

Classification of Corrosion due to Damp Heat in Phosphate Glasses

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Corrosion disturbs the performance of optical surfaces. However, the pattern varies strongly with chemically distinct glass types. Different techniques for description and quantization are discussed. There is no universal measurement, instead, comparative tests need to be conducted. Results may vary from one laboratory to another.

1 Introduction to corrosion via damp heat

Humidity at increased temperatures can lead to corrosion in sensitive glasses. Fig. 1 illustrates an advanced stage of corrosion observed on an optical filter glass sample. This corrosion represents a chemical degradation process that starts at the surface and progressively penetrates into the bulk of the material over time.

Such corrosion cannot be cleaned off. Instead, affected glass components require repolishing to restore their optical quality.

In technical applications, a critical consideration is the onset of corrosion as well as the point at which it leads to optically detectable effects, including:

- increased global scattering
- formation of localized scattering centers
- development of localized surface defects
- alteration of the wavefront
- formation of a liquid film or, alternatively, the development of a crystalline layer.

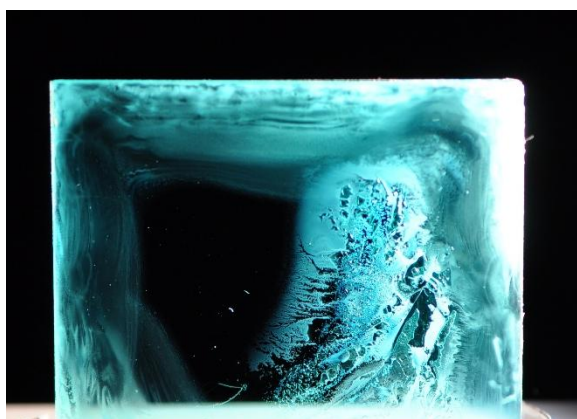


Fig. 1 Corrosion of a coated NIR cut filter after 96 h in a climate chamber at 85 °C / 85 %rh. The progression of the chemical reaction beneath the coating is from the edges towards the center.

2 Model of corrosion mechanism

Corrosion is a chemical process and is therefore primarily governed by glass composition. Since all

glass types differ chemically, no universally applicable model for corrosion exists. Nevertheless, certain systematic trends can be observed, allowing the process to be divided into distinct phases. For a phosphate glass, the following sequence applies:

1. The polished glass exhibits a pristine, surface (e.g. polished and cleaned surface). No corrosion is detectable.
2. Moist air reacts with the surface causing oxygen and hydrogen species to be incorporated into the glass matrix. As a result, the surface properties are altered.
3. Diffusion processes commence. Increasing amounts of water penetrate into the near-surface region where the species interact with the glass network. The glass chemistry is modified within a near-surface layer. As a consequence, the glass network progressively decomposes. Simultaneously, weakly bound elements diffuse from the bulk into the hydrated layer. Certain elements may migrate to the surface and accumulate there. This can result in the formation of a uniform film or in localized coagulation or precipitation. Under certain conditions, 'defect centers' may develop within and/or on the surface.

At this stage, corrosion becomes optically visible and begins to impair the functional optical performance. Since the nature of the corrosion products depends on the specific glass composition, the resulting optical effects vary significantly between different glass types.

In technical practice, corrosion is typically detected and evaluated by visual inspection. Analytical techniques such as time-of-flight secondary ion mass spectrometry (ToF-SIMS) can be employed to characterize both the chemical reactions and the penetration depth of the corrosion layer.

3 Methods for characterization: HAZE measurement

For certain glass types, direct measurements of the scattered light fraction (HAZE) can yield inconsistent results when a liquid film forms on the

surface. In such cases, the measured HAZE value may decrease despite a progressing corrosion process. For this type of corrosion, the HAZE measurement is not applicable.

Additionally, the method cannot be used to compare different glass types, due to differences in chemical composition, which can cause different corrosion topologies, thus influencing the HAZE measurement.

