

Glass Reactivity and its Potential Impact on Coating Processes

Dr. Paul F. Düffer's article addresses, explains, and offers practical suggestions and recommendations for three significant problem areas related to glass surface reactivity and chemistry:

- *Stage 1 Corrosion in Glass Racks and Cases*
- *Damaging Effects of Glass Fines (Glass Particulates) from Glass Edging Operations*
- *"Hard" Water Silicates Deposits and Their Effect on Subsequent Glass Coating Operations*

This article will benefit all Vitro Architectural Glass (formerly PPG Industries) glass customers, particularly distributors, fabricators and those who coat glass.

Abstract

It is generally unknown that commercial flat glass exhibits distinct behavioral characteristics which warrant that it be classified as an "active" rather than "passive" substrate for coating applications. As a consequence, this paper sets out to present an overview of several key aspects regarding glass surface behavior and reactivity with coating processes in mind. The effects of storage and aging of glass are reviewed, along with the deleterious impact of classic surface corrosion. In addition, the ramifications of process water attributes and itinerant silicate materials on surface quality in pre-coating functions such as mechanical washing, tempering and heat strengthening are given equal consideration.

Introduction

Since the Middle Ages, flat glass products have maintained a well deserved reputation for longevity and reliability in service for a wide variety of end-uses. From the intricate patterns of stained-glass cathedral windows to the design and performance challenges presented by the architectural and transportation markets of more recent history, glass has been applauded as one of the most noble and dependable of building materials. Therefore, except for occasional breakage, it is not surprising that the archetypal consumer views glass as being essentially immutable and virtually impervious to chemical attack. However, there are specific environments commonly encountered by flat glass producers and fabricators wherein the vitreous surface willingly reveals its unique reactive characteristics. The following discussion reviews important aspects of these special environments and the salient features of glass surface reactivity and the potential impact on coating operations.

Glass Storage and Surface Corrosion

The discovery that chemical processes are initiated when glass and water come into prolonged contact has been known to scientists for several hundred years [1]. However, it has only been within the past 30 years that details of these reactions have been elucidated. In 1967, Douglas and El Shame [2] reported that glass undergoes moisture-induced corrosive attack via a two-step process. Today, it is a well known fact that this corrosive process is characteristic of stagnant environments in which glass and moisture can remain in contact for days and even weeks. This observation is particularly important to the glass manufacturer and

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fabricator especially when consideration is given to the tiny spaces that exist between stacked glass sheets such as those shown in Figure 1. Poised for transport and storage, these interstitial regions, which are on the order of 0.0008" to 0.090" in width, collectively represent one of the most striking examples of a potentially stagnant and damaging environment if CONDENSATE is entrapped [3]. On the other hand, the typical end-user or consumer is never confronted with the task of handling and storing large amounts of packed glass. Consequently, glass surface corrosion is a phenomenon which usually remains outside the realm of common, day-to-day experience.

Stage I Corrosion

Whenever commercial flat glass (soda-lime-silica glass) comes in contact with water, an ion exchange process begins in which sodium ions in the glass are displaced by hydrogen ions from the water. The immediate outcome is hydration, or dealcalization, of the glass and depletion of hydrogen ions from the water. This process is accompanied by a shift in the aqueous equilibrium



to produce more H^+ and OH^- ions. However, since a significant number of the H^+ ions are consumed by the glass via ion exchange, there is an overall increase in the number of OH^- ions in the contact water which exhibits a commensurate increase in pH. The ion exchange process is noticeably temperature dependent as demonstrated in Figure 2 where the increase in solution pH is plotted against time for several float glass samples exposed to water at temperatures of 72°F, 140°F and 195°F respectively. If the pH

level remains below 9.0, Stage I corrosion results in nothing more than a dealcalized glass surface. There is no physical damage and no adverse effects occur during most present-day coating and fabrication processes. However, a finite possibility exists that acutely sensitive coatings could be negatively impacted by surface dealcalization although documented occurrences of this are very rare. Of course, if Stage I sensitivity was common, it would present a monumental dilemma to the coating industry since all soda-lime-silica glass undergoes some degree of Stage I corrosion unless kept absolutely dry from the time of manufacture to the moment coating is completed.

