

## PROTECTIVE COATINGS FOR MEDIEVAL STAINED GLASSES

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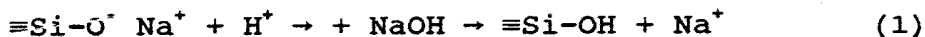
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## ABSTRACT

The corrosion protective effect of the surface modification of corrosion sensitive glass surfaces and of ORMOCER (= organically modified ceramic) coatings is investigated. The surface modification provides a modest protection, perhaps useful for additional protection in combination with external glazing. The advantage is the "invisibility" of the modification due to the thickness of several molecular layers. An effective protection can be obtained by a diffusion barrier pigmented ORMOCER coatings. First outdoor results on medieval glasses are very hopeful, but long period experience is necessary for wider application.

## INTRODUCTION

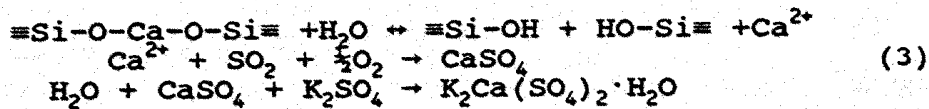
The corrosion of glass under the influence of H<sub>2</sub>O is a well known phenomenon. An ion exchange process takes place between a proton and an alkali ion, as a rule, according to (1).



The sodium ion in an aqueous environment forms NaOH, which can lead to a network dissolution of the silica matrix (2).

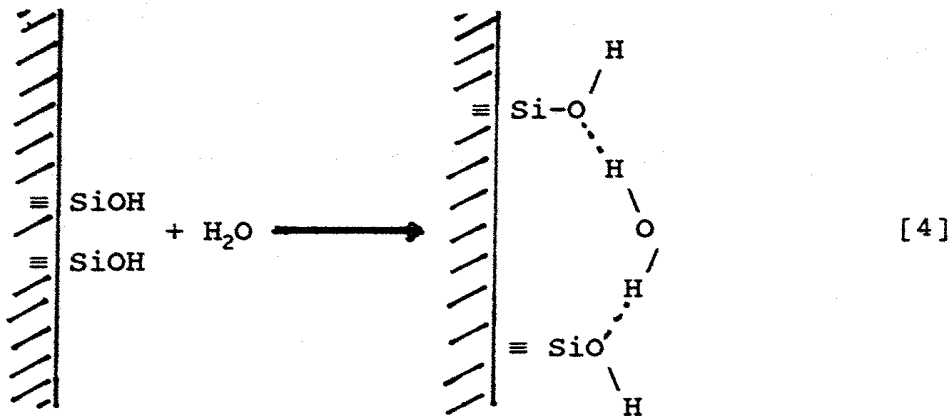


In presence of CO<sub>2</sub>, sodium carbonate will be formed. Potassium containing glasses basically react in the same way. Whereas in hydrolytic stable glasses, e.g., modern calcium silicate glasses the ion exchange is mainly restricted to the alkaline ions [1, 2], in glasses with high potassium and high calcium contents calcium ions are exchanged, too, as shown in [3] by ESCA measurements. In these glasses with about 18 mole-% of K<sub>2</sub>O as well as of CaO, in a corrosion experiment in humid air, K as well as Ca is leached out. As shown in this investigation, too, the leaching out of Ca is enhanced in the presence of SO<sub>2</sub>. This can be explained by the formation of syngenite, a potassium-calcium sulfate, which is almost insoluble in water. This leads to a drastic decrease of the Ca<sup>2+</sup> ion concentration in the diffusion path and to an increased driving force for the process in equation (3).



ESCA analysis including depth profiling shows that corrosion in presence of  $\text{SO}_2$  leads to a much stronger decay in Ca concentration in the glass surface than in a  $\text{SO}_2$ -free atmosphere. These findings explain the fact, that during the last decades a dramatic increase of corrosion on medieval glasses was observed. Most of these glasses have high potassium and high calcium contents as well.

