

# Effects of alkaline solutions on tin oxide coated glass surfaces\*

G. L. Smay & J. S. Wasylyk

American Glass Research, Inc., Butler, Pennsylvania, USA

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*Heated soda-lime-silica glasses were treated with vapours of anhydrous stannic chloride to produce tin oxide coatings on their surfaces. The coated surfaces were exposed to various solutions of sodium hydroxide and changes in visual appearance of the coatings were noted. These changes were correlated with Auger compositional profiles through the coating and the substrate, coating surface microstructure changes observed with a scanning electron microscope, and x-ray diffraction results. The changes in the visual appearance of the coated surfaces were attributed to sodium hydroxide attack of the coating/glass interface which affected the light reflectance properties of the coated glass.*

Tin oxide coatings are applied to glass surfaces to produce a variety of effects, such as decorative multi-coloured coatings and transparent semiconductive films in electrical applications. On glass containers, tin oxide coatings in combination with organic lubricants increase the lubricity and scratch resistance of the surface. The thickness of the coatings in the decorative examples is generally greater than 150 nm in order to produce brilliant iridescent colours by a light interference phenomenon. Tin oxide thicknesses on glass containers must be considerably less than 150 nm to avoid such effects, thus providing essentially invisible coatings. However, it has been observed that even though tin oxide coatings may be applied to glass surfaces in thicknesses for which no interference colours result initially, exposure to solutions of sodium hydroxide over a period of time causes the coatings to exhibit a blue coloration. The purpose of the work summarised in this paper is to determine the mechanism of the change in visual appearance of tin oxide coatings.

## Experimental procedure

Soda-lime-silica glass samples of the wt% composition 73.3SiO<sub>2</sub>, 12.8Na<sub>2</sub>O, 11.0CaO, 1.8Al<sub>2</sub>O<sub>3</sub>, 0.9(K<sub>2</sub>O + MgO) and 50 × 50 × 5 mm in size were heated for 20 min in an electric muffle furnace main-

tained at 640°C. Each sample was removed from the furnace and treated with vapours of anhydrous stannic chloride in an air stream at 55% relative humidity after the glass surface temperature had cooled to 565°C as measured by an Ircon 710 (Ircon Inc., Niles, Illinois) infrared pyrometer. Coating parameters were adjusted to deposit 18 and 50 nm of tin oxide on the glass surfaces as measured by an American Glass Research Inc. Hot End Coating Meter. Following coating, the samples were heat treated in the muffle furnace as it slowly cooled from 640 to 430°C at a rate of 2 degC/min. The samples were then removed from the furnace and allowed to cool to room temperature. Selected coated samples were withheld from the heat treatment process and used as comparative standards in the structural evaluation portion of the investigation.

The coated and heat treated samples were exposed to the solutions listed in Table 1 for 30, 60, or 120 min at various solution temperatures. These tests were performed to determine the activation energy of the caustic attack mechanism and to ascertain the effect which additives to the caustic solution have on the overall reaction rate. Titration measurements showed that the sodium hydroxide concentration in each solution remained constant over the maximum exposure time. Sets of identically prepared coated samples were withheld from caustic exposure and were used as comparative standards.

All samples were then subjectively evaluated visually in reflected light to determine the degree of change in coating appearance relative to the appearance of the standard untreated coated samples. Each sample was viewed in a hooded chamber against a flat, black background under diffuse daylight

**Table 1.** Additives to the basic 4.5 w/o NaOH + 0.5 w/o Na<sub>3</sub>PO<sub>4</sub> solution

Solution	Additive	Concentration
A	None	—
B	PD-3675*	0.38 w/o
C	PD-3675	2 w/o
D	PD-3675	4 w/o
E	Aluminium	0.27 g/litre
F	Aluminium	2.7 g/litre

\*BASF Wyandotte Corp., Wyandotte, Michigan 48192

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fluorescent lighting and the appropriate changes in appearance noted.

Compositional profiles were obtained transversely through the coating/glass interface by Auger electron spectroscopy for 18 and 50 nm thick tin oxide coatings following a 60 min exposure to a caustic solution with no additives and for a 50 nm coating which had been exposed to a dilute solution of hydrofluoric acid. These profiles were compared with profiles obtained from the standard unexposed samples.

The physical microstructure of the 18 and 50 nm coatings exposed to caustic solutions A, C, and D for various times were investigated under high magnification using a scanning electron microscope. Various surface microstructural features were also analysed qualitatively with an energy dispersive x-ray spectrometer. The surface microstructures of as-deposited and heat treated samples not exposed to caustic solutions were also studied. Each of the sample areas examined was chosen to be representative of the general visual appearance of the sample.