4 Methods for characterization: visual inspection

The most widely used method is subjective visual inspection under grazing illumination, or diffuse light against a dark background. This method is applied to determine the onset of corrosion at a level that is no longer acceptable from an application perspective.

However, the results are strongly dependent on the individual examiner. Additionally, the visual inspection is a test method, leading to “good” or “no good” results.

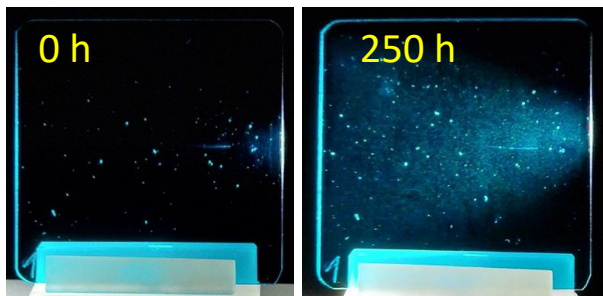


Fig. 2 Fluoro-phosphate glass before and after climate chamber testing at 85 °C and 85 % rh

Despite all the disadvantages of this method, it is widely used in the industry (see [1] for example), because of the simplicity of the setup.

5 Methods for characterization: gravimetric analysis

In particular, pure phosphate glasses readily absorb moisture from the ambient atmosphere and consequently exhibit a significant increase in mass during the course of corrosion. This mass gain can be used as an indicator of the corrosion rate. However, relatively fresh samples (showing little or no corrosion) and highly corroded samples do not exhibit linear behavior. Thus, this technique can provide measurement values. However, the range of linearity needs to be evaluated first.

Note: The samples must be equilibrated to room temperature after removal from the climate chamber in order to ensure accurate mass measurements.

Although the gravimetric analysis provides meaningful measurement values in the linear range, the onset of corrosion cannot be deduced from those results. Additionally, this method is only applicable

for large samples and glasses that absorb a significant amount of water.

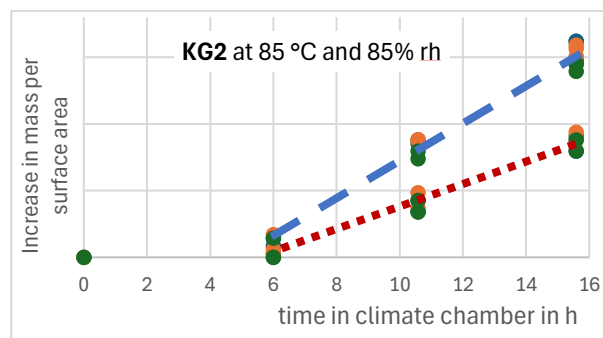


Fig. 3 Gravimetric analysis of corroded glass samples (phosphate glass KG2). The results depend strongly on the difference in temperature of environment and sample. The red curve depicts the warm samples and the blue curve depicts results of samples in thermal equilibrium.

6 Conclusion: only comparative measurements are feasible

Environmental conditions, glass composition, and surface properties represent the principal factors influencing corrosion susceptibility. To ensure reliable reproducibility and comparability of results across different workshops and laboratories, a standardized polishing and cleaning procedure would be essential. However, this is not feasible, as sensitive glass materials require application-specific manufacturing and cleaning processes. Also, each manufacturer produces surfaces with distinct chemical composition and morphology.

Accordingly, the following conclusions can be drawn:

- Measurements obtained from different laboratories / manufacturers are not directly comparable.
- Only samples originating from the same polishing and cleaning process can be meaningfully compared.
- Environmental conditions: results obtained under different temperature and humidity conditions are not transferable.
- Visual inspections can be used to determine the onset of corrosion that is technically unacceptable.
- Gravimetric measurements can provide a comparative indicator of the corrosion rate, but the onset of corrosion cannot be determined.

References

- [1] “Optical filter glass 2026” (SCHOTT AG; product catalog