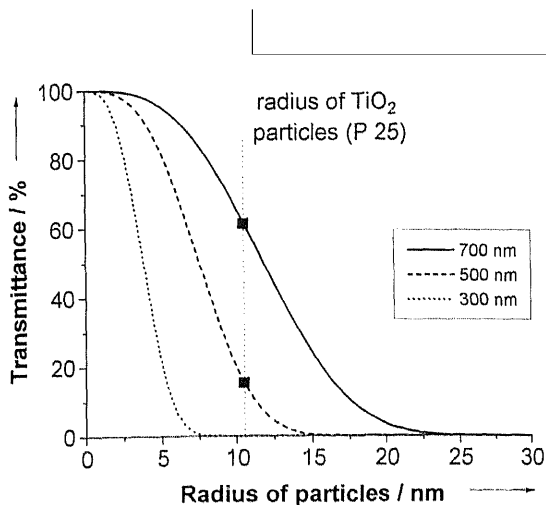


Fig. 1. Dependence of the transmittance upon the radius of particles in a composite material according to Eqs. (1) and (2) assuming 15 vol.% of  $\text{TiO}_2$  particles ( $\rho = 4.506 \text{ g cm}^{-3}$ ,  $n_D = 2.47$ ) in a 20  $\mu\text{m}$  thick silica matrix ( $\rho = 2.20 \text{ g cm}^{-3}$ ,  $n_D = 1.46$ ) including the particle radius of  $\text{TiO}_2$  P25 from Degussa.

small particles (Rayleigh scattering) and because the state of agglomeration of the particles is not known.

For the densification or for the firing of decorations a thermal treatment is necessary. During this treatment residual organic groups of the sol-gel matrix have to be removed. For the determination of the corresponding decomposition temperatures a DTA/TG measurement of the sol-gel material was carried out and is shown in Fig. 2.

The exothermic peak at 285°C represents the removal of residual ethoxy groups from TEOS and MTEOS. At 527°C the  $\text{CH}_3$ -groups from MTEOS

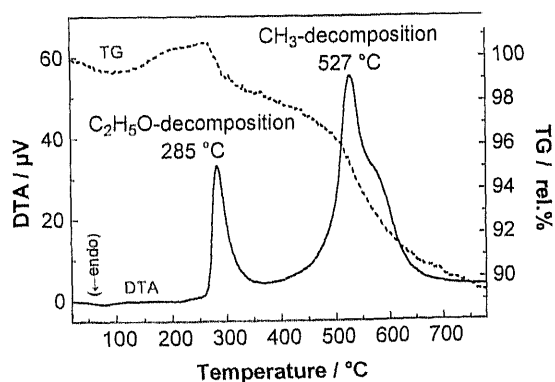


Fig. 2. DTA/TG-measurement (DTA straight line, TG dashed line) of the matrix system after drying at 120°C (heating rate 10 K/min in  $\text{Al}_2\text{O}_3$  crucibles in synthetic air).

decompose, which results in a total weight loss of about 10%. Heating rates of 1 K/min and 0.5 K/min and stops at 280°C (30 min) and 500°C (2 h) were used to allow a defect free burn off of the organics and densification of the coatings. This treatment results in a total processing time of about 23 h for the thermal densification, which is not suitable for industrial application. However as shown in Refs. [11,12] no pyrolysis was obtained of methyl group oxidation or decomposition leading to carbon or coloring effects. For this reason fast firing experiments were carried out.

In practice enamels are usually fired with heating rates up to 20 K/min allowing rapid processing. In first tests the decorations were fired in a preheated muffle furnace at 560°C for 12 min for the simulation of such processing parameters. The resulting decorations showed optical properties and adhesion equal to decorations fired using small heating rates. Because this method provided the possibility for a fast processing, decorations were fired in a tunnel furnace with a temperature-time-profile typical for the firing of enamels. From the DTA/TG curve shown in Fig. 2 it has to be concluded that  $\text{CH}_3$ -groups still remain in the coating, but do not affect the optical properties.

## 5. Conclusion

The investigations showed, that by using sol-gel coating compositions which allow the preparation of thick layers, white coatings can be prepared. Due to the fast firing these coatings are suitable for being used as lead-free white enamels or to substitute the fluoride coloring process in glass melting. Based on this results, an industrial process is being built up in present.

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