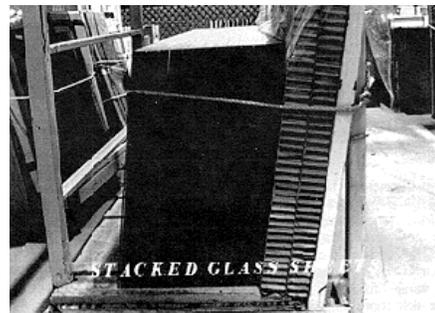


Fig. 1

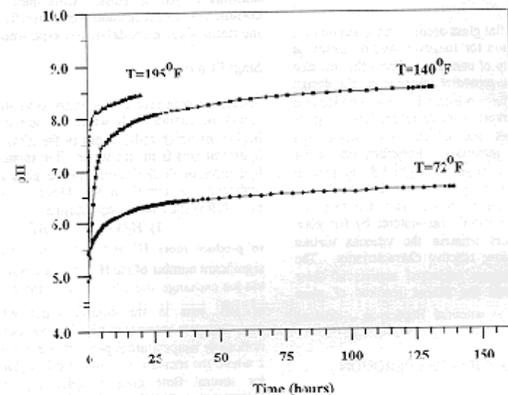


Fig. 2

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Stage II Corrosion

If the Stage I process is allowed to proceed with no provision to control pH levels below 9.0 through the judicious use of anti-corrosive interleaving materials [4], it will not be long before Stage II corrosion materializes and permanent surface damage occurs. This degradation in surface quality is the result of alkali attack on the glass silicate network and is manifest in several forms which range from a subtle iridescence to a distinctive milky white haze. A good example of classic Stage II corrosion is illustrated in Figure 3.

During the incipient phase of Stage II corrosion, microscopic pitting of the glass occurs. Invisible to the naked eye, this degree of damage poses little problem for the fabrication of non-coated residential and transportation vision units. On the other hand, such damage can impose serious difficulties upon coating applications where there is little or no latitude for aberrations in surface quality. As Stage II corrosion advances, the microscopic pits develop into tiny crevices that grow and eventually undercut the surface, forming islands of glass which can exfoliate from the underlying bulk material. Figure 4 shows an example of severe Stage II corrosion with exfoliation magnified 200 times. Viewed with the naked eye, this glass is characterized by extensive milky white regions with iridescent fringes.

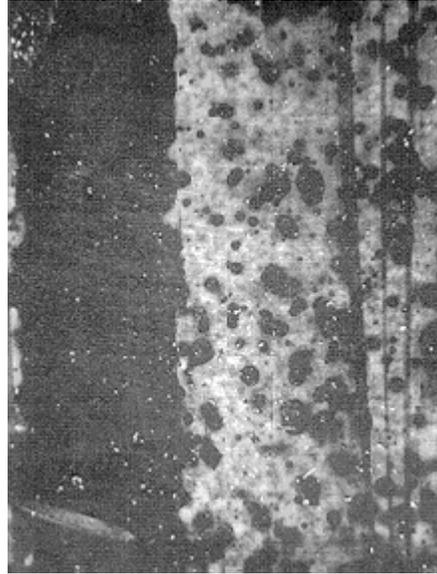


Fig. 3. Stage II surface corrosion

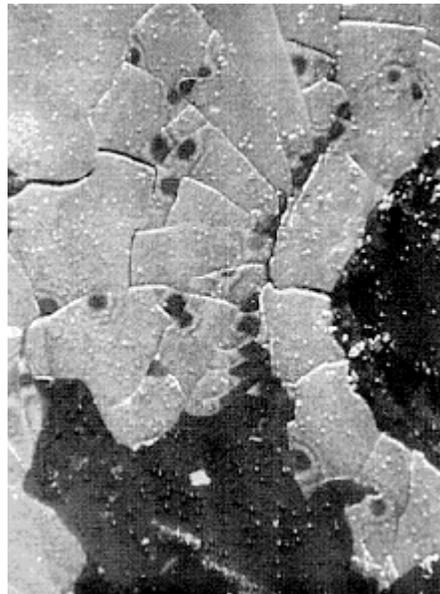


Fig. 4. Stage II surface corrosion 200X; field of view = 0.5 mm x 0.3 mm.