The ion exchange with protons as the basic origin of the corrosion process at room temperature is not restricted to the liquid phase, but can take place with the humidity of the air. Due to an adsorption/desorption equilibrium on a glass surface, water molecules are present up to  $200^\circ\text{C}$  (4).



As a consequence of this leaching process, an almost alkaline-free high silica layer with a gel structure is formed, and by further condensation of  $\equiv\text{SiOH}$  groups within the gel layer stresses are built up, leading to cracks and loss of adhesion of the layer.

From the considerations above, a simple conclusion can be drawn: for successful corrosion protection of glass surfaces, the surface has either to be chemically stabilized or the presence of water on the surface has to be excluded. The simplest way of excluding  $\text{H}_2\text{O}$  seems to cover the glass surface with a transparent coating [4-6]. These coatings, however, have to be organic polymers, since low curing temperatures have to be employed not to deteriorate the glass surface gel layers. But it is well known that organic polymers are more or less permeable for  $\text{H}_2\text{O}$  diffusion due to their open structure. That means, at the interface between the glass surface and the coating  $\text{H}_2\text{O}$  molecules are present, and the exchange process can take place. It is only a matter of the permeability of the coating layers whether a decrease of the corrosion rate is obtained or not. If  $\text{Na}^+$  ions are transported to the interface, they cannot be removed by natural processes like rain. In this case, at the interface a highly concentrated corrosive alkaline solution can be formed,

leading to an even higher corrosion rate after a while than without protection layer. Therefore, if a coating technique is employed, one has to look very carefully for the  $H_2O$  permeability of the coating.

The progress of the gel layer formation can be followed by IR spectroscopy, as shown in fig. 1, by the formation of the OH stretching vibration ( $\Sigma SiOH + HOH$ ).

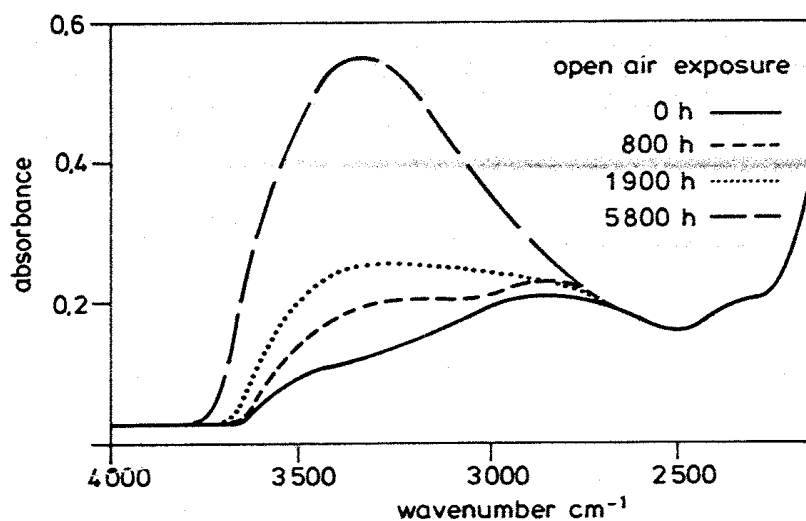


Fig. 1 IR spectra of corroded glasses of the composition (I) 48,0  $SiO_2$ /25,5  $K_2O$ /3,0  $Na_2O$ /15,0  $CaO$ /1,5  $Al_2O_3$ /4,0  $P_2O_5$  (wt.-%) [10].

This provides an easy mean to control the corrosion progress even in a very early stage. The corrosion follows a  $\sqrt{t}$  dependance and a diffusion controlled mechanism is assumed [11].

#### MOLECULAR LAYER PROTECTION

As already mentioned, the stabilization of the glass surface has to be regarded as a hopeful mean to protect the glass. In [7-9] is shown that the adsorption of  $Zn^{2+}$  on the glass surface leads to a remarkable decrease of the corrosion rate. This effect can be observed on low chemical durability composition (II), too, as shown in fig. 2.

