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Original article

A new cleaning method for historic stained glass windows

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Abstract

Historical stained glass has a clear tendency to form a crusted layer on its surface due to the environmental exposure. One of the most delicate aspects to be faced during the restoration of historic glass windows is the cleaning of these thick corrosion crusts.

For several centuries, stained glass windows have been cleaned using damaging mechanical (scalpel) and chemical (high acidic or alkaline solutions) methods. Today's understanding of the cleaning process comprises two complementary aims: improving the readability of the glass and reducing the weathering process of the historical glass. The act of removing deposits and encrustations resulting from corrosion should not endanger the artwork itself. Mechanical methods, cleaning solutions or gel pads are now being developed. However, these methods could present further problems.

In this study, we examine a new cleaning method that can be employed to remove encrustations in a quick and efficient way. Results up to now, obtained on specific stained glass windows are promising; further researches are in process for other cases. We propose an optimized solution to dissolve calcium carbonates and lead sulphates from Avila Cathedral glass windows crust. This system is tailored to control pH, temperature, conductivity and concentration of Ca^{2+}. Continuous on-line analysis of these parameters allows us to monitor the cleaning process. In particular, the Ca^{2+} concentration in the cleaning solution is controlled by means of a Ca^{2+} ion selective analyzer.

Keywords: Glass cleaning; Glass crust; Accelerated glass weathering; Grisaille; Laminar flow; Crust solubility

1. Introduction

In the mid XII century, some glass workshops emerged within Spanish cathedrals such as León and Toledo. Subsequently, independent workshops were developed in Burgos and Seville. Stained glass had been imported into Spain, which explains the presence of German, Flemish and French glass artists who worked and taught their craft in these workshops [1]. Nowadays, Spain preserves relevant artworks made by great Flemish artists, although in some cases, their state of conservation is precarious due to the fragility of both the glass and its pictorial layers.

Glass decoration is accomplished by applying a mixture called grisaille which consists of a low-melting glass powder, a binding agent and colouring pigments of iron and copper. Grisaille is used not only to paint details on faces, hands, cloths or patterns, but also to modify glass tonalities. After applying the mixture, the glass piece is again heated at around 600 °C. If the firing and/or the composition are not appropriate, tensions will arise, causing the detachment of this pictorial layer [2].

One of the most delicate stages in the restoration–conservation of stained glass is the cleaning process, whereby both slightly-adhered debris (usually, inside painted glass faces) and strongly-fixed crusts (usually, outside on non-painted glass) of crystallized materials should be removed from the glass surface without irreparably damaging it or its grisaille. The aim of this removal of surface crust is to avoid further

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artwork deterioration and to allow its iconographic reading. Nevertheless, this process should not be aimed at giving shine or transparency to the glass, since this would ''strip'' the weathered protective layer surface of all the protection, making the glass piece more vulnerable to future attack and remove possible thin original grisaille layers [3]. Furthermore, original stained glass is likely to have been almost completely painted with more or less dense cold-applied patinas which modulate light, thus avoiding glare.

The durability of a glass and, subsequently, the crusts that will form on its surface depend on a series of factors such as: glass composition (relationship between formers, modifiers and stabilizers), production process; environmental parameters; previous restorations, and biological attack.

The chemical stability of a glass depends on its composition, the presence of water on its surface and on the pH of the medium where it is located. In an acidic medium, the alkali ions migrate to the solution (dealkalinisation or leaching) and form leached hydrated silica glass layer. The alkaline medium is much more aggressive because the break down of the glass network occurs very quickly [4].

