Does glass rust?

The insulated glass window is one of the most important components of modern life. On the one hand, it connects us with our environment by allowing us to see it (instead of a wall). On the other, it protects us from undesired environmental influences such as cold, heat or noise. Its transparency thus obscures the fact that insulating glass consists of a variety of materials, which only as a whole can satisfy the various demands of technical, highly complex end products. Each of these materials shows how it reacts once the product is assembled, whereby this reaction also always depends on how the raw materials were initially processed. And so glass too has a past life; everybody knows that luck and glass shatter easily and luck can rust easily… but glass? Dr Michael Emonds considers the possibilities.

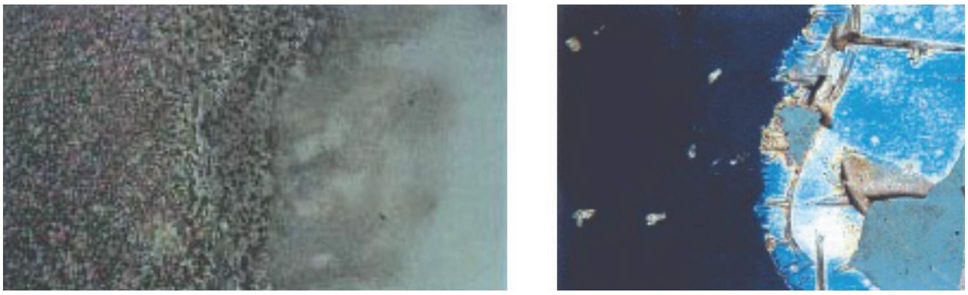

Figure 1: What is corrosion, how does it occur and how can it be prevented? The left picture shows visible, rainbow colour glass corrosion on the left glass side - the right glass side was corrosion protected so shows no corrosion. The right picture shows glass with a low-E coating; after immersion in hydrochloric acid, the corrosion protected left part stays intact, the non-protected right part peels off.

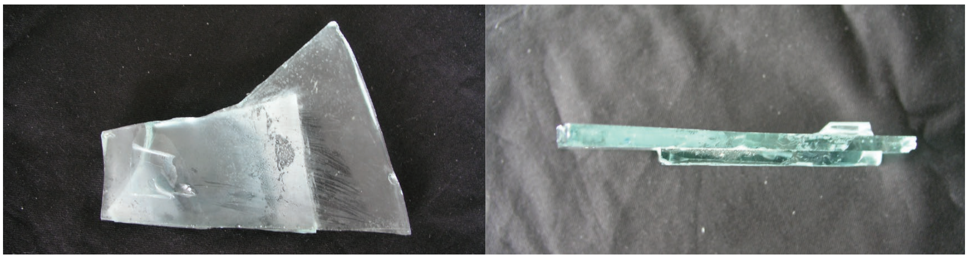

Figure 2: Glass corrosion in the end state; heavy, white staining, destacking not possible without breakage.

The surface of freshly produced float glass is highly reactive. While the glass is being stored or transported, it may react with humidity that has penetrated the spaces between the layers of glass, which can lead to highly adhesive blotches of corrosion. If the corrosion is distinctive, the glass cannot be processed any further. The level of corrosion depends on the humidity, temperature, conditions of storage and transport and the quality of the glass (composition, hydrolytic class etc).

Furthermore, corrosion in the early stages is not recognisable to the eye and only becomes visible when the glass is processed further (eg by low-E coating, silvering or tempering). In the Chemetall development laboratory, corrosion-protected sheets were compared to non-protected sheets as to any reactions following application of a thin film coating (figure 1). In stress tests, the untreated sheets showed signs of flaking much sooner than sheets that were given an initial protective coating. The disturbance in film build-up that was responsible for this can, during further processing into insulation glass, also have a negative effect on the sealant on the glass surface.

CORROSION

The normal definition of corrosion is the 'reaction of a metallic substance with the environment, causing a measurable change to the substance', eg the build-up of rust on steel surfaces. A more precise definition describes corrosion as 'a quality-reducing change in a material, occurring on the surface, caused by an unintentional, chemical or electrochemical action'. This definition can apply to the reaction undergone by float glass due to environmental humidity during storage or transport (figure 2).

HOW CORROSION OCCURS

The effects of water on glass surfaces is a combination of two processes, which take place almost at the same time; the exchange of H+ ions in the water for Na+ ions on the surface of the glass (initial phase) and an alkaline reaction by the hydroxyl ions left over in the water to the silicate network on the surface of the glass (corrosion stage) (figure 3).

In the initial phase, the silicate network remains unchanged and an SiO_x-rich layer with low Na^+ content builds up. A constant replacement of the layer of water adhering to the upper layer of the glass, eg due to rain then leads to a stabilisation of the glass.

What happens however, when a thin film of water remains on the glass over a longer period and is not constantly replaced? The sodium hydroxide is no longer washed off by the rain but becomes more concentrated. When the pH level reaches 9-10, the glass structure starts to decompose. This process, called glass corrosion is consolidated by high humidity in connection with vastly varying temperatures (temperatures below dewpoint). >

1. Ion exchange

$$\equiv\text{Si-O-Na} + H^+ + OH^- \longrightarrow \equiv\text{Si-OH} + Na^+ + OH^- \text{ (soda lye)}$$

2. Condensation

$$\equiv\text{Si-OH} + \text{HO-Si}\equiv \longrightarrow \equiv\text{Si-O-Si}\equiv + H_2O \text{ (silicate rich layer)}$$

3. Network dissolution

$$\equiv\text{Si-O-Si}\equiv + OH^- \longrightarrow \equiv\text{Si-O}^- + \text{HO-Si}\equiv$$

Figure 3: Glass corrosion chemistry: The condensation step stabilises the glass surface but the third step destroys it.