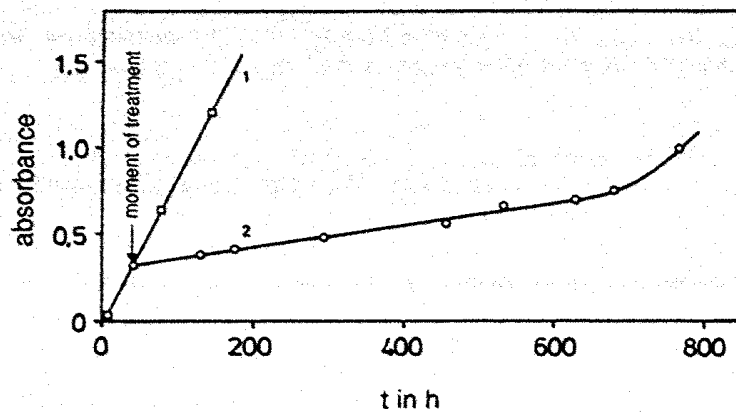


Fig. 2 Corrosion behaviour of a glass of the composition (II) 72,4 SiO<sub>2</sub>/22,7 K<sub>2</sub>O/0,3 Na<sub>2</sub>O/3,6 CaO/0,2 Al<sub>2</sub>O<sub>3</sub>/0,8 P<sub>2</sub>O<sub>5</sub> (wt.-%) treated with a Zn(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> solution at 40°C and heating to 150°C for 1 hr; 1 = untreated, 2 = treated glass [10], corrosion parameters: 80°C, 76% r.h.

The treated glass shows a remarkable lower corrosion rate, which lasts for about 700 hrs. Similar results are obtained with composition I (fig. 3).

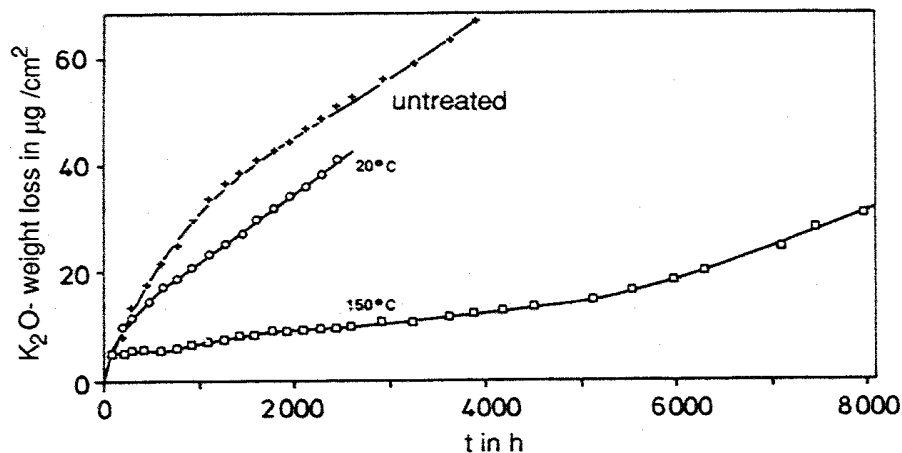


Fig. 3 Comparison of the untreated and treated glass composition I Zn(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> room temperature storage after treatment 150°hr temperature treatment after Zn treatment.

Fig. 3 shows clearly the effect of the treatment, and baking is necessary for a sufficient effect. This causes problems since a 150°C temperature treatment is critical for medieval glasses. The Zn treatment in the previous experiments was carried out at pH 8.4. Treatment at pH 5 leads to an improvement of the room temperature treated glasses (fig. 4).

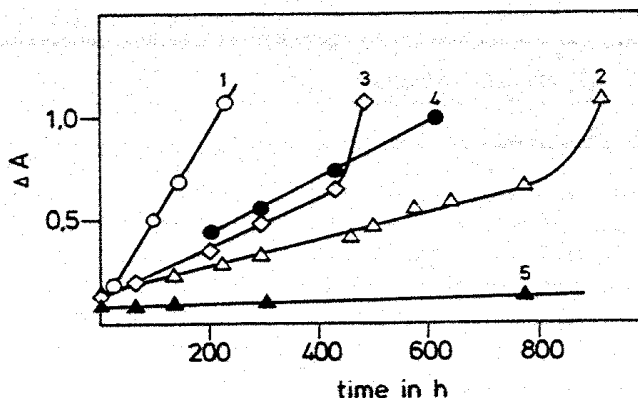


Fig. 4. Corrosion of medieval model glasses  
 1: (I) untreated;  
 2: Zn treated + 80°C treatment;  
 3: Zn + 25°C treatment;  
 4: 2 x Zn + 25°C treatment;  
 5: model glass of the composition  $60\text{SiO}_2/15\text{K}_2\text{O}/25\text{CaO}$  (III).