Historical stained glass windows are in permanent contact with water. Condensation of environmental humidity generally takes place in the form of dew drops on the inside glass face, whereas the outer side of the glass is affected also by rain washings. The state of conservation that each side presents is usually very different. Also the paint layers are very different. The most of the paint is on the inside of the windows and the crusts are mainly outside. This directs cleaning actions: transparency can be achieved by cleaning the crusts outside but more gentle cleaning actions are required for cleaning painted areas. Apart from that, crusts or dirt inside are never so dense and difficult to clean, so that different cleaning methods could be used on cleaning inside and outside surfaces. The reason for this difference in the degree of surface alteration is based on ion exchange reaction which occur between the water and the glass, generating significant changes in pH and favouring the processes of dealkalinisation and break down of the glass network. However, a shorter time of wetness does not allow a chemical balance reducing glass leaching [5]. In fact, by using a convenient solution volume during a short time, insoluble salts could be solved. Based on this, we designed a system to remove corrosion crusts consisting of the use of an over saturation volume of neutral or slightly acid solutions, allowing them to flow on one side of the glass to avoid saturation and changes in surface pH.

Methods for cleaning stained glass should be chosen according to the composition of both the glass and its crusts. Most of the reported crusts have a composition consisting of silica (30–50%), SO_3 (17–28%), CaO (9–15%) and K_2O (10%) [6]. Poorly soluble salts, which darken the glass, are mainly SiO_2 xH_2O (hydrated silica), $CaSO_4$ $2H_2O$ (gypsum), $CaSO_4$ $1/2H_2O$ (basanite), K_2SO_4 (arcanite), $K_2Ca(SO_4)_2$ H_2O (syngenite), $K_2Pb(SO_4)_2$ (palmierite), $PbSO_4$ (anglesite) and $CaCO_3$ (calcite). Nitrates, other carbonates and other sulphates are more soluble and do not form crusts [7]. Grisailles also develop crusts, generally consisting of $CaCO_3$, $CaSO_4$ and/or $PbSO_4$. If the grisaille is also detached, the cleaning process can be very difficult.

In any case, a previous crust analysis is needed for every conservation–restoration on glass windows. A careful adaptation of cleaning conditions has to be made for every case.

Once the state of conservation of glass and adherence of the grisaille has been established, the least fixed debris can be removed using very soft natural bristle brushes. The most adhered deposits must be removed using carefully selected ''chemical'' methods as complexing solutions (EDTA, thiosulphates, citrates, etc.) or gel pads, which allow greater control over the application areas. This method is highly effective for cleaning very small and damaged areas [8]. However, the application conditions must be carefully controlled to avoid dissolution of lead and iron cations that could affect the grisaille or the calcium in the glass. Gel pads and complexing solutions may leave some debris that might end up damaging the glass in the long term [9,3]. Also laser cleaning has been studied, concluding that cleaning of stained glass windows with lasers is possible within limits [10].

The choice of a cleaning method also depends on the fact if the window has to be dismantled to replace the lead cames. In this case the glass pieces can be cleaned before placing them back in a new lead structure. Conservation ethics require, however, that the lead cames shall be kept as long as possible and for these cleaning campaigns, a method which allows cleaning ''in situ'' of the glass-lead composition has to be applied.

2. Research aims

In view of the difficulties to fix grisailles, and the current lack of effective and guaranteed methods to do it, the method proposed here allows one to clean only unpainted sides of the stained glass being restored, avoiding thus any intervention on the damaged grisaille.

Application conditions were optimized using current glass pieces and grisailles with diverse manufactures and compositions which had previously undergone an accelerated weathering process. The optimized method was subsequently applied to clean the outside of stained glass window from Avila Cathedral which is currently being restored by the studio Vetraria Muñoz de Pablos, S.L. This method requires that the glass to be taken out from its lead structure.

The relative composition of all materials, as well as the crystalline phases of the corrosion products were determined using portable and/or non-destructive methods for analysis without sampling, so that they could be applied to real samples of cultural heritage artworks. The techniques used in this work meet several of these requirements. We applied portable X-ray fluorescence analysis (EDXRF) and focused-XRD diffraction systems. Some destructive analyses (SEM-EDX) of model glass have been done to prove the absence of leaching after cleaning.

3. Experimental section

3.1. Instrumental techniques

Non-destructive focused diffraction analyses (f-XRD) were carried out using a SEIFERT XRD 3003 TT diffractometer,