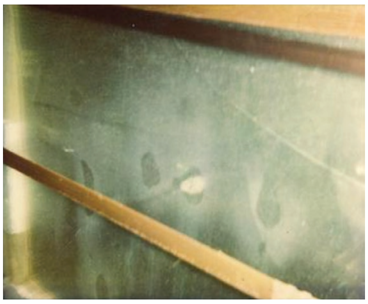

Figure 4: The analytical problem of glass corrosion; corrosion never shows a regular distribution.

Figure 5: Heavy glass corrosion after transport under unfavourable climatic conditions; high humidity, extreme temperature changes.

HOW TO RECOGNISE CORROSION

While corrosion in the end phase is clearly recognisable by multi-coloured changes on the surface of the glass to white coloured deposits, the initial phases of corrosion are not visible but make further processing of the glass difficult, if not impossible.

Corrosion in the initial phase is characterised by various physical changes to the surface of the glass, eg a change in thermal expansion, refractive index and surface energy. Furthermore, already existing microscopic cracks are strengthened by the corrosion. A porous layer several micrometers thick occurs, in which various deposits can settle, making further processing difficult. Physical methods of measuring, such as ellipsometry, IR, REM, AFM or the measurement of the contact angle allow a very sensitive location of corrosion (figure 4).

HOW TO REDUCE CORROSION

In order to reduce production loss due to corrosion, the glass industry uses various procedures, eg:

- Only freshly produced float glass is used for further processing. However, this is only possible for float glass manufacturers, even though there are problems for them also, eg in thick glass processing.
- The glass is stored and transported at a constant temperature and humidity (figure 5). Due to the capacity of the float glass lines and the jumbo sizes produced, this solution is only partially applicable.
- The stacks of glass are sealed off at the ends in order to prevent humidity from entering between the glass sheets. This method is mainly used to transport laminated glass but is hardly ever used for untreated glass.
- The glass is polished prior to further processing. The surface of the glass is refreshed using a suspension of cerium oxide, aluminium oxide or other oxides, before being given its silver plating or low-E coating finish. Because a fresh glass surface is very reactive, further treatment must take place as quickly as possible.
- Finally, it is also possible to reduce the pH value on the glass surface using acid. Mixtures of separating agents with adipic or boric acid in various concentrations allow the separation of the glass sheets on the one hand and the application of a corrosion protection on the other, in the same phase. Recently, people have started to apply a liquid corrosion protection, applying the separating agent in the second phase (figures 6 and 7). In this way, a better distribution of the acids on the surface is achieved. Due to the use of polyvalent acids, the buffer capacity of the protective acids can be improved.

Much can be done to protect glass from corrosion but it is not possible to exclude it completely. While corrosion in the initial phases can be removed using suitable polishing agents, visibly corroded glass can no longer be repaired to a reasonable standard.

As float glass available on the market can vary, (eg they can possess various hydrolytic qualities, or the year of manufacture may simply be different), polishing, in order to clean the surface of the glass is surely a reasonable step to take prior to further processing of the glass into a higher quality product. It must be pointed out once more that due to initial corrosion, defects on the glass surface will be increased, which may not become visible for some time after the end product has been completed unless silver layers start to flake off, colour defects of low-E glass or adhesion problems with insulating glass occur. Chemetall's experience shows that corrosion can be reliably held back using tailor-made, anti-corrosive interleavants. However, one must remember that the corrosion protection must be totally washable, leaving no residue, prior to further treatment. The same applies to all other auxiliary agents such as cutting fluids, separating agents or coolants and of course, contamination of the glass surface due to dust, fingerprints, roller prints, gloves etc. This is no longer possible using just water alone; special detergent, used for treating glass is also required. It must also be possible to wash this off completely.

As can be seen, things can go wrong right at the beginning in the final production of insulating glass windows. It is certainly not easy to find a solid, overall approach. However, each individual stage must be carefully observed and its effects on the subsequent stages of the process assessed if one wishes to locate defects and to avoid them. ■

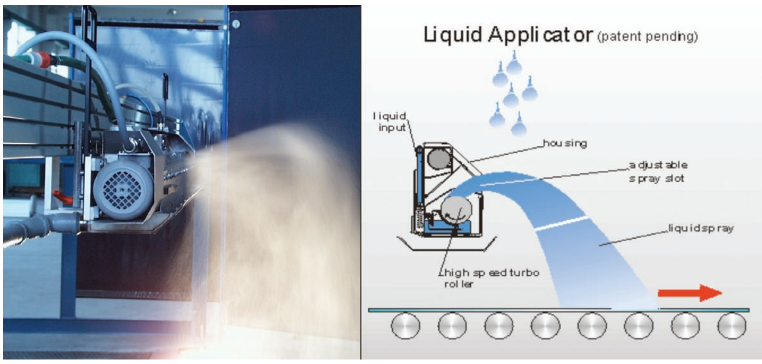

Figure 6: The Grafotec Liquid Applicator produces a spray 'curtain' that covers the glass surface with AC Resistain TC.

Figure 7: The Liquid Applicator, installed on a float line.

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