GLASS CORROSION EFFECTS FROM DISHWASHING AND THEIR TECHNICAL SOLUTION

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ABSTRACT

Glass corrosion from automatic dishwashing has been investigated by atomic force microscopy (AFM) and other surface sensitive methods. The results show completely different basic causes of glass attack. Local clouding at the mouth rim or line corrosion can be traced back to the production process of the glass. Components of cleaning agents were found to be responsible for iridescence and clouding all over. The comprehensive knowledge of the corrosion mechanism was used to establish one possible technical solution to avoid glass corrosion. Using the so called Protector Dual Protection, the cleanness and brilliance of glass can be conserved even if the glass passed many cycles in automatic dishwashing. The mechanism to prevent the glass surface and enamels are described below.

1. INTRODUCTION

The following essay will give an overview of the glass corrosion problem. First there will be shown some examples of glass corrosion of drinking glasses and the various reasons therefore. Followed by a solution to prevent this corrosion and in a final step, examples which illustrate the condition before and afterwards are given.

2. BODY

Milky glasses form dishwashing machine? That's not a layer of lime, that's corrosion. The automatic dishwashing brings glasses in close contact with water, high temperature, lime and cleaning agents. Small parts of the glass dissolve. The outcome of this is an edgeless and cracked glass surface. To prevent the product from the beginning a special protection is necessary. Using the Protector Dual Protection, the cleanness and brilliance of glass can be conserved even if the glass passed many cycles in dishwashing.

In 1974, Lohmeyer [1] pointed out that differences in chemical composition, due to melting and annealing, produce local differences in resistance to attack by various media. The research work was carried out with an optical microscope, making it impossible to explain all effects in detail. Gebhardt [2] published in 1985 a paper on dishwater resistance investigated by scanning electron microscope and infrared reflection spectroscopy which put the research much further than ever before. Gebhardt pointed out that the mouth rim clouding of a drinking glass could be due to the formation of holes in this area. The infrared spectroscopy showed after round-melting of mouth rim that an enrichment of the alkali ions took place and was responsible for the clouding after dishwashing. However, the experimental methods deployed are not sufficient to fully justify the proposal. The line corrosion was elevated by washing and consisted of Al_2O_3 and ZrO_2 from refractory materials of the glass melting process.

With the rapid development of modern characterization methods in recent years, such as the field emission scanning microscope (FE-SEM) and the atomic force microscope (AFM), many phenomena can be clarified much better. Buchmeier [3] showed that the damages by

clouding and iridescence were more serious when washing with a high disilicate-containing detergent (already after 50 cycles). However, the conventional and carbonate-containing detergent did not cause visible corrosion after 1000 washing cycles. The x-ray photoelectron spectroscopy (XPS) indicated that the disilicate built a coating layer on the glass surface with a structure similar to the basic glass structure.
Investigation by Wang [4] and Martinek [5] were done with the atomic force microscope (AFM) and secondary neutral mass spectroscopy (SNMS) to confirm several hypotheses of corrosion during dishwashing process.

There are different kinds of glass corrosion which depend on the type of liquid like acid, water, base and organic chelating agent. The corrosion mechanism of drinking glasses, mostly affected from automatic dishwashing, was investigated in detail. Typical defects shown in figure 1-4 are cloudy bands and films that can iridescence and have slightly yellow areas, non-regularly stain and unsuitable glass composition. Another defect is line corrosion. It can appear after several numbers of cleaning cycles in automatic dishwashing.


Figure 1: Cloudy mouth


Figure 2: Non-regularly stain


Figure 3: Completely cloudy


Figure 4: Bad composition

The corrosion is either local restricted at the rim (figure 1), at the stem or the bottom plate of the glasses or can be found more or less at the complete glass surface (figure 2 to 4). To react to the different corrosion effects the cause of them is very important to know.

During the automatic dishwashing the glass reacts with water and detergent for much longer time than during hand washing. The uniform glass dissolution results in weight loss but does not affect the appearance of glass. Recent studies indicated two main reasons that can generate visible glass corrosion.
Compounds (atomic scale) are leached from the glass surface by the dishwashing procedure. The result is a leached “rough” glass surface with visible clouding as light is scattered. This inhomogeneous degradation occurs only at the outer surface relating to compositional and structural inhomogeneity created by manufacturing process.
The other cause is the forming of a permanent layer on top of the glass surface. This layer made from hydrated SiO_2 generates after frequent washing an effect of clouding and iridescence.

