The characterization of a XVth century stained glass panel from the Monastery of Santa Maria da Vitória in Batalha is performed. With the identification of the corrosion products, it is proposed a study of ionic liquids as a cleaning method for the corrosion crusts.

Introduction

Medieval stained glass production in Portugal begins in the 15th century, late in the European context. The oldest conserved remains come from the Monastery of Santa Maria da Vitória, in Batalha. The stained glass panel "Figura Aureolada" dates from 1440-1448 and was originally installed in the south aisle of the monastery church. Its condition is bad/fragile, presenting, among several other phenomenas, corrosion crusts, fractures and browning of the surface [1].

Medieval stained glass is characterized by a high amount of alcali and alcali-earth ions, mainly potassium, and low contents of silica. In the presence of water and an environment with pH>9, begins the extraction of the alcali ions from the glass network, with the formation of a hydrated surface layer rich in silica. In the presence of pollutant agents, CO₂ and SO₂, insoluble salts as calcium carbonate and calcium sulfate are formed [2].

Nowadays the methods for the cleaning of corrosion crusts tend to be agressive, whether with the aid of scalpels or the application of chelant agents such as EDTA, oxalic or citric acids, or the piranha solution, a mixture of sulfuric acid and hydrogen peroxide[3].

Ionic liquids are formed by a combination of an organic cation and an anion (organic or inorganic) with a melting point below of 100ºC. The main advantages for this work are related with their low vapor pressure and low volatility, variable solubility and viscosity rates, depending on which cation and anion selected. Additionally many of these materials can be liquids at room temperature, so called RTILs (Room-Temperature Ionic Liquids)[4].

Experimental Procedure

The experimental studies included: a) Characterization of the detected corrosion at the glass surface, b) selection of seven ionic liquids for dissolution tests of calcium salts and their possible effect on glass and grisaille models of similar composition found in Batalha, and c) cleaning of glass samples that were corroded in laboratory.

The RTIL's selected were chosen among three families of cations (ammonium, phosphonium and imidazolium), combined with several anions (e.g. chloride, ethylsulfate and dicyanamide). The analytical techniques used were: Optical Microscopy (OM), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray spectroscopy (XRF), Fourier Transform Infrared Spectroscopy (FTIR), Raman spectroscopy and Inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Results and Discussion

The characterization of the corrosion crusts was performed by non-destructive analysis, with the identification of white opaque crystalline forms of great adhesion to the surface, constituted mainly of calcium carbonate, calcium sulfate and calcium oxalate.

FTIR and Raman characterization of ionic liquids show their ability on the dissolution of calcium salts.

No significant effects on the glass surface after the application of each ionic liquid were reported. Cleaning tests over corroded glass samples revealed good results.

Ionic liquids can be used as alternative greener solvents over the conventional toxic cleaning solvents, because their very low vapor pressure and also as designer solvents. Preliminary results have shown a relevant cleaning performance, with a significant controlled removal of the corrosion layer at the surface. A more detailed analysis of glass models and corroded samples with SEM is in progress. The application of each ionic liquid over the grisailles is being performed. After these experiments the application of RTIL's will be tested over the stained glass panel of the Monastery of Batalha, named "Figura Aureolada".

Acknowledgements

The authors wish to thank Prof. Rui Silva from the Department of Material Engineering for the support in the optical microscopy.

References