

# CORROSION OF SiO<sub>2</sub> AND TiO<sub>2</sub> SOL-GEL LAYERS IN WATER AND DILUTED HCl

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Submitted November 22, 2001; accepted January 29, 2002

**Keywords:** Glass corrosion, Sol-gel, Glass surface layers

*In the preparation of sol-gel layers based on SiO<sub>2</sub> and TiO<sub>2</sub>, use was made of alkoxides (tetraethoxysilane and tetrabutoxytitanium), which were hydrolysed with distilled water under the catalytic effect of HCl. The layers were applied on glass by the dip coating method. Following the drying of applied layers and their final heat treatment, their resistance to the effects of distilled water (pH = 6.1) and to aqueous solution of HCl (pH = 2.2) was studied by determining the content of sodium ions and silica in the leachates. The data obtained were compared with the values corresponding to untreated glass surface. It was found that the sol-gel surface layers reduce significantly the content of sodium ions and silica in leachates produced by the effect of the aggressive solutions. The anticorrosive protective effect in acid media depends on the composition of the coating. The best protection was provided by the silica layer, while the layers based on titanium dioxide were less effective.*

## INTRODUCTION

Sol-gel layers prepared on the surface of glass affect favourably the properties of the glass substrate, thus expanding the possibilities of utilizing glass in optics, communication technology, electronics and other additional fields of technology [1]. The inorganic sol-gel layers may also be used to protect the glass surface from the effects of aggressive solutions. Their performance in this respect depends primarily on their chemical composition, porosity and thickness of the layer. Layers containing SiO<sub>2</sub> and TiO<sub>2</sub> exhibit a very good resistance to atmospheric effects [2] but show a poor chemical durability with respect to alkaline solutions. This applies in particular to silica layers which dissolve completely when immersed for long periods of time in saturated Ca(OH)<sub>2</sub> solution [3]. In contrast to this, it may be expected that SiO<sub>2</sub> layers will resist acidic solutions. The present study had the aim to assess the chemical durability (with respect to acid solutions) of inorganic layers based on silicon dioxide and titanium dioxide. For this purpose, the content of sodium ions and silicon dioxide in leachates from glasses protected by the layers was determined and compared with the content of the components in solutions eluted from the original unprotected surface of glass.

## EXPERIMENTAL

The layers were prepared on microscope slides 75'25'1 mm in size, made of sodium-calcium glass by the firm Marienfeld. Before application the glasses were cleaned with a detergent, rinsed with distilled water and an 0.5M HCl solution, and after final rinsing with boiling distilled water dried in a drying oven.

Tetraethoxysilane Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> (TEOS) of purity exceeding 98% and a density of 0.933 g cm<sup>-3</sup> was the starting compound for the preparation of SiO<sub>2</sub> layers. The layers of titanium dioxide were prepared from tetrabutoxytitanium Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub> (TBuT), also of better than 98% purity and a density of 1 000 g cm<sup>-3</sup>.

The preparation of silicon dioxide layers consisted of hydrolysis of the tetraethoxysilane by distilled water, in which hydrochloric acid played the role of catalyst (e.g. [4,5]). TEOS was mixed with ethanol and water at a ratio of 1:5:9. Following adjustment of pH by hydrochloric acid the resulting mixture was transferred to a polypropylene vessel and homogenized for 40 minutes in the Heldolph electromagnetic mixer at 150 r.p.m. The layers were applied on the glass substrate by dip coating [6]. The glass specimen was immersed in the reaction mixture, whose viscosity had been adjusted by an additional admixture of ethanol, for a period of 30 seconds and then withdrawn at a rate which allowed a homogeneous continuous coating of the gel to be formed (20 cm/min.). The specimens with the layer applied were dried for 20 minutes in a drying oven preheated at 60°C. The final heat treatment consisted of 45-minute exposure of the specimens in a horizontal electric furnace at 450°C.

In the preparation of titanium dioxide layers [7], use was made of TBuT solution in ethanol (1:50) acidified with HCl. The subsequent procedure was identical with that employed in the preparation of silicon dioxide layers, with the exception of heat treatment which was effected at 500° C for a period of 45 minutes.

