How to Prevent Glass Corrosion

In the article below "How to Prevent Glass Corrosion" by Paul F. Duffer (Glass Digest, November 15, 1986), Dr. Duffer explains the chemical mechanisms causing glass corrosion and the conditions under which it can exist. The article also covers interleaving systems and the restoration of lightly corroded glass. This article should be of particular interest to fabricators of mirrors or MSVD coated glass since these products are highly sensitive to even very light stains.

How to Prevent Glass Corrosion
Glass + Moisture = Stain
by Paul F. Duffer

During the past 100 years, commercial flat glasses have acquired a reputation as being among the most durable of materials used in the construction and fabrication industries. This is not surprising, for our common, day-to-day experiences tell us that glass seems to be immune to any form of degradation.

Except for those of us involved in glass research, the mere mention of glass corrosion or staining to most people receives a skeptical response. Unfortunately, glass really can corrode. In fact, glass damaged by staining and corroding has resulted in losses to glass manufacturers and fabricators amounting to millions of dollars. Although the phenomenon itself is often misunderstood, the end result of the corrosion process is a glass product that is unsuitable for fabrication or installation.

Thus, the particular circumstances under which staining or corroding occurs need to be addressed, so that glass handlers and others who may encounter corrosion-related problems when dealing with glass can know the best way to prevent them.

For years, scientists have known that water reacts with commercial soda-lime-silica glass compositions. While the interaction may be subtle and slow paced, appearing to be neither significant nor spectacular to the casual observer, the outcome can be serious to glass manufacturers and fabricators.

Whenever water is permitted to remain on a glass surface for longer than a moment, several unique chemical reactions can occur that cause corrosion damage, or stain. The first of these begins almost immediately after water contacts the glass, even at room temperature.

In technical terms, this initial reaction at the glass surface is characterized by a diffusion-controlled ion-exchange process involving sodium ions in the glass and hydrogen ions from the water. Stated more simply, water readily leaches, or takes, sodium ions from soda-lime-silica glasses. This leaching process, which glass scientists commonly refer to as Stage 1 corrosion, can be expressed by the following reaction scheme:

$$SiONa \text{ (glass)} + H_2O \text{ (solution)} \longleftrightarrow SiOH \text{ (glass)} + NaOH \text{ (solution)}$$

If Stage 1 corrosion is allowed to continue uninterrupted for only a few minutes, pH levels gradually increase from an accumulation of hydroxide ions (OH^-) in solution. Eventually, the increase in alkalinity of the contact solution will initiate other, more damaging reactions. Therefore, the leaching process needs to be examined more carefully.

The reason solution pH increases can be explained by basic chemistry principles. Pure water is a weak electrolyte that

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spontaneously breaks down partially into hydrogen ions (H^+) and hydroxide ions (OH^-) according to the simplified expression: $H_2O \longleftrightarrow H^+ + OH^-$. At 25° C (77° F), this equilibrium condition is described by an ionization constant, Kw, as given by the equation $K_w = 1 \times 10^{-14} = (H^+)(OH^-)$.

In other words, at a given temperature, the product of the hydrogen ion and hydroxide ion concentrations remains constant. For water in contact with a glass surface, however, the exchange process tends to deplete the supply of hydrogen ions in solution, causing an imbalance in the equilibrium represented by the equation just given.

In order to reestablish equilibrium, more water molecules dissociate, producing additional H^+ and OH^- species. As the original quantity of OH^- was not affected by the exchange process, further dissociation of H_2O results in an increase in hydroxide ion concentration and a commensurate rise in pH.

Recent experiments with commercial float-produced glasses have shown that an unsubdued ion-exchange reaction can produce contact solution pH values as high as 9.9, which is highly alkaline.

As long as solution pH levels remain well below 9.0, Stage 1 corrosion proceeds as the predominant reaction at the glass surface. During this period, optical quality and surface integrity remain essentially unaffected. In fact, extensive laboratory studies have revealed that the leaching process can be carried out on float glasses for several months at 140° F without any adverse effects on surface quality being observed, so long as increases in solution pH levels are controlled. However, unrestrained State 1 corrosion can lead, as previously mentioned, to highly alkaline conditions.