The acid treatment seems to be a method to be discussed as a corrosion inhibitor for easy cases; especially the double treatment results in a corrosion rate reduction over a 600 hrs period without change of mechanisms. Composition (III) is surprisingly stable compared to (I). This is due to the lower K and higher Ca content. The protective mechanism of Zn is unknown, but it correlates to the fact that Zn can improve the hydrolytic stability of glasses substantially. The better performance of the acid treatment can be explained by a better gel layer formation on the surface and in these gel layers,  $\text{Zn}^{2+}$  can be adsorbed. At higher pH values a network dissolution takes place, removing the gel layer whenever formed. As shown by ESCA analysis with a glass covered with a gel layer of several  $\mu\text{m}$ , a 15 min  $\text{Zn}^{2+}$  solution treatment leads to a  $\text{Zn}^{2+}$  infiltration depth of about 2 nm.

The chemical stabilization leads to a remarkable, but time limited decrease of the corrosion rate. Another principle to be tested is a surface modification to reduce  $\text{H}_2\text{O}$  adsorption on the surface. It is known from hydrophobing agents like  $(\text{MeO})_3\text{SiCH}_3$ , that a limited corrosion inhibiting effect can be observed. In [12], the effect of more voluminous modifying groupings was investigated. A model of the surface coverage is shown in fig. 5.

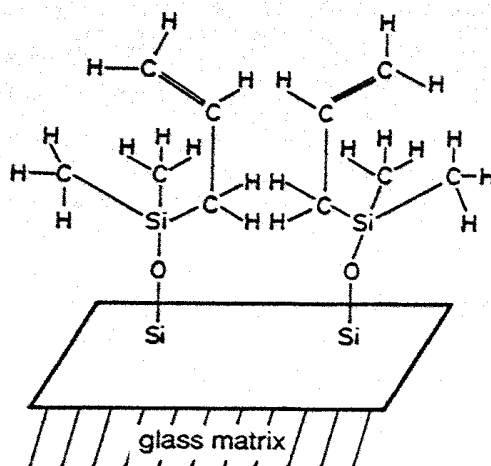


Fig. 5 Model of the surface coverage of allyl-dimethyl silane.

The allyl group, in addition to its sterical effect, should be able to be polymerized to form an organic polymeric structure. But, as experiments have shown, this is difficult to achieve. In fig. 6, the effect of the allyl silane modification for corrosion inhibition is shown compared to a methyl silane treatment.