X-ray diffraction studies were also performed on a sample with a 50 nm coating to determine if any crystallographic changes had occurred in the coating due to a 60 min exposure to caustic solution A.

## Discussion of results

### *Visual appearance*

The visual evaluations showed that the appearance of the 18 and 50 nm coatings changes with time of exposure to caustic solutions. Prior to exposure, both coating thicknesses were so thin that the only optical effect observed was a slight metallic grey sheen on the surface. This initial appearance changes with time of exposure to the caustic solutions first to a blue colour, then to a purple-brown colour, and finally to a crazed, easily removed film. This progression was interpreted as an attack of increasing severity upon the coating/glass system as exposure time increased. If this is true, the times at which specific changes in appearance occur might be used as measures of the reaction rate of the attack by caustic solutions on glass specimens coated with SnO<sub>2</sub>.

The results of the exposure of the 18 nm coating to caustic solutions containing additives C and D exhibited the same general trend as was seen with solution A, that is, increasing severity of attack with longer exposure times. However, the presence of the proprietary additives in these solutions inhibited the attack, the reaction rates generally decreasing with increased concentrations of additive.

### *Auger spectroscopy*

The Auger profiles obtained from samples exposed to caustic solution A did not show any significant differences when compared with those obtained from unexposed samples. However, Auger profiles obtained from coated glasses subjected to a dilute hydrofluoric acid solution, and which were observed to form a deep

blue coloration, revealed a concentration of fluorine at the coating/glass interface. The presence of fluorine suggests HF attack on Si-O-Si bonds at the interface to form Si-F bonds and an interfacial layer having compositional and optical properties different from those initially present.

### *Scanning electron microscopy*

Examination of the variously exposed coated surfaces revealed a wealth of detail. Heat treated coatings of both 18 and 50 nm thicknesses were found to have numerous angular holes as may be seen in Figure 1(a). Only samples with the 50 nm coating are shown since the same surface features are present with both coatings.

When the beam was placed in the centre of one of the holes, the x-ray spectrometer showed the presence of only the elements normally found within the glass: sodium, aluminium, silicon, and calcium. No tin was detected. Moving the beam to one side of a hole by a distance of approximately one hole diameter resulted in the detection of a tin x-ray signal with a corresponding attenuation in the glassy element intensities. Examination of the tin oxide coatings which had received no heat treatment showed that the holes are initially filled with sodium chloride crystals.<sup>(1)</sup> These crystals are formed during deposition by the reaction of chloride ions in the anhydrous coating material with sodium ions in the glass surface. Either a specific heat treatment subsequent to coating or exposure to aqueous or caustic solutions removes the sodium chloride, leaving a hole in the tin oxide coating.

The study also indicates as have others<sup>(2)</sup> that tin oxide coatings adhere firmly to glass substrates. This is indicated in our study by the uniformity of the electron emission from both the coating and the edges of the holes as seen in Figure 1(a). In general, tin oxide coatings which have been exposed to caustic solutions and exhibit a visual blue coloration, have essentially the same microstructural characteristics as heat treated coatings which have not been exposed to caustic solutions.

However, further examination of the two microstructures reveals that the coatings exposed to caustic attack exhibit a brightening effect around the edges of the holes in the coating as seen in Figures 1(b)-(d). This effect is due to enhanced secondary electron emission resulting from the existence of a sharp undercut edge surrounding the periphery of the hole, indicating that the coating is being undermined near each hole and is not bonded to the glass surface to the same degree as before exposure. Only the lower edges of the holes in the micrographs appear brightened due to the orientation of the sample in relation to the electron beam and the electron detector. Rotating the samples under the beam of the scanning electron microscope indicated that the lower edges of the holes as viewed always exhibited enhanced electron emission.