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The surface damage just described is often referred to as "stain". It is usually observed, as mentioned earlier, in conjunction with stacked glass sheets that have been allowed to remain in storage after condensate has formed between the individual units having insufficient interleaving protection. Curiously, the capillary-like spaces within the packed glass case do not have to be completely filled with moisture in order for the corrosion process to begin. On the contrary, it is more common to find evidence of corrosion in situations where a large population of distinct and separate condensate droplets have been in contact with the glass. These droplets are very, very small; so small that it would require from 50,000 to 1,000,000 to fill a 1 ml vessel. A representative view of such condensate on glass is presented in Figure 5 magnified 100 times. It has been observed in this laboratory that, at a given temperature, the Stage I and Stage II corrosion reactions can occur in each droplet at rates which vary with the glass surface area to droplet volume ratios. In other words, micro-regions covered by individual droplets that are spread over a relatively large area are corroded more rapidly than domains where the droplets are more rounded in shape. This phenomenon accounts for the "Swiss cheese" corrosion pattern exhibited in Figure 3 where condensate formed in the unprotected areas between protective interleaving particles and ultimately caused irreparable damage.

It is important to mention at this point that situations develop where even properly interleaved glass can undergo "staining". This is due most often to the selection of

poorly maintained storage areas that have no ventilation or environmental controls. Here the atmosphere may be brimming with moisture to the point that protective interleaving materials can actually be dissolved from between the stacked glass sheets. It is often quite easy to detect this problem by looking for a characteristic "picture-frame" effect in which corrosion appears around the perimeter of the glass where interleaving removal has been most extensive. Therefore, it should come as no surprise to learn that warehouses with roof leaks and poor ventilation, as well as outdoor holding areas where glass is exposed to rain, stand as vivid examples of some of the worst storage conditions to which glass can be exposed.

In order to maintain surface quality for coating applications, it is imperative that glass be transported and stored with sufficient interleaving in place to infuse a twelve month shelf-life. It is also critical that ventilation be provided whenever possible and contact with vagabond water streams be avoided. Temperatures above 110°F in combination with a humid atmosphere should also be avoided.

Pre-Coating Processes

In today's flat glass arena, there are frequent occasions when glass destined to serve as a substrate for high performance coatings is first subjected to a heat strengthening or tempering process. However, the stringent requirements associated with "coating quality" glass place unique demands upon these pre-coating operations that deserve special attention in order to avoid potential pitfalls.

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Tempering and heat strengthening procedures usually involve some form of cold-end edge working prior to firing. This step can range from simple belt seaming to more intensive diamond wheel grinding for a "pencil-edge" finish (See Figure 6). In each of these processes, glass fines are generated which can present a particularly severe threat to glass surface quality unless dealt with appropriately. For example, edging byproducts are extremely small -- on the order of a few microns in diameter assuming spherical geometry -- and, as a result, are very difficult to wash from a glass surface. This is due to capillary forces that tenaciously hold the particles in place. Consequently, an effective cold-end washing system becomes an extremely important factor in achieving high quality tempered glass surfaces.

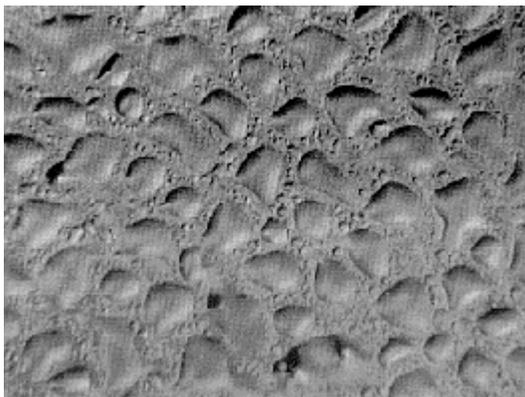


Fig. 5. Field of view measures 1 mm horizontally

Apart from the fact that fines are extremely difficult to remove physically, there are even more important ramifications which emanate from their rather pronounced chemical reactivity. The noticeably enhanced reactivity of "fines" over that of bulk glass surfaces is due to the relatively

large surface areas per unit mass which are characteristic of collections of tiny particles. For example, a gram of glass particles with an average diameter of 3 microns has a total surface area of more than 4 square feet (3700 cm²) whereas a similar quantity of 3.0 mm thick window glass would exhibit an approximate surface area of only 4.0 cm². Since it would take only one drop of water, or roughly 0.1 ml, to easily wet this amount of material, huge surface area to volume ratios would develop within this system -- on the order of 40,000 cm⁻¹ or larger. For a comparison with a bulk glass sample, consider that a 128 cm² (20 sq. in.) glass sample exposed to 235 ml of water (less than 1/2 cup) yields a surface area to volume ratio (SA/V) of approximately 0.544 cm⁻¹. The SA/V ratio has a direct influence on the rate at which glass reacts with water. Consequently, at a given temperature, glass fines react much more quickly and enter into Stage II corrosion more readily than does bulk glass.