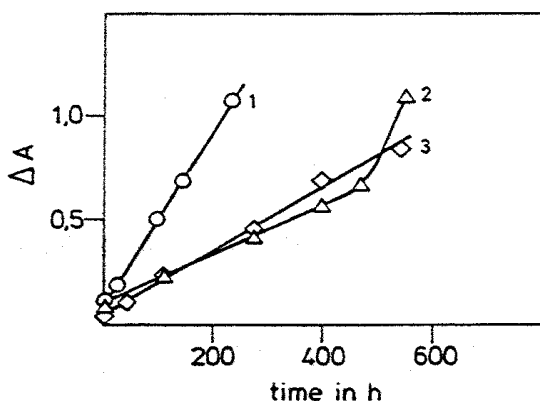


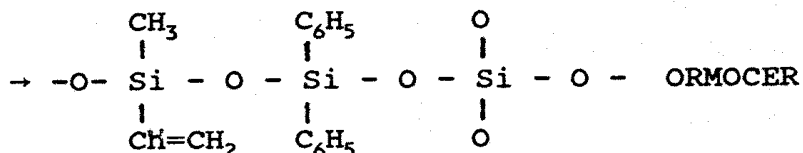
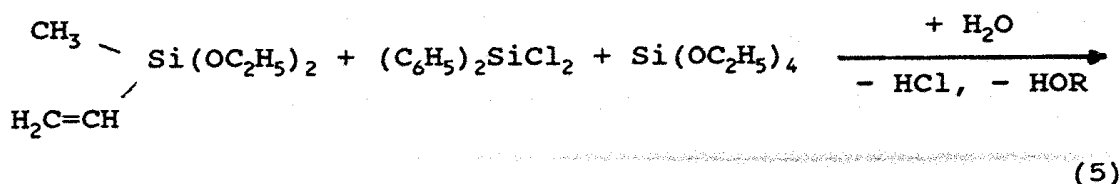
Fig. 6 Corrosion of modified glass surfaces; composition (II); 80°C, 76% r.h.; 1 = without, 2 = allyl, 3 = methyl modification.

The corrosion experiments show a corrosion inhibition similar to that obtained from the Zn modification experiments. No distinct advantage could be observed from the allyl modification.

Summarizing one can say that the surface modification by molecular layer obviously is not sufficient for a full protection of glasses with medieval compositions against weathering. But the question arises, whether this concept should be overthought in connection with external glazing, which is considered to be the choice number one, but which, how first results show, is not able to stop corrosion completely. The advantage of such treatments would be that they are invisible due to their molecular dimensions and that the amount to be employed is negligible compared to the amount of the bulk glass.

## THICK LAYER PROTECTION

In order to meet the requirements of conservation, thick layer protection has to be reversible and has to be able to be adapted to the pearance of the piece of art. In addition to this, from the material science point of view the coating has to provide a perfect adhesion to the corroded (or corroding) glass surface and the diffusion of H<sub>2</sub>O to the glass surface has to be decreased substantially. In [13] an ORMOCER has been developed (composition 35CH<sub>3</sub>(CH=CH<sub>2</sub>)SiO/62,5(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SiO/2,5 SiO<sub>2</sub>; molar ratio), which shows a perfect adhesion to glass surfaces even under extremely corrosive conditions. The material is prepared by a sol-gel reaction according to (5).



The vinyl group can be crosslinked, too. Adhesion tests on all three compositions (I, II and III) proved the excellent adhesion of coatings even under heavy corrosive conditions. The material can be employed from toluene or acetic acid ethyl ester solutions by dip or spray coating or by painting. But as one can see from fig. 7, the formation of crystalline corrosion products cannot be stopped.

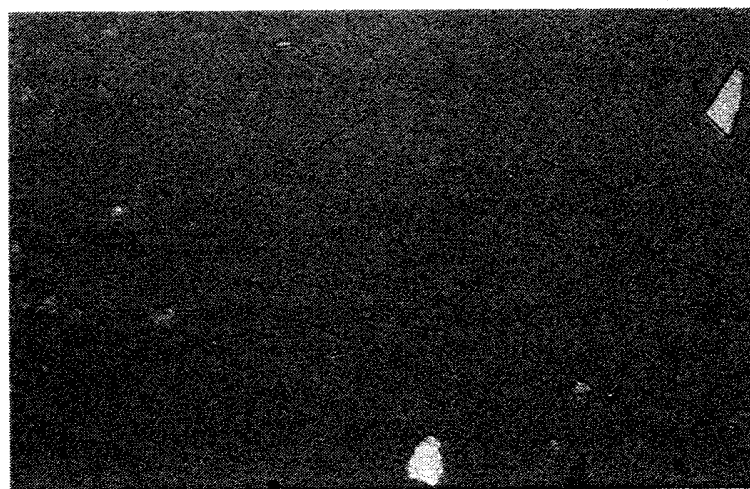


Fig. 7 Composition (I) coated with an ORMOCER after corrosion.