Upon continued exposure to caustic solutions, the tin oxide coatings became hazy in appearance and were found either to flake spontaneously from the glass surface or to be easily removed by a light

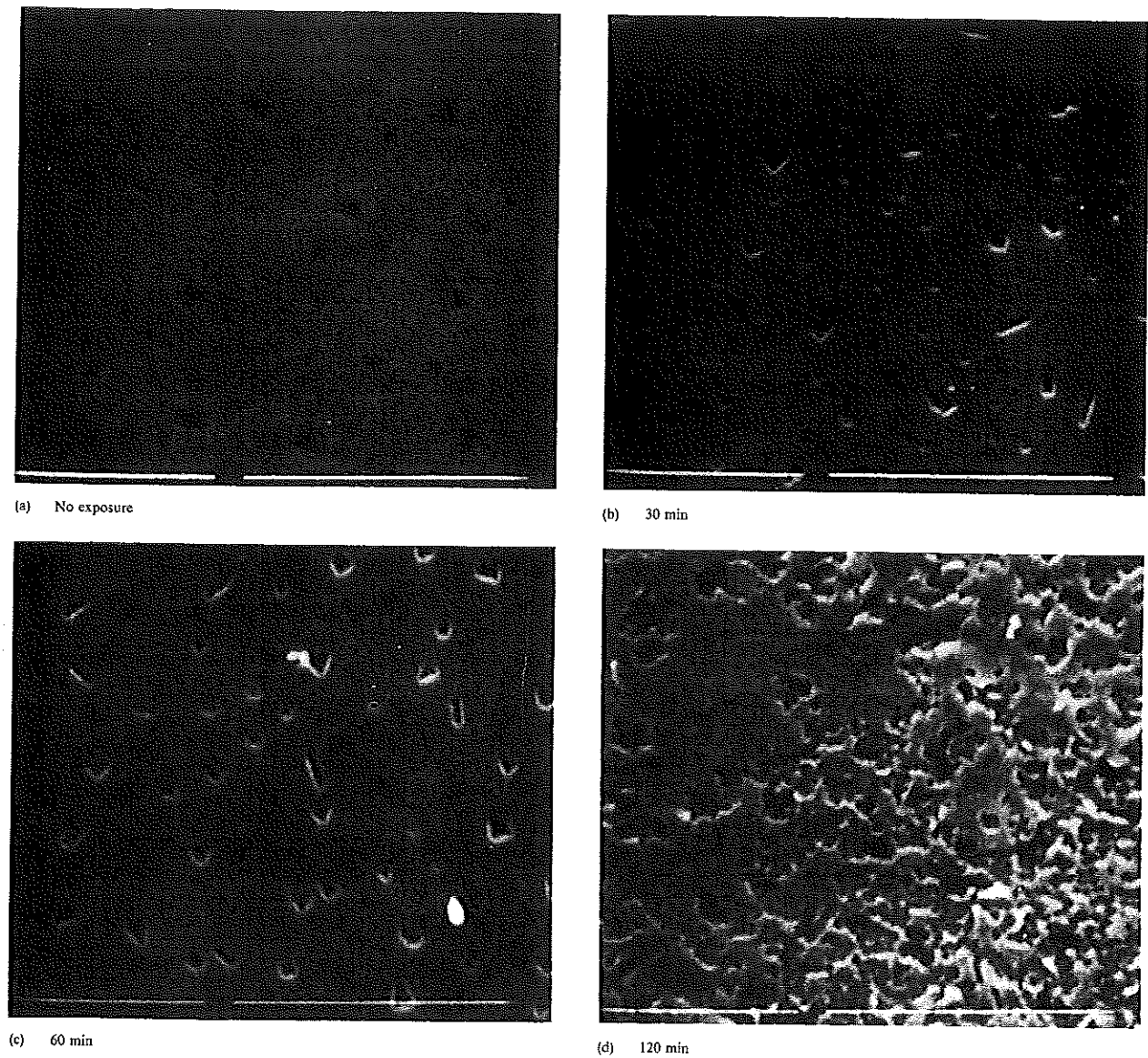


Figure 1. Micrographs of 50 nm tin oxide coatings after exposure to solution A for various times. Space between markers =  $0.5 \mu\text{m}$

rubbing. These advanced stages of caustic attack were correlated with microstructural disruption in the continuity of the coating as seen in Figure 1(d).

The micrographs of the tin oxide coatings exposed to caustic solutions C and D indicate that the microstructural changes which took place in these coatings were the same as those in coatings exposed to caustic solution A. However, brightening of the edges of the holes was delayed to 120 min.

Examination of HF treated coatings revealed microstructures virtually identical to those found in samples exposed to the caustic solutions, together with the same edge brightening effect. These results, interpreted with the HF Auger results and the fact that HF solutions are not known to attack tin oxide coatings,<sup>(2-4)</sup> indicate that an attack on the interface between the coating and the glass is responsible for the visual blue coloration.