Once solution pH levels reach 9.0 or greater, the second important reaction in the glass corrosion process - Stage 2 - begins. At this point, hydroxide ion concentration is sufficient to begin attack of the silicate network. As shown in the following equation, the main reaction is the severing of silicon-oxygen bonds (the glass itself is slowly dissolved): Si-O-Si (glass) + OH^- (solution) $\longleftrightarrow$ Si-OH (glass) + O-Si (dissolved glass; sodium and calcium silicates).

During the beginning stages of this reaction, microscopic pitting of the surface occurs. If the reaction is allowed to continue, surface damage will become more apparent, and the glass may have a widespread iridescence or a dense, translucent haze like that shown in Fig. 1.

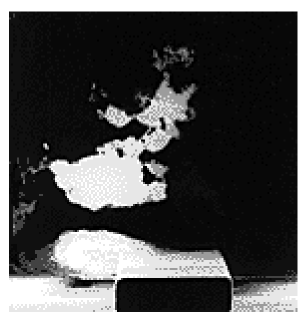

Fig. 1

In each case, the optical quality of the glass is destroyed even though overall mechanical integrity of the glass is maintained. What actually occurs is a combination of Stage 2 phenomena: The glass network dissolves, and by-products such as sodium and calcium

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silicates work together to affect the appearance of the glass. Carbon dioxide in the atmosphere can also react with moisture on the glass surface to form additional surface residues, typically of sodium and calcium carbonates.

Restoring the pristine surface quality to severely corroded glass is at best a formidable task. Grinding and polishing could, with much time and effort, restore the optical characteristics of glass corroded like that shown in Fig. 2. However, this solution is not practical nor economical; it is simply easier to discard all heavily corroded glass.

Fig. 2

Restoring Corroded Glass

Yet, there are occasions when it is advantageous to restore lightly corroded surfaces. With a little practice, anyone should be able to identify lightly "stained" glass that can be successfully restored.

The degree of surface corrosion that is acceptable in any glass fabrication process is directly related to the surface quality required by the end use of the glass. Mirror silvering, vacuum coating, and chemical etching processes are all highly sensitive to the presence of even minor surface damage, which can be invisible to the naked eye. On the other hand, lightly corroded glass may, in many instances, be cleaned sufficiently with acidic detergents or abrasive agents, such as pumice or cerium oxide, so that it can be used in less critical applications where no coatings are involved.

When lightly corroded glass is successfully restored, the sodium and calcium silicates are removed as well as any carbonate residues that may have precipitated on the glass surface as by-products of the Stage 2 reaction. The actual network damage affecting optical quality is so slight that it is of no consequence in less critical applications.

Conditions for Corrosion

Once the glass has been properly cleaned and dried, the corrosion process is suppressed. It is unlikely that it will begin in the finished glass product.

Obviously, the average homeowner, car driver, or commercial building owner does not usually observe surface corrosion damage on finished glass products. When, then, is glass most likely to corrode, and when is it most likely to be noticed?

In order for glass to corrode, certain conditions must exist that are not usually found outside glass manufacturing or fabricating. The single most important difference between the manufacturers' and fabricators' experience with glass from that of the end user is storage and handling of glass packages containing several individual lights. In fact, it is the glass package where the corrosion process is most likely to occur.

In packaged glass, it is the spaces between adjacent glass lights where the conditions for corrosion can exist. If no environmental controls are set up during storage, these spaces can readily trap and retain moisture

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if temperatures drop below the dew point (when daytime temperature is 80° F and relative humidity is 61 %, the dew point is 65° F). Once this occurs, Stage 1 corrosion begins, which soon will lead to Stage 2 activity and ultimate surface damage unless the process is stopped.

The reason that glass corrosion is not usually observed on fabricated glass products stems from the fact that moisture in contact with installed units is not trapped or stagnated, as it is in a glass package. With most glass products, the environment is such that water in contact with a glass surface either quickly evaporates or is highly diluted by normal weathering conditions. In any case, the critical pH levels required to promote Stage 2 corrosion are not reached, and the glass remains undamaged.

For most casual observers, the two most likely situations in which glass corrosion may have been observed are in double-light sealed insulating units in which the seal has failed (Fig.2) and narrow neck bottles containing liquid that have been allowed to set for long periods of time (Figs. 3a and 3b).

