Journal of Cultural Heritage 16 (2015) 365–371

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Case study

17th century blue enamel on window glass from the cathedral of Christ Church, Oxford: Investigating its deterioration mechanism

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ARTICLE INFO

Article history:
Received 25 February 2014
Accepted 26 June 2014
Available online 23 July 2014

Keywords:
Blue enamel
Painted glass
Cracking
Thermal expansion coefficient
SEM-EDS
Van Linge

ABSTRACT

A chance discovery beneath Christ Church Cathedral, Oxford has brought to light some very well-preserved 17th century van Linge enamel-painted glass fragments. Deterioration was in most cases minimal and largely limited itself to the blue areas of the fragments. Here, cracking in both the enamel and the glass surface beneath it was observed, which resulted in detachment of the painted enamel