Microscopic investigations show that the crystallite formation occurs in the interface. This was attributed to the fact that the H<sub>2</sub>O permeation could not be stopped completely. In order to reduce H<sub>2</sub>O permeation, mica and glass flakes were added to the ORMOCER. These pigments with plate like geometries should be able to form an efficient diffusion barrier within the ORMOCER matrix according to fig. 8, which shows a three layer system including the pigmented barrier coating, especially developed for corroded medieval glasses according to [11].

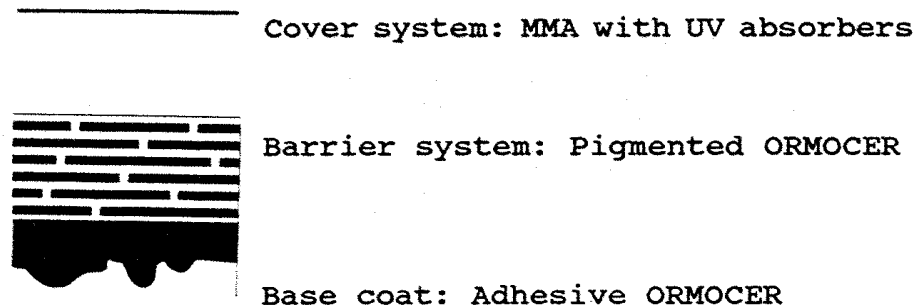


Fig. 8 Three layer protective system.

The mica pigmented coating system can be applied with spray guns, several layers are necessary. The refractive index of the coating system can be adapted to mica by blending the ORMOCER with soluble PMMA polymers. Glass flakes can be used, too, but they have to be employed layer by layer onto ORMOCER precoated, wet substrate by electric field assistance. The processing is shown in fig. 9.

The H<sub>2</sub>O permeability was investigated by permeation experiments. Therefore the H<sub>2</sub>O permeation was calculated according to (6) and (7).

$$\frac{1}{Q_{tot}} = \frac{1}{Q_L} + \frac{1}{Q_{carr.}} \quad (6)$$

$$P = \frac{m \cdot d}{F \cdot \Delta p \cdot t} \quad (7)$$

m = flux  
d = thickness  
F = area  
Δp = partial pressure difference  
t = time



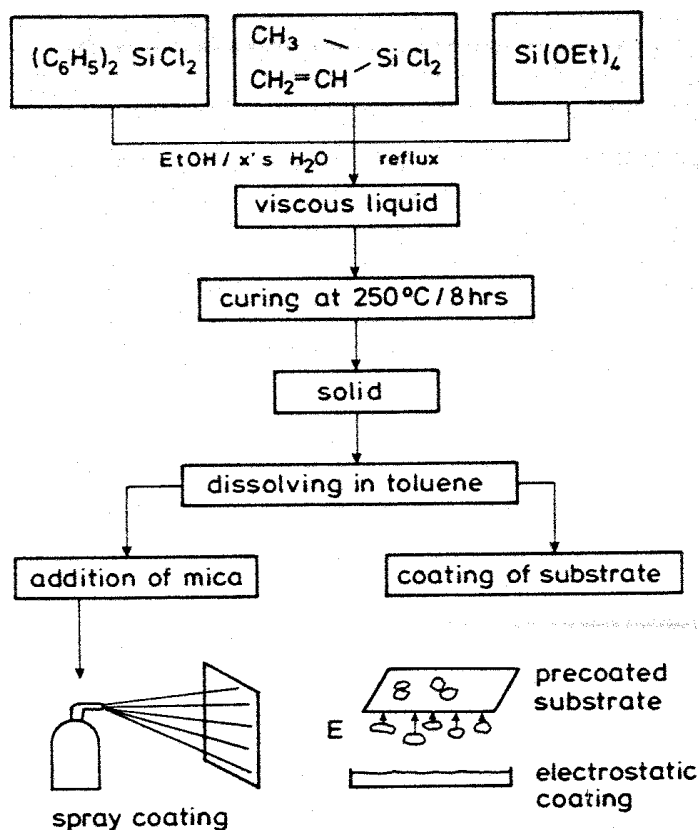


Fig. 9 Preparation and coating procedure for pigmented ORMOCER coatings

In Fig. 10, the results are given.

