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SURFACE FILM FORMATION ON E GLASS

By

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## Surface Film Formation on E Glass

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### Abstract

As part of a program concerned with the influence of surface properties of glass on the behavior of reinforced plastics, we report here on the formation of films on the surface of E glass on exposure to Oxalic acid solutions. No such films have been observed with 994 glass treated under identical conditions. As is well known, both of these glasses are employed in the production of glass reinforced plastic.

Evidence is provided that the film is associated with the  $\text{Ca}^{+2}$  ions in E glass. Experiments indicate that this ion is deficient in the surface of E glass. Thus fractured E glass exhibits much more rapid film formation than the native surface. Moreover, prior removal of the native surface on treatment with NaOH solution also results in more rapid film formation.

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## Introduction

Evidence that the surface structure of many glasses differs from that of the bulk material is found in work by Hensley<sup>(1)</sup> in 1951 and more recently by Anderson and Kimpton<sup>(2)</sup> and Trebilcock<sup>(3)</sup>. Hensley's work on the adsorption of tagged phosphate ions on "Pyrex" and soft glasses showed that adsorption is very weak on the surface except at cracks or other imperfections which penetrate the glass surface and expose the bulk glass. It was also shown that after alkaline attack on the glass, the adsorption is greatly increased. This difference in adsorption is thought to be due to the absence of polyvalent cations in the surface structure even though they are present in the bulk material, since polyvalent ions would normally act as adsorption sites for the doubly negative phosphate ions is due to the bulk structure being exposed by the dissolution of the surface.

## Results

Visual observation of this structural difference has been obtained by the authors of this paper. Treatment of fractured E and 994 glasses in a boiling pH 2 oxalic acid solution yielded the formation of an insoluble calcium salt on the E glass fracture surface. This surface layer did not appear on the 994 glass or on the native surface of the E glass. After removing the layer from the glass, spot tests (4), (5) were made which revealed  $\text{Ca}^{++}$ ,  $(\text{SiO}_3)^{--}$  and  $(\text{C}_2\text{O}_4)^{--}$  ions in this layer. Subsequent rinsing, however, removed the oxalate ion. Treatment of both glasses with

HCl produced no surface film on the 994 glass while a film did form on the E glass fracture surface. Spot tests again revealed  $\text{Ca}^{++}$ ,  $(\text{SiO}_3)^{-}$  in the layer.

Figures 1, 2, and 3 show microphotographs of untreated E glass, the oxalate treated free surface, and the treated fracture surface respectively. The network of lines seen in Fig. 2 are Griffiths' microcracks which have been made visible by the etching action of the oxalic acid. No film has formed on this surface. It is noted that the microcracks are also seen on this surface but are masked somewhat by the surface layer.

Figure 4 shows the native surface of the E glass after 48 hours treatment. The microcracks have widened and a slight film has started to form. This film begins at the crack lines and grows toward the interior of the matrix elements formed by the cracks. This is believed to be caused by a higher concentration of  $\text{Ca}^{++}$  ions in the region of the cracks, since not only do the cracks penetrate the surface into the bulk material, but diffusion of  $\text{Ca}^{++}$  ions would also be accelerated in these regions.

The native surface of E glass pretreated for 10 minutes with a .25N NaOH solution before treatment in the oxalic acid is shown in Fig. 5. A rather well developed surface film is seen covering about 80% of the glass. This indicates that the NaOH treatment has dissolved the native surface of the glass exposing the  $\text{Ca}^{++}$  ions of the bulk material.

## Discussion

There are three possible explanations for the absence of  $\text{Ca}^{++}$  ions in the surface structure.

1. The  $\text{Ca}^{++}$  may be removed by an ion exchange with  $\text{H}^+$  ions.
2.  $\text{CaO}$  may be vaporized during the formation of the glass.
3.  $\text{Ca}^{++}$  ions may produce a high surface energy and therefore tend to reside away from the surface.

It seems likely that the ion exchange mechanism is important in forming the surface structure.  $\text{Ca}^{++}$  atoms residing within an atomic layer of the surface would likely be effected by this mechanism, but since the ion exchange mechanism is diffusion controlled for  $\text{Ca}^{++}$  atoms more than an atomic layer away the effect would be negligible away from the surface monolayer. Volatilization of glass constituents is known to occur at elevated temperatures<sup>(6)</sup>, i.e. during formation. The process is generally considered to consist of two steps. First volatilization from the native surface and secondly volatilization from the surface layer now of a different composition. In some extreme cases, the surface created by the volatilization of certain constituents may be subject to extensive devitrification. It is seen, therefore, that volatilization may cause structural difference in the surface.

The final possibility for the absence of  $\text{Ca}^{++}$  in the surface is explained by Yates and Trebilcock<sup>(3)</sup>. It is well known from the Gibbs' isotherm that constituents which lower the surface energy

will concentrate in the surface region. Since the negative surface charge due to non-bridging oxygen atoms are probably effectively neutralized by  $H^+$  and monovalent ions the more highly charged  $Ca^{+2}$  ions may result in an increase in surface energy. However, more data is required concerning the influence of various ions on surface energy.