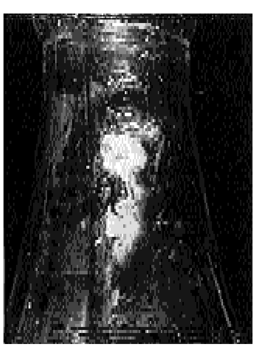

Fig. 3a

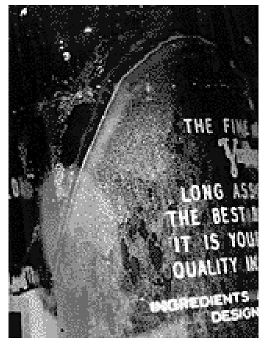

Fig. 3b

A double-light window unit that has seal failure will show a milky white haze on the interior surfaces. The white haze is actually surface corrosion damage. When double-pane units fail, moisture is allowed to enter the airspace separating the glass lights. The relative humidity in the airspace can reach levels where evaporation is not resulting in a net loss of moisture, and water-induced corrosion reactions take place.

A similar situation can occur in narrow-neck bottles where the rate of evaporation is greatly reduced by the constricted opening. Solution pH can, in time, reach critical levels, where it is between 9.0 and 9.9, and can cause permanent surface damage. Perhaps you have found an antique bottle lying in a field with milky white surface deposits that could not be removed no matter what cleaning agents were used.

Interleaving Systems

While the end-user customer has little need to be concerned about glass surface corrosion, glass manufacturers and fabricators do need to be. As stacked glass provides the most common environment for corrosion, and storage conditions cannot

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always be controlled, manufacturers use techniques to retard stain damage in packaged glass.

They do so by using any of a variety of powdered and paper interleaving systems. Interleaving materials used in glass packaging today serve two purposes. First, they mechanically separate individual lights to prevent abrasion and other mechanical damage during shipping and handling. Second, functional interleaving systems also contain relatively harmless acidic chemicals to neutralize Stage 1 alkali buildup and provide pH control.

Paper interleaving materials in general are excellent separators that prevent mechanical damage during handling and transport. Some papers, like newsprint, also effectively reduce the probability of chemical attack by keeping pH levels below critical values during storage. This occurs because of the presence of naturally occurring organic acids that typically give the paper a pH value of 5.0.

Because of its favorable characteristics, paper interleaving was once the preferred packaging material in the glass industry. Today, however, because of new technological developments in glass production and fabricating, and rising materials and labor costs, the use of paper interleaving has, for the most part, become limited to the packaging of fabricated products.

It was the advent of float glass technology, as well as the emergence of automated procedures for unpacking and handling glass before fabrication, that necessitated the need for new interleaving systems. Today, powdered interleaving has become the preferred one.

Powdered interleaving systems offer many advantages. Powdered interleaving can be readily applied to glass surfaces with automatic dispensing equipment without interrupting float glass production, and it is compatible with automatic unpacking systems. Paper interleaving is more than 30 times more expensive to use than today's most popular powdered materials. Handling and disposing of paper interleaving can be expensive and problematic for the glass fabricator as well as the producer.

The developer of powdered interleaving systems began in earnest about 22 years ago. Initially, materials such as polystyrene beads blended with salicylic acid were tested. More exotic systems using ground coconut shells or wood flour combined with an organic acid were also investigated.

It was about 12 years ago that powdered interleaving systems first appeared. They use **polymethylmethacrylate (PMMA)** beads as the separator medium and provide excellent protection against mechanical damage. PMMA beads are highly resilient; beads ranging in size from -60 to +120 mesh have been shown to be able to withstand pressure of 10,000 pounds per square inch (psi) for one hour without being permanently deformed.

PMMA beads are also chemically inert under the conditions found in typical glass storage environments. Today's most popular powdered interleaving also includes adipic acid as a defensive measure to retard increases in pH levels should Stage 1 corrosion ever begin within the packaged glass. Adipic acid, a weak organic acid, is a solid-form food additive. It is blended with the PMMA beads in equal portions by weight. Together, these materials offer the full complement of performance characteristics required of any effective glass interleaving system.

How does a powdered interleaving system actually prevent glass staining as well as mechanical damage, such as surface scratches? In order to understand, it may be helpful to know what happens if interleaving is not used, a question asked by some buyers of primary glass. If no interleaving is used, the stage is set for development of the most severe glass corrosion environment imaginable.