From a practical point of view, these examples simply point out that glass fines and moisture represent a very reactive system wherein Stage II corrosion can occur quite rapidly, even at room temperature. Partial dissolution of the glass network ensues forming a dilute solution of glass components that includes silicates. Table I illustrates this effect for 2 grams of glass fines placed in 100 ml of distilled water at 72°F for solution samples taken at 0.75, 6 and 24 hours respectively.

In many cold-end operations prior to tempering or heat strengthening, a mixture of glass fines and water, or coolant, is deposited on the bulk glass surface. This situation is of no specific consequence if the

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material is washed away before any appreciable drying. On the other hand, should complete evaporation occur, one will observe that it is impossible to remove all surface debris via ordinary cleaning methods. Any success in this effort usually results from polishing the glass; hydrofluoric acid may also work but the dangers associated with this aggressive reagent makes its use impractical in most production situations.

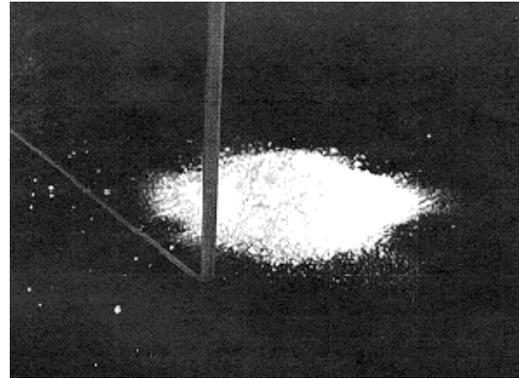


Fig. 6

Element	Control	45 min.	6 hrs.	24 hrs.
Si	<.01	1.2	5.2	1.4
Mg	0.2	0.3	0.3	0.6
K	0.2	0.2	0.2	0.2
Na	0.1	0.9	5.0	6.2
Al	<0.1	<0.1	<0.1	<0.1
Ca	0.8	3.1	3.3	4.1

Table I: Glass fines in distilled water (parts per million)

These severe cleaning problems are due to the reality that silicate solutions, when permitted to evaporate on glass, engage in chemical reactions which leave deposits that become what are essentially "glass-on-glass" defects. Figure 7 presents an example of such a residue deposited on glass by evaporation of a droplet of water taken from the "24 hour" leachate solution listed in Table 1. Magnified 200 times, this photomicrograph shows the result of attempts to cleanse the surface with 5% acetic acid.

There are repeated instances in practice where glass fabricators have purchased sophisticated equipment for V-grooving or beveling purposes only to be frustrated the first time attempts were made to clean unwashed finished parts that had been allowed to rest for only a few hours. This problem occurs because it only takes a short time, even at room temperature, for silicate deposits to react with a glass surface. In fact, observations have been made in this laboratory which suggest that the reaction takes place almost immediately upon evaporation to dryness. Needless to say, these reactions can be potentially devastating to the surface quality of coating substrate glass. Therefore, it is essential that all pre-coating edge-work be followed by immediate washing in an effective washer system using good quality water.

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Fig. 7. Silicate deposit after evaporating solution containing 14, PPM Si from "glass fines" and water mixture exposed 24 hours at 72°F; after 5% acetic acid wash; 200X

Glass Washing and Surface Preparation

A detailed treatment of all the major factors associated with operating and maintaining a flat glass washing system, especially for coating substrate preparation, is beyond the scope of the present discussion. Nonetheless, there is one very important aspect of washing and surface preparation that needs to be considered. This relates to the short-term, non-corrosive interaction of glass and process water.

The mere act of sending glass through a mechanically sophisticated washer apparatus before a tempering or coating process does not necessarily mean that the associated surface is sufficiently clean. Ponder the reality that both complex and even rather simple washer systems can actually serve as sources of contamination if not rigorously maintained on a continuous basis. Unfortunately, in many situations a disproportionate amount of effort is devoted to preparing washers for the anticipated

removal of "exotic" debris that is expected to reside on incoming glass (Indeed, if "exotic" residues do exist, it may be time to return the glass to the supplier and give consideration to alternate sources). As a consequence, much energy may be unnecessarily devoted to the selection of detergents and optimized operating temperatures while other, equally important aspects of system operation are overlooked. For example, consider that many fabricators continue to use tap water in glass washers on production lines that produce tempered products for coating applications. Apart from the obvious risk that hard water salts may be "fired" into the surface, there is a relatively unknown, yet very significant, hazard that can be associated with the incidental drying of itinerant tap water droplets on glass.