Glass producers influence the glass corrosion with their chemical composition. Figure 4 above shows a complete cloudy surface after 100 cycles in automatic dishwashing as a result of unsuitable glass composition.

Table 1 below gives an overview about composition with bad and excellent durability. The hydrolytic class (ISO719) measures the durability of glass in water. Higher class means higher weight loss and therefore more solubility of the glass.
The lifetime and durability of the glass can be increased by adding elements of high coordination state like Al_2O_3 and using alkali oxide with lower quantity.

Components	Content [wt %]	Barium crystal
SiO_2, TiO_2, ZrO_2	74	71
Na_2O, K_2O	18	14
CaO, MgO, BaO, ZnO	8	13
Al_2O_3, Fe_2O_3	<<1	1
Others	<1	1
Hydrolytic class	4	3
Results dishwashing	cloudy 60 cycles	**brilliance 1.000 cycles**

Table 1: Glass composition

During the melting process small amounts of refractory material can be solved from the liquid glass. After the production of drinking glasses the surface is clean and brilliant. The line corrosion, shown in figure 5, appeared after numerous cycles of dishwashing.

Figure 5: Photo of line corrosion

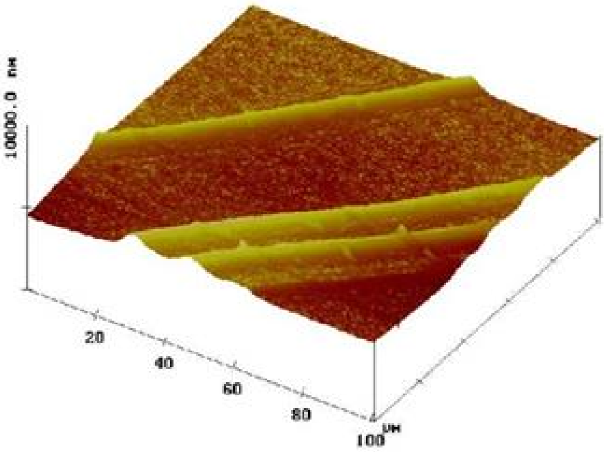

Figure 6: AFM of line corrosion

Figure 6 shows line corrosion, elevated by washing, consisting of Al_2O_3 and ZrO_2 from refractory materials of the glass melting process. Inhomogeneity in the surface and their different dissolubility are able to generate line corrosion.
The glass producers are in the situation to prevent such an appearance using high quality refractory material, drainage systems in furnace and feeders as well as to reduce the chemical inhomogeneity with stirrers next to the spout.

After cracking off the rim area the glass is fire polished. Figure 7 below is the schematic drawing of burner and glass [5]. In the re-melting area the alkali and the earth alkali ions might evaporate and condense on the colder area. Between these two areas a certain zone might be long enough at temperatures which favor ion migration and phase separation could take place. Due to melting and annealing, the surface may give rise to localized differences in chemical composition and results in diverse resistances to attack by various media. However, this area is not cloudy yet. It is possible that the cloudiness here occurs later, after several cycles in automatic dishwashing. The enrichment of the alkali ions could also be confirmed by infrared spectroscopy.

