Attack on Glass: Corrosion Attack Mechanisms

Section: Glazes, Subsection: Food Safety

Description

Max Richens outlines the various mechanisms by which acids and bases can dissolve glass and glazes. He provides some information on stabilizing glazes against attack.

Article

The corrosion attack mechanisms on glasses and glazes can vary greatly depending on the pH and strength of the attacking medium as well as other factors. Water can be very aggressive especially when it reaches the critical pH of 9 by dissolution of alkalis from the glass surface. Under these conditions even vitreous silica (which will protect from boiling acids) will be attacked. If the surface area in contact is large and the volume is low (as, say, a stack of glass sheets) then this can happen fairly rapidly.

Acid solutions (ignore HF for the moment) attack the fluxes in the glass dissolving them by substituting hydrogen Ions for the alkali ions and opening up the silica skeleton (You get a dull finish where attack has taken place.) The strength of the acid can be crucial. With boiling Sulphuric Acid solutions the attack increases up to 25% and the drops to not a lot at full strength because the acid is no longer ionic therefore fewer hydrogen ions for substitution. When the glass/glaze is high in silica and low in alkali the silica / hydrate film formed will protect the surface from further attack.

Culinary acids such as Citric (orange, lemon,etc) and Acetic (vinegar) can be worse than sulphuric or hydrochloric as they will chelate with the metals present and make them into soluble complexes. That is why comments about orange juice and metal release are important. The calcium, magnesium and aluminium ions which increase the chemical durability of the glass will react and allow a clear path to further attack. Tannic acid (possibly in tea and red wine) acts in a similar manner. Other complexing agents are sucrose (sugar) and alcohol. A small amount of leached copper oxide (10ppm) will sufficiently taint fruit juice to make it unpalatable.

Alkali solutions attack the silica skeleton. Although the attack on the alkali structure doesn't take place; by breaking the silica skeleton down more alkalis are released to join the attack on the glass. Additions such as Zircon can inhibit this attack more effectively than Alumina in alkali silicate glasses. The opacifying effect would, however, be detrimental in a clear glaze.

(Molten NaOH eats glass, as will a 50% boiling solution of NaOH; though at a lower rate. Doesn't touch stainless steel though. This is a well tried process for de-enamelling sheet iron articles which cannot be shot-blasted)

A lot more work could probably be done on comparing slightly different glazes for the changes in chemical resistance and also the effects of under and over firing the glaze. For example take the Lead Bisilicate used as a source for lead. The effect of raw lead oxide on pottery workers led to experiments to make it safer to use. The results showed that the lead-silica ratio of one lead to two silica was the least soluble of the mixes. (ref 2) It was also found that by adding Alumina to the combination the solubility dropped again by a large factor. If, however, borax is used in the lead frit it can increase the solubility of the lead from the frit (ref 3).

This is the traditional reason for having separate borax and lead frit components in preparation of 'Raw' glazes. (ref 4) This is not to say that the final fired glaze will be more soluble because it has borax and lead in it. The balance of the final glaze will determine that. Copper oxide in the glaze will greatly increase the leachability of lead.

Generally speaking using calcium, magnesium, and zinc in the glass formula will increase the chemical resistance over that with sodium and potassium. This is why low fire glazes, which contain more group 1 (periodic table) fluxes and less glass formers, are more susceptible to attack. In these cases lead, barium, zinc etc help improve the chemical resistance.

Special effect finishes can sometimes be more prone to attack than the base glaze. From porcelain enameling experience (bear in mind that enamels are formulated frits that generally fire onto steel at 750-850 degrees Celcius in 4-10 minutes) : a matte finish can be obtained by mixing two dissimilar glasses, one a normal alkali boro-silicate glass with excellent acid resistant properties, the other an alumino-phosphate glass also chemically good. Combined they gave a matte finish with very little acid resistance.

Reading

The book by Bull and Taylor (ref 1) is a good general read on glazes from experienced commercial people. There are references in it which would take you further than this article has on the whole matter of glazes. (ref 5)

There are further works on the structure of glass and glazes by Zachariasen, Warren, Andrews, Mellor etc but you can start getting in quite deep.

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References

1 A good general text 'Ceramics Glaze Technology' J R Taylor & A C Bull, Pergamon, ISBN 0-08-033465-2

1 ibid Page180

2 'The use of lead in the manufacture of pottery' T H Thorpe, 1899, UK govt paper 8383-150093/1901 wt 32982 Da S-4

3 Harkort, Sprechsaal 67 621 1934

4 'Ceramic Glazes', Felix Singer & W L Geman. (A Borax Monograph), Borax Consolidated Limited. 1960

5 (No.. I don't have any shares in it ;-) I just think it's an excellent book)