The preparation of the SiO<sub>2</sub> - TiO<sub>2</sub> layer containing 90 mol% SiO<sub>2</sub> was complicated by the considerably different rate of hydrolysis of the respective alkoxides, and by the poor solubility of TBuT in ethanol [2]. In the procedure eventually employed, the slowly reacting TEOS

was first hydrolysed in the mixture of ethanol, water and HCl while stirring for a period of 40 minutes. Only then TBUt was added to the reaction mixture together with a large excess of ethanol slightly acidified with HCl, and the resulting mixture was again agitated for 30 minutes. After diluting with ethanol, the mixture was suitable for dip-coating the glass specimens. The binary mixture was dried and heat treated under the same conditions as the single-component SiO<sub>2</sub> layer. We have failed to prepare homogeneous and integral layers with a higher TiO<sub>2</sub> content (50 mol%) by this procedure.

Chemical durability of the specimens with the surface layers with respect to distilled water ( $pH = 6.1$ ) and to hydrochloric acid ( $pH = 2.2$ ) was established by determining the content of silicon dioxide and sodium ions in the leachates. The conditions of the corrosion test are summarised in table 1.

Table 1. The conditions of the corrosion test.

$pH$	6.1 and 2.2 respectively
temperature (°C)	85
exposed area (cm <sup>2</sup> )	12
volume of solution (ml)	100
time (h)	3, 8, 16, 24, 48

During the static test, five specimens at a time were exposed to the aggressive solution in a polypropylene vessel. Sodium ions in the leachate were determined by atomic absorption spectrometry (AAS), and the content of SiO<sub>2</sub> by means of the SHIMADZU UV 1201 spectrophotometer by measuring absorbance of the blue form of molybdate-silicic acid at  $\lambda = 800$  nm wavelength.

## RESULTS AND DISCUSSION

The chemical durability tests were carried out on specimens with the surface layers and on slides with the original untreated surface, always in parallel on several specimens. The values of SiO<sub>2</sub> and sodium ions content in the leachate are means of four independently prepared samples. The time dependence of the content of sodium ions in leachate following exposure to distilled water is plotted in figure 1. The diagram shows that the surfaces provided with the protective layers exhibit a substantial decrease of Na<sup>+</sup> content in the leachate. The lowest content was found in leachates from glass protected by the SiO<sub>2</sub> layer, a somewhat larger one in leachates from glass with SiO<sub>2</sub> - TiO<sub>2</sub> layer, and relatively the highest content in the case of glass protected by the TiO<sub>2</sub> layer. Even in the latter case the values of Na<sup>+</sup> content in the leachate amounted to approximately half of the Na<sup>+</sup> content in leachates from original, untreated glass. The protective layers therefore slow down the process of interdiffusion Na<sup>+</sup> (glass)  $\rightleftharpoons$  H<sup>+</sup> (l) by obviously forming a barrier to diffusive movement of ions.

Figure 2 shows the time dependence of SiO<sub>2</sub> concentration in leachate during corrosion in distilled water. The specimens provided with the protective layer exhibit a significantly lower SiO<sub>2</sub> content in the leachate. The best protective performance was again shown by silicon dioxide layers. The distinctly lower content of SiO<sub>2</sub> in the leachate is indicative of the resistance of the layer proper, as well as of its retarding effect on dissolution of silicon dioxide from the original surface of glass. The layer of titanium dioxide prevents the dissolving of silicon dioxide to a significantly lower degree. However, even this layer, similarly to the case of sodium ions, resulted in reducing the content of silicon dioxide in the leachate, in the least favourable instance to half the value compared to the original unprotected surface.

Figure 3 shows the time dependence of the content of Na<sup>+</sup> ions in the leachate following exposure to HCl solution of  $pH = 2.2$ . The specimens provided with the protective layers again exhibited a distinct reduction of the content of sodium ions compared to the original surface, particularly in the case of the single-component SiO<sub>2</sub> layer. As demonstrated by figure 4, the SiO<sub>2</sub> content in the leachate was again significantly lower compared to the untreated glass surface.