#### X-ray diffraction

These data indicated slight differences between the 50 nm coating before and after exposure to caustic solution A. Before exposure, the coated sample exhibited a pattern characteristic of an amorphous silicate material with no evidence of any crystalline tin compounds, the tin oxide coating being too thin to produce any tin oxide diffraction peaks. However, after 60 min exposure, the diffraction pattern for  $\text{CuK}\alpha$  radiation exhibited a small peak centred at  $2\theta = 26.6^\circ$  superimposed on an amorphous background. This peak is characteristic of a crystalline or ordered  $\text{SiO}_2$  structure. These results indicate that the caustic treatment produces a modification at the interface, creating a more ordered silica structure following an alkaline attack process than exists prior to caustic treatment.

### Reaction rates

As mentioned earlier, the time necessary to attain the faint blue colour can be used as a measure of the reaction rate of the caustic attack and this was determined as a function of additive concentration for various temperatures. It was found that the reaction rates increase with increasing temperature of the caustic solution and decrease with increasing additive concentration. The increase in reaction rate with increasing temperature suggests that the reaction of sodium hydroxide solutions with coated glass surfaces is an energy activated process and should follow an Arrhenius type of behaviour. A semilogarithmic plot of the time to create the blue coloration should therefore yield a linear relationship with temperature, whose slope can be used to determine the activation energy of the sodium hydroxide attack.

Such plots showed an excellent linear fit of the data, as may be seen in Figure 2. Activation energies of 18.7, 19.1, and 18.8 kcal/mole have been calculated for the solutions containing 0, 0.27 and 2.7 g Al/l and 18.7, 21.3, and 20.9 kcal/mole for the solutions containing 0, 0.38, and 2 w/o of the Wyandotte additive. These values are in good agreement with the literature values of  $18 \pm 2$  kcal/mole for the reaction of sodium hydroxide solutions with soda-lime-silica glass surfaces.<sup>(5,6)</sup> Since these activation energies are all similar and could be fitted to one linear function, one may infer that the general reaction mechanism is the same regardless of the additives in the caustic solution. The presence of the additive serves simply to reduce the overall reaction rate. The basic reaction mechanism, therefore, must be an attack by the hydroxyl ions from the caustic solutions on the Si-O-Si bonds of the glass at the coating/glass interface.

### Mechanisms of attack

Additional evidence not shown here has demonstrated that the occurrence of the blue coloration as a function of exposure time also applies similarly to SiO<sub>2</sub> and TiO<sub>2</sub> coatings on soda-lime-silica glass, indicat-

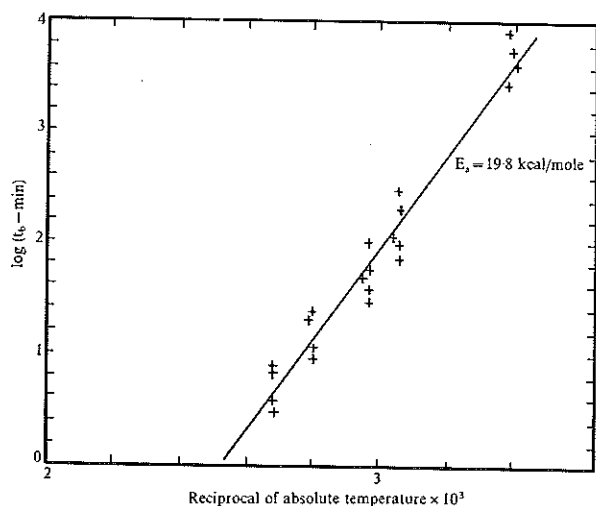


Figure 2. Arrhenius plot for the onset of blue coloration

ing that the change in visual appearance is independent of the type of coating material.

Hudson & Bacon<sup>(7)</sup> and, recently, Hench<sup>(8)</sup> showed that the addition of aluminium ions to sodium hydroxide solutions retards the attack on and dissolution of soda-lime-silica glass surfaces. The retardation is attributed to the formation of aluminosilicates on the surface. It is likely that an aluminosilicate layer is being formed in the interfacial region in our tests with the aluminium additive since the change in appearance results from an interfacial attack and the addition of aluminium ions to the caustic solutions retards this change. A similar mechanism is also proposed for solutions with the Wyandotte additive, in which zinc is believed to be the active metal. In this case a zinc silicate layer is assumed to be responsible.

As indicated in Figure 3, the caustic attack is directed at the coating/glass interface, changing its light reflectance characteristics. The caustic solutions cause compositional changes at the interface in which Si-O-Si bonds are attacked by the hydroxyl ion to form SiOH groups.<sup>(4)</sup> These silanol groups then recombine to form a more ordered Si-O-Si structure. The altered region increases in thickness with time and it possesses optical properties sufficiently different from those of the untreated coated glass to cause interference phenomena with the tin oxide film. The coated surface now exhibits a visual blue coloration. No changes in Auger profiles were noted for the caustic attack on coated glass since little or no change in the oxygen or silicon content of the interface would occur as a result of the attack.