Without interleaving materials, the distance between non-contacting points on adjacent glass surfaces can be as little as 0.0007 to 0.0009 inch, which is about a third of the thickness of a sheet of newspaper. Fig. 4 shows a unique cross-sectional view of non-interleaved glass.

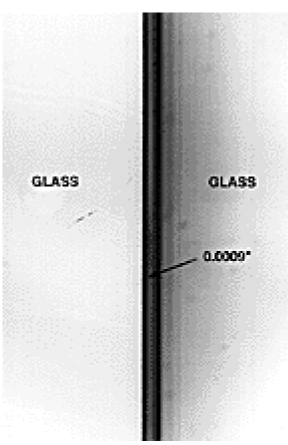

Fig. 4

Under these conditions, the quantity of water found in a small droplet -0.1 milliliter, or about the amount of water in two raindrops - could come into intimate contact with more than 16 square inches of glass surface. In a very short time (several days at room temperature), pH levels would reach the critical stage -pH of 9.0- and the glass would soon suffer irreparable corrosive damage. The absence of interleaving also leaves the glass highly susceptible to being scratched.

What happens when a neutral, non-reactive separation medium, such as PMMA beads, is applied between stacked glass lights as shown in Fig. 5. Notice how the beads act as tiny ball bearings that prevent sliding friction between the glass. The distance between adjacent surfaces has been increased to 0.01 inch; a 0.1-milliliter water droplet would cover only 1.6 square inches of glass surface, tenth that for non-interleaved glass. In other words, it would take an entire milliliter of water to achieve intimate contact with 16 square inches of glass surface area.

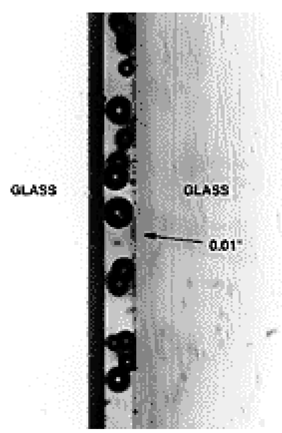

Fig. 5

However, this "spacing" effect does not significantly act to prevent glass staining. The additional space between the glass lights permits more condensate to form on a

Fig. 4

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given surface area. As a result, the by-products of Stage 1 corrosion, when evolved, accumulate in a greater volume of moisture than they would when non interleaving is used. The net result is that it takes slightly longer for critical pH levels to be reached.

This may mean an additional shelf life of one to two weeks, at most, compared to glass that has no interleaving. In order for increased separation to be effective in preventing stain, spacing between packaged glass lights would have to be increased to at least a quarter of an inch or larger in order to allow a dynamic weathering environment to exist between stacked glass lights.

This would be impractical. If, for example, this spacing were used with an average case of 135 patio door lights measuring 34 by 76 inches, with 3-millimeter glass, the case width would increase from 22 inches to more than 4 feet. Obviously, neutral, nonreactive interleaving materials alone cannot meet performance levels required to prevent glass corrosion during storage.

It is for this reason that effective glass interleaving systems include acidic materials. Without them, Stage 2 corrosion would begin to wreak havoc on the surface quality of stored glass.

Glass cannot be safely stored for any length of time without an acidic interleaving material being in place unless it is stored in an environmentally controlled warehouse. On the other hand, powdered interleaving, when properly distributed to a glass surface (see Fig. 6), can provide corrosion-free storage for 12 months or longer.

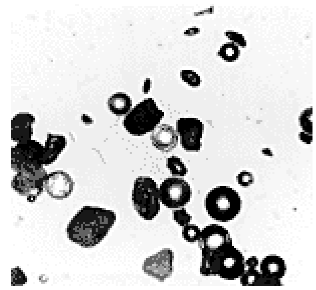

Fig. 6

Even if packed glass comes in contact with moisture, no surface damage will occur so long as sufficient quantities of acidic interleaving materials are present to maintain pH control. The longer glass is to be stored, the larger the amount of interleaving that should be applied. Judicious use of interleaving materials is key to success in storing flat glass products.

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HISTORY TABLE		
ITEM	DATE	DESCRIPTION
Original Publication	11/15/1986	
Revision #1	1/17/2002	Transferred to TD-105
Revision #2	2016-10-04	Updated to Vitro Logo and format