A comparison of the corresponding diagrams shows that the highly acidic solutions ( $pH = 2.2$ ) somewhat increased the content of both SiO<sub>2</sub> and Na<sup>+</sup> ions in the leachate compared to distilled water. However, the SiO<sub>2</sub> layer has almost completely eliminated this effect, resisting the effect of the highly acidic solution almost identically as those of distilled water. Examination of the exposed samples under the microscope showed that even a 48-hour exposure produced no discernible changes in the surface. The results obtained show that the SiO<sub>2</sub> layer protects the surface of glass from attack by acid solutions, by slowing down the processes decisive for the corrosion rate, namely elution of sodium ions and dissolution of SiO<sub>2</sub>. In the case of specimens protected by the SiO<sub>2</sub> layer the corrosion rate is almost independent of time and much lower than in the case of samples with the original surface.

## CONCLUSION

The sol-gel layers of silicon dioxide and titanium dioxide, applied on the surface of glass by dip coating, reduce the content of sodium ions and silicon dioxide in the leachates following exposure to distilled water and aqueous solution of hydrochloric acid. The best protection was provided by layers of silicon dioxide, while combined layers of silicon dioxide and titanium dioxide were less effective, and the smallest retarding effect on corrosion by acidic solutions was attained by layers of titanium dioxide. The content of sodium ions and SiO<sub>2</sub> in leachates from glasses with a surface layer of silicon oxide was reduced to roughly one tenth of the values obtained with the original untreated glass.

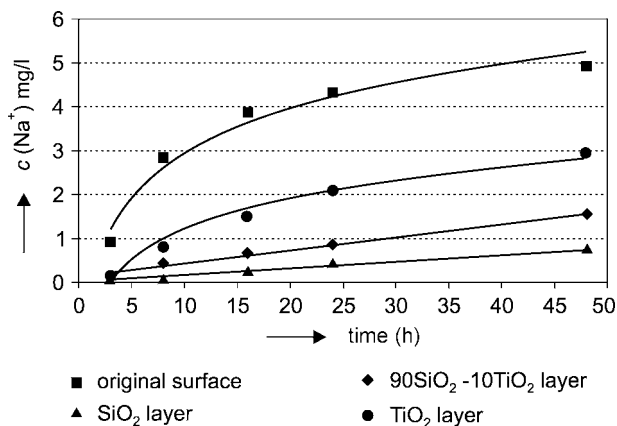


Figure 1. Concentration of Na<sup>+</sup> ions vs. time of exposure to distilled water of  $pH = 6.1$  at  $85^{\circ}\text{C}$ .

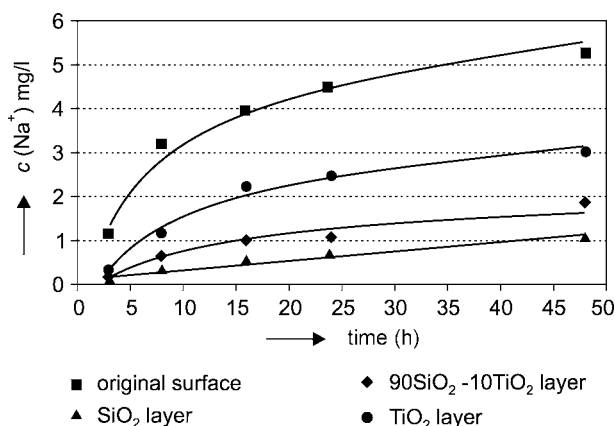


Figure 3. Concentration of Na<sup>+</sup> ions vs. time of exposure to HCl solution of  $pH = 2.2$  at  $85^{\circ}\text{C}$ .

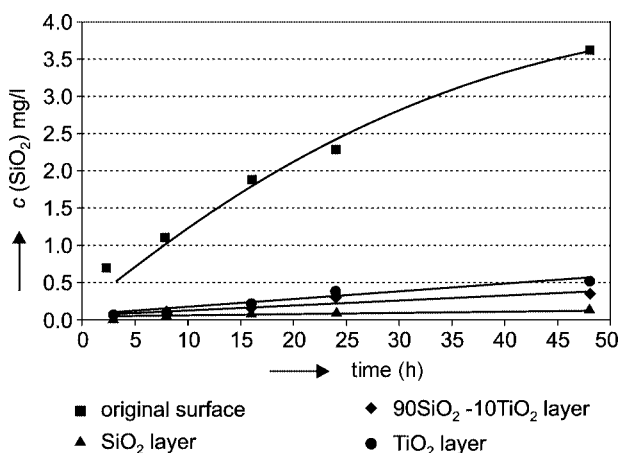


Figure 2. Concentration of SiO<sub>2</sub> vs. time of exposure to distilled water of  $pH = 6.1$  at  $85^{\circ}\text{C}$ .