When tin oxide films exhibiting interference colours ranging from third order at the centre of the sample to first order or less at the edges were prepared and then subjected to caustic solutions, the coatings were affected only where they were thinnest. The coating was observed to flake away from the glass surface in those thin regions after prolonged exposure. This result

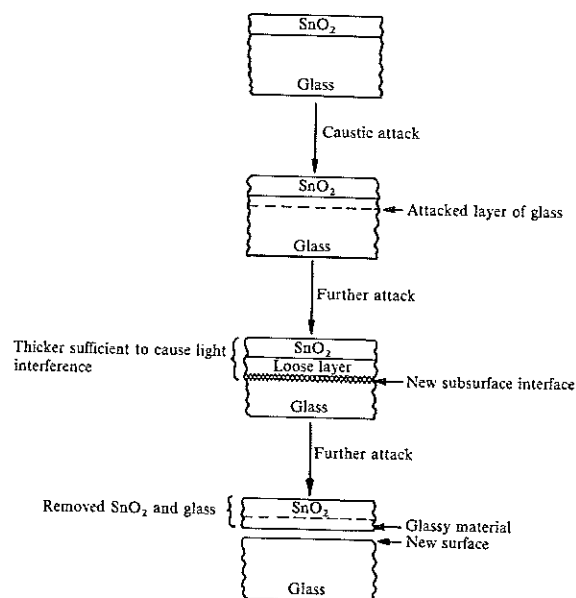


Figure 3. The physical mechanism of blue coloration

indicates that tin oxide layers with thicknesses that yield third order colours are less permeable to caustic solutions than the thinner layers which give first order colours.

The holes in the tin oxide coatings provide the caustic solutions with an obvious avenue of attack to the coating/glass interface. To determine whether the coating itself is permeable, a series of tin oxide coatings were deposited on soda-lime-silica glass samples using dibutyl tin diacetate. Since this material is free from chloride ions, no sodium chloride would be formed, the result being a continuous, hole-free SnO<sub>2</sub> coating on the glass surface. Examination by the scanning electron microscope of the coatings deposited by this method revealed complete surface coverage. However, exposure to caustic solution A at 65°C resulted in the appearance of a blue coloration. This indicates that such tin oxide coatings, ranging from 18 to approximately 50 nm thick, are permeable to caustic solutions, most probably along columnar grain boundaries or other defects in the structure of the coating.<sup>(2,9)</sup>

### Conclusions

Sodium hydroxide solutions attack the interface between metal oxide coatings and the soda-lime-silica glasses on which the coatings are deposited. The mechanism is postulated to be a hydroxyl attack on the Si-O-Si bonds, creating SiOH groups which can recombine into a more ordered Si-O-Si structure possessing physical and optical properties different from those of the bulk glass.

The increase in depth and differences in physical and optical properties of such a reaction layer, combined with the thickness of the tin oxide layer, leads to an optical interference phenomenon which produces a change in the visual appearance of the coating. For prolonged exposure times, the reaction layer reaches such a depth that mechanical forces arising from differences in expansion characteristics between the tin oxide coating and the glass surface cause the coating to be removed from the surface.

Caustic solutions gain access to the tin oxide coating/glass interface through holes left in the coating by the removal of sodium chloride crystals, either by sublimation during heat treatment or by dissolution during exposure to caustic solutions; alter-

natively they may permeate through structural defects such as grain boundaries in the tin oxide coating.

The onset of the blue coloration was found to be independent of coating thickness and method of depositing the metal oxide over the range 18 to 50 nm. However, coatings with thicknesses corresponding to third order interference colours were found to be less permeable to caustic solutions.

The change in appearance of tin oxide coatings was dependent on the temperature of the sodium hydroxide solution. The time to form a blue colour decreased (the reaction rate increased) with increasing temperature.

The reaction rate decreased with increasing concentrations of aluminium or Wyandotte additive in the caustic solution. This effect is postulated to be due to the formation of an aluminium or zinc silicate interfacial layer which slows the overall reaction.

Even though the reaction rate is different for caustic solutions containing different amounts and types of additive, the activation energies were generally the same for all solutions tested. This suggests that the mechanism causing the change in appearance is basically the same regardless of the concentration or type of additive in the sodium hydroxide solution.

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