The potentially negative aspects associated with the use of tap, or "hard", water in cleaning glass can be reinforced by recalling observations from personal experience. For example, the undesired white spots seen on a recently washed automobile or the futile attempts made to clean lawn sprinkler residues from windows. Even more striking are the gross deposits of chalk-like material found inside a hot water tank or tea kettle. In each of these annoying situations, it is ultimately the presence of calcium and magnesium carbonates in the water supply to which blame is usually attached. When one installs a water softener, the objective is to replace calcium and magnesium ions with sodium ions to forego the precipitation of insoluble carbonates in hot water systems and also improve the performance of soaps. However, water quality improvements that may be suitable for sundry residential and

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commercial uses may not meet the requirements for effective glass washing.

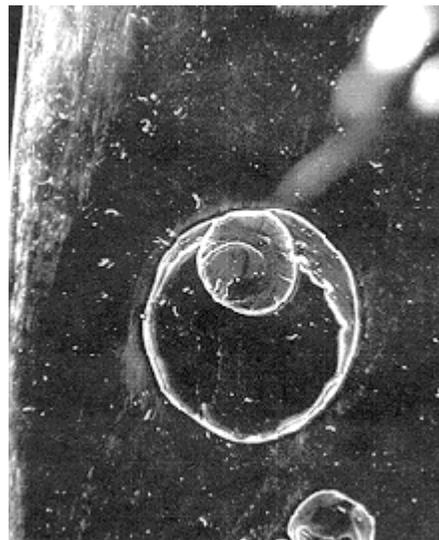
When engaged in overseeing sensitive processes that utilize flat glass products, one must think about other dissolved species that are usually found in both public and private water supplies. Of particular interest is the presence of dissolved silicates that are normally overlooked as a potential source of difficulty. This state of affairs quite likely stems from the fact that dissolved silicates, up to now, have had a limited documented history, of adversely affecting water users outside the domain of flat glass processing. However, it is plausible to suggest that even within the glass dominions, fabricators have experienced the adverse effects of dissolved silicates in process waters without ever having been aware of the actual cause.

In a previous section, it was pointed out how silicates emanating from glass fines can lead to washing problems during fabrication. In like fashion, tap water deposits can present the same sort of cleaning difficulties. To develop a better perspective of the relative quantities of dissolved materials in various water supplies, Table H has been compiled which presents analytical data for the cationic species found in samples taken from a lake in Florida and a public well in the state of Washington.

Element	Well	Florida Lake
Ca	23	20
Mg	2.4	6.8
Na	16	7.2
K	3.2	3.4
Si	3.9	20

Table II: Cationic species in water (Parts Per Million)

Note that the sample from Washington contains about five times as much Si as the Florida lake water illustrating that dissolved silicate levels can vary significantly from region to region. Typically, one observes from 4 to 10 PPM Si in most water supplies analyzed from North America. In addition, the other species listed in Table H can also vary from region to region; water samples with more the 40 PPM Ca and 15 PPM Mg have been evaluated by the author. To illustrate the impact of tap water silicates on glass cleansing, attention is directed to Figures 8 and 9. These close-up photographs show deposits formed by the evaporation of several droplets of the Washington state well water sample before and after cleaning with a 5% acetic acid solution. Note the significant amount of material that remains unaffected in spite of the rigorous cleaning procedure undertaken. If the deposit in question was composed primarily of calcium and magnesium carbonates, there would have been no problem in dissolving the material with the weakly acidic cleaning solution.



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**Fig. 8. Tap water spot close-up view
20PPM Si, before washing**

The fact that tap water can produce such unyielding deposits on glass should raise concerns regarding any preparation of coating substrates where untreated process water is employed. For example, incidental distribution of tap water droplets can create deposits that will escape removal in a coating line washer. Unfortunately, these deposits most likely will not be noticed until inspection of the coated article is initiated. A very good example of such an occurrence is illustrated in Figure 10. Magnified 50 times, the subject of this photomicrograph is a spot defect in a MSVD coating on glass. Measuring approximately 0.5 mm in diameter, this aberration was created by the unintentional evaporation of tap water