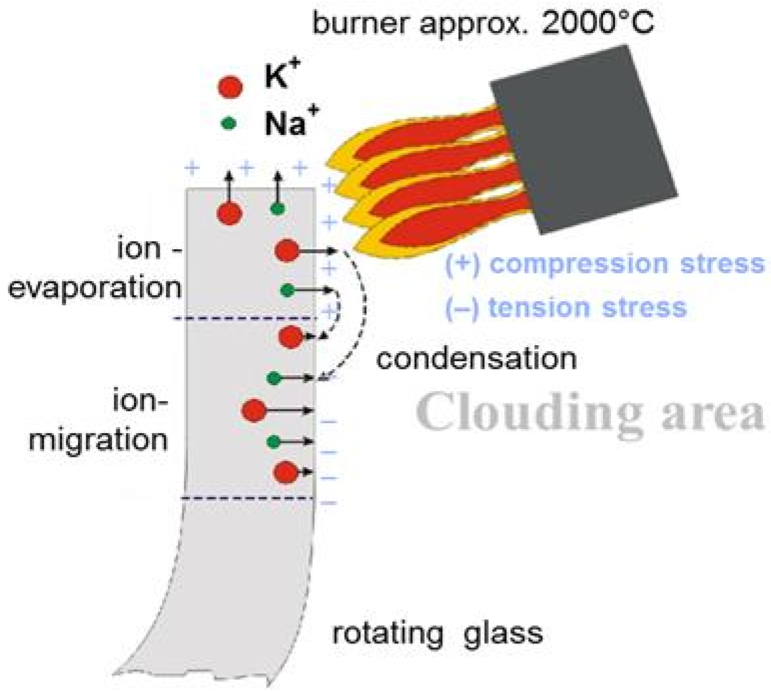

Figure 7: Schematic drawing of thermal treatment at mouth rim [5]

Phase separation can be identified by AFM at different kinds of glasses and different areas after thermal treatment. During the dishwashing the surface structure with different solubility was modified. This hole structure of a bottom plate of barium crystal is shown in figure 8. The mouth rim of lead crystal in figure 9 shows the similar hole structure but in a smaller size.

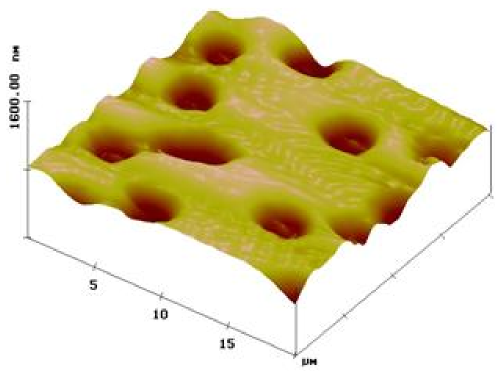

Figure 8: AFM from bottom plate of barium crystal

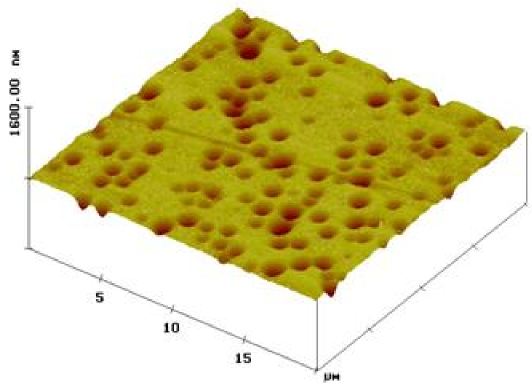

Figure 9: AFM from mouth rim of lead crystal

It can be summarized that the phase separation by thermal treatment and the generation of holes within the glass surface from dishwashing should be prevented e.g. with a short time in fire polishing at mouth rim area and at other parts of the glass surfaces.

So far, if the production process is optimized from glass melting and glass forming, local clouding can be prevented.
Now there is only one reason to get glass corrosion in dishwashing: the glass structure gets damaged during the dishwashing and generates hydrated gel layer. This process can be delayed if the dissolving process of the gel layer is influenced. Nachtmann and ReckittBeckiser developed a special patentee glass [6, 7]. In contrast to the technical glasses made from silicon dioxide, this glass is a phosphate glass and can be solved in water much better than silicate glasses. This phosphate glass contains the protecting agents and brings the glass and decor protecting agents directly into the dishwashing water. The higher the temperature and duration of dwell, the higher the corrosion of the drinking glass. This can be antagonized through a better dissolubility of the phosphate glass.

To avoid permanent damage and give the drinking glass a protection from the beginning the Finish Protector Dual Protection was invented by ReckittBenckiser and Nachtmann. The water of the dishwasher flows through the opening of the protector thus glass and decoration protecting agents are set free. Thereby glass damaging components get "neutralized". This protects colors and decors from desaturation, so the brilliance is kept.