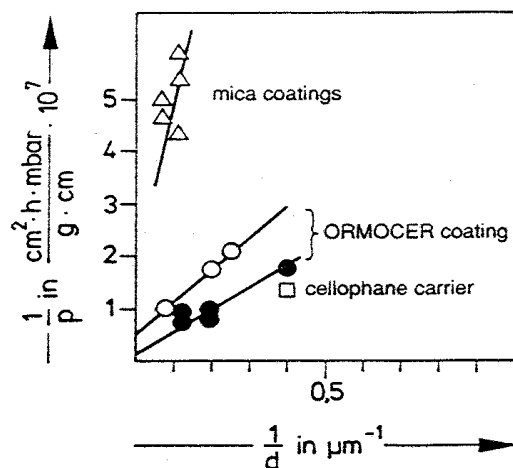


Fig. 10  $H_2O$  permeation at  $25^\circ C$  as a function of coating thickness for the cellophane carrier ( $\square$ ); two types of unpigmented ORMOCER coatings according to [12] ( $o$ ,  $\bullet$ ) and the mica pigmented ORMOCER coating.

The effect of the mica pigmented ORMOCER coatings is remarkable as the permeation decreases almost for one order of magnitude. The coating system is fully reversible and has been tested for several years in open air experiments and in lab crash tests. No negative experiences have been seen so far. In fig. 11, the open air exposure corrosion rate of the very sensitive

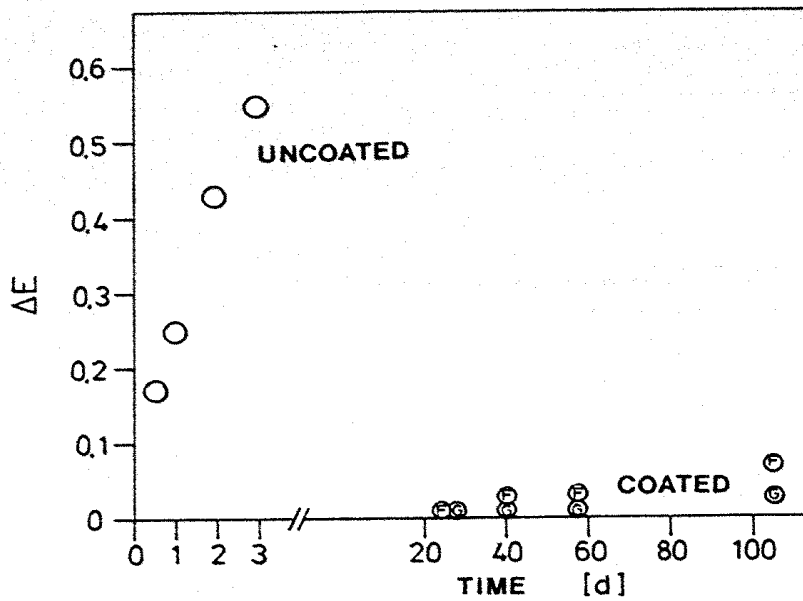


Fig. 11 Corrosion of coated and uncoated composition (I)  
 F: mica pigmented; G: glass flake pigmented  
 composition (I) is shown.

The experiments show, that especially the glass flake pigmented coatings show corrosion rates which are close to the experimental error. Outdoor experiments on an experimental glazed unit with medieval glasses do not show any signs of corrosion even after years (fig. 12).



Fig. 12 Experimental glazed unit from York Minster, UK; upper part: protected, lower part: unprotected.

## CONCLUSION

The experiments have shown, that only diffusion barrier coatings lead to a substantial decrease of the corrosion rate of the glass surface. This could only be achieved by the incorporation of barrier pigments. The coating in its present state is the end of a consequent development based on material science knowledge and on the input of restoration needs. How far these systems can be widely used cannot be predicted at the moment, since the period of experience is not long enough. Some special pieces of art, e.g., the King's windows of the dome of Cologne are already protected and future will show the long term effectiveness.

## ACKNOWLEDGMENT

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