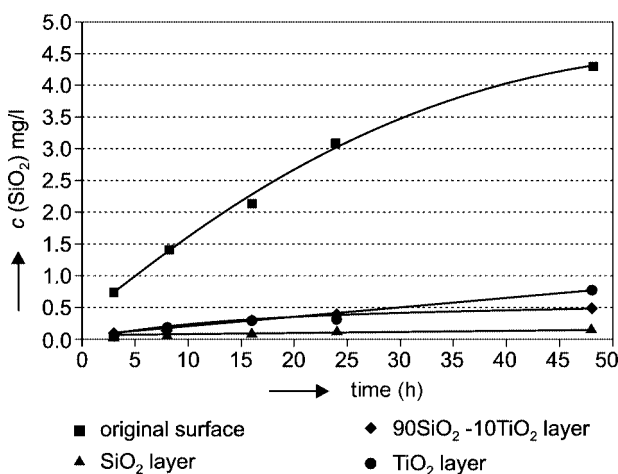


Figure 4. Concentration of SiO<sub>2</sub> vs. time of exposure to HCl solution of  $pH = 2.2$  at  $85^{\circ}\text{C}$ .

#### Acknowledgements:

The present study was financially supported by the Grant Agency of the Czech Republic (Grant No. 106/99/1419) and also is a part of Research Project CEZ:MSM 223100002.

#### References

- Uhlman D.R., Teowee G., Boulton J.: J.Sol-Gel Science and Technology 8, 1083 (1997).
- Wellbrock U., Beier W., Frischat G.H.: J.Non-Cryst. Solids 147&148, 350 (1992).
- Carturan G., Della Mea G., Paccagnella A., Soraru G.D., Rizzo C.: J.Non-Cryst.Solids III, 91 (1989).
- Nikolic L., Radonjic L.: Ceramics International 24, 547 (1998).
- Hsuaan Fu Yu, Shenq Min Wang: J.Non-Cryst. Solids 261, 260 (2000).
- Briker C.J., Scherer G.W.: The physics and chemistry of sol gel processing, Academic Press Ltd., London 1990.
- Zhai J., Zhang L., Yao X.: J.Non-Cryst.Solids 260, 160 (1999).

#### KOROZE SiO<sub>2</sub> A TiO<sub>2</sub> SOL-GEL VRSTEV VE VODĚ A ZŘEDĚNĚ HCL

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K přípravě sol-gel vrstev na bázi SiO<sub>2</sub> a TiO<sub>2</sub> bylo použito alkoxydů (tetraethoxysilanu a tetrabutoxitanu), které byly hydrolyzovány destilovanou vodou za katalytického účinku HCl. Pro nanášení vrstev na povrch skla byla použita metoda dip coating. Po vysušení nanášených vrstev a jejich konečné tepelné úpravě byla sledována jejich odolnost vůči působení destilované vody ( $pH = 6,1$ ) a proti vodnému roztoku HCl ( $pH = 2,2$ ) stanovením obsahu sodných iontů a oxidu křemičitého ve výluzích. Tato data byla porovnána s údaji o obsahu sledovaných složek ve výluzích z původního, nechráněného povrchu skla. Bylo zjištěno, že sol-gel vrstvy podstatně snižují obsah sodných iontů a zvláště výrazně obsah oxidu křemičitého ve výluzích po působení korozních roztoků. Ochranný efekt vůči korozi v kyselém prostředí závisí na složení vrstvy. Nejúčinněji brání korozi vrstva oxidu křemičitého, méně účinné jsou vrstvy s obsahem oxidu titaničitého.