To understand this effect it is very important to know how the protecting agents work in detail. Without using the Protector Dual Protection, water and alkaline solution dissolve the glass network. The surface structure becomes damaged and a hydrated layer is created. Furthermore water molecules and alkaline solutions attack the existing surface structure.
Using the Protector, glass and decor protecting agents are set free. They move to the glass surface and built a layer to protect it. A big amount of tests has shown that only one combination of components improves the anticorrosive coating significantly – zinc and bismuth (Zn^{2+} and Bi^{3+}). As seen in figure 10 the smaller zinc-ions (GPA) infiltrate the glass structure. They help to protect the glass surface next to the glass network. Bismuth-ions (DPA) are bigger, remain on top of the surface and build a helpful protection for the hydrated layer. The result of this process is two protection layers which are difficult to pass for damaging elements.

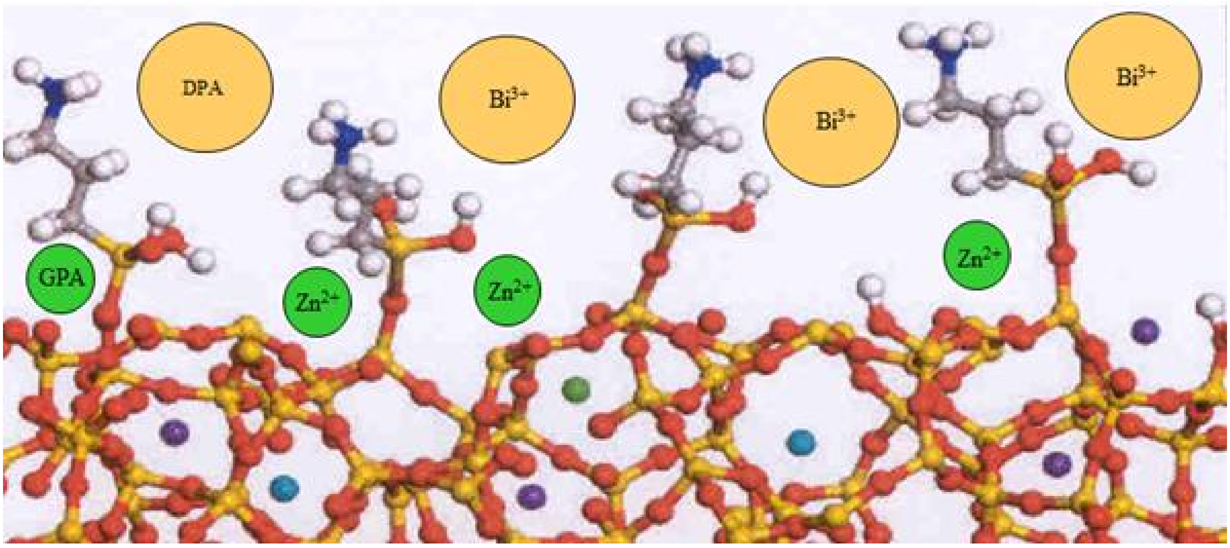

Figure 10: Schematic structure of glass surface with protecting agents [8]

Washing with the dishwasher but without the Protector Dual Protection can lead to irregular material loss at the surface of the drinking glass. A “rough” surface, scattering of light as well as severed clouding are very likely to occur. Using the Dual Protection this effect can be reduced or even completely prevented.

Lab and consumer-tests show the effectiveness of the Protector Dual Protection. Already after 50 washing cycles in the consumer-test corrosion is clearly visible. The lab-test confirms this result arrestingly after 100 cycles as seen in figure 11. Figure 12 shows that not only the glass is attacked, also the decor becomes damaged and loses brightness and color intensity.

Figure 11: Glass protection in lab-test (100 x)

Figure 12: Glass & decor protection in consumer-test (50 x)

3. CONCLUSION

All in all we can retain that glass corrosion is a complicated procedure and often has various reasons. Cloudy glass surface may occur in a short time, after permanent using or not using the glass at all. Unfavorable glass structure can be avoided during the glass melting and glass production process. Also the conditions in dishwashing as temperature, water hardness and time are very important and have a big influence.
To delay or even avoid glass corrosion optimized cleaning agent and glass protection additives are helpful.

4. REFERENCES

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