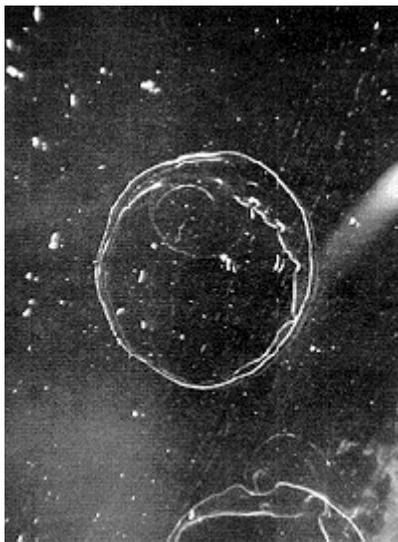


Fig. 9 Tap water spot after 5% acetic acid wash

droplets on the substrate glass, prior to delivery to the coating facility. The water in question contained only 4 PPM Si, yet the

impact was significant enough to lead to the rejection of numerous coated units. It is worthwhile to note that this was not an isolated incident. In recent months, there have been a number of similar events investigated by the author that have originated within the Pacific Rim as well as various areas of North America.

It should be obvious at this juncture, that diligence must be exercised at every step in the production of coated glass products to avoid incidental contact with omnipresent silicate bearing materials. A key point in achieving success is to employ process waters which are essentially free from silicates (<1.0 PPM) and avoid accidental contamination by untreated water supplies near those production lines engaged in coating related operations. The level of awareness regarding the impact of water borne silicates on glass surface quality must be raised to the status where coated products are no longer ravaged by reactions that heretofore have escaped widespread notice in the world of flat glass fabrication.

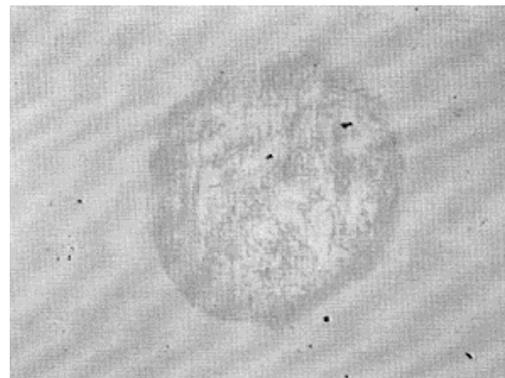


Fig. 10. MSVD coating defect from silicate deposit; field of view is 2mm x 1.5 mm, 50X

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Conclusions

It has been shown by means of several examples that glass has reactive characteristics which are not usually observed by persons outside the realm of flat glass production and fabrication. Stacked glass sheets packed in boxes or on steel racks present the most potentially hostile environments for glass. If moisture forms between the glass units, an ion exchange process, or Stage I corrosion, occurs during which the pH of the condensate begins to increase. Whenever this pH increase is controlled by application of protective interleaving materials, no permanent damage appears. However, uncontrolled increases in pH above the 9.0 threshold soon result in microscopic pitting and the eventual deterioration of surface quality by what is commonly referred to as Stage II corrosion. However, surface corrosion can be prevented for a year or more by judicious use of protective interleaving materials combined with the selection of dry, well-ventilated storage areas.

Edging and belt seaming operations present unique problems for maintaining glass surface quality in that the glass fines by-products are extremely reactive with water and yield substantial levels of soluble silicates, even at room temperature. When dilute solutions (4 PPM Si) of silicates evaporate on glass, deposits remain behind which react with the glass creating "glass-on-glass" defects that are impossible to remove except by means of abrasive polishing or dissolution in hydrofluoric acid. Arising from the very large surface area to mass ratios characteristic of large numbers of minute particles, the intense reactivity of glass fines is most effectively

controlled by washing all glass articles immediately after edging or seaming.

The third and final pitfall encountered in the production, tempering and washing of "coating quality" glass is the presence of soluble silicates in process waters. Here again, evaporation to dryness results in a glass-like deposit that does not yield to practical methods of glass cleaning. Accidental splashing of glass with tap water can result in silicate deposits that escape detection until inspection of the finished coated article. In a similar vein, intentional use of silicate bearing water to process substrate glass is a practice begging for problems to ensue. Every effort should be made to use silicate free process water anytime one is engaged in preparing glass for sensitive coating applications.

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HISTORY TABLE		
ITEM	DATE	DESCRIPTION
Original Publication	1996	
Revision #1	1/17/2002	Transferred to TD-106
Revision #2	2016-10-04	Updated to Vitro Logo and format

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