It is clear on the basis of the above work and that of others that the surface structure of E glass and other borosilicate glasses varies significantly from the bulk structure. As yet, however, the reasons for this are unclear. Since it is the surface structure which influences glass-coupling agent bonding, it would be of value to determine the reasons for this structural difference.

#### Acknowledgments

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### References

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Composition of Glasses, percent by weight

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	F <sub>2</sub>
E	54.5	14.5	10.0	15.9	4.4	0.5	0.4	0.3
994	64.0	26.0			10.0			

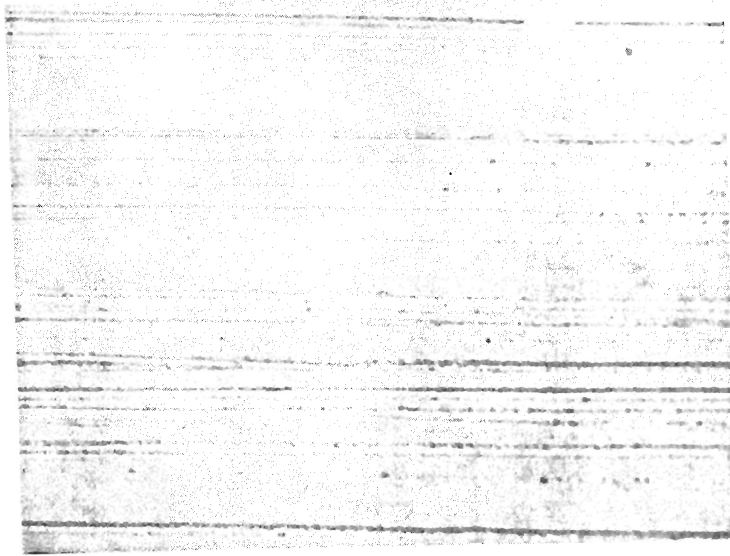


Fig. 1 Untreated E glass native surface 240X

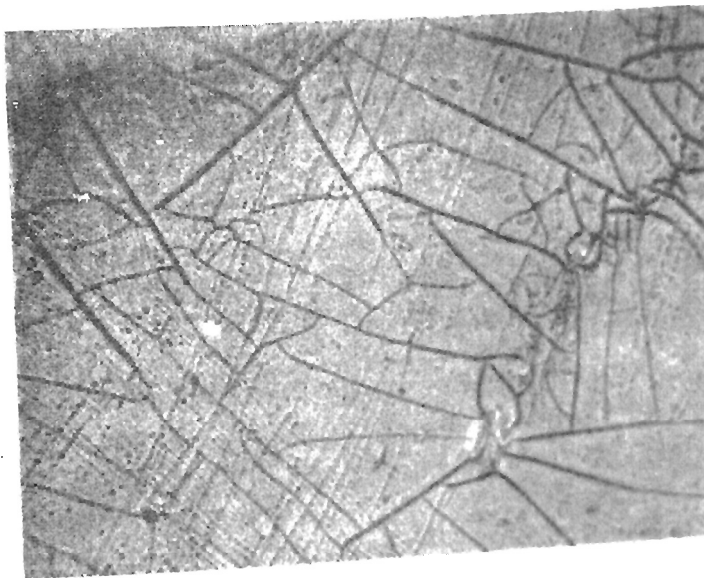


Fig. 2 E glass native surface after 24 hr. boiling in pH 2 oxalic acid buffer solution. 240X



Fig. 3 E glass fracture surface  
after 24 hrs. boiling in pH 2 oxalic  
acid solution. 240X



Fig. 4 E glass native surface after  
48 hr. boiling in pH 2 oxalic acid  
solution. 240X

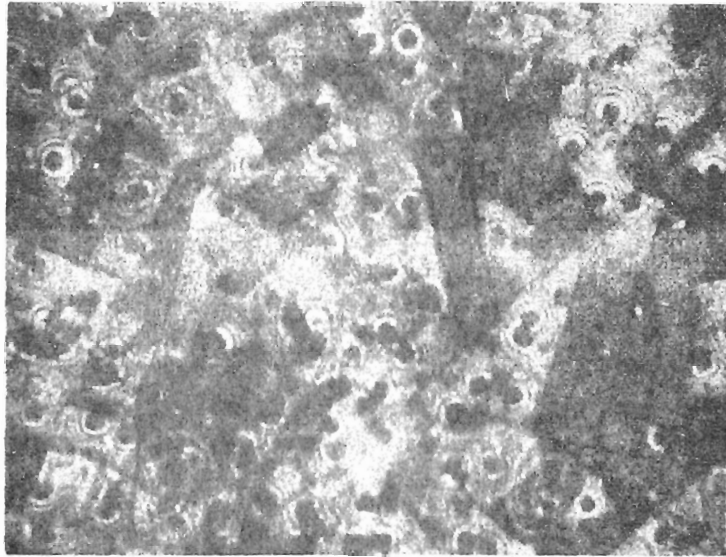


Fig. 5 E glass native surface  
pretreated 10 minutes in .25N NaOH  
before treating 24 hrs. in pH 2.  
oxalic acid solution. 240X



Fig. 6 E glass fracture surface  
treated 24 hrs. in boiling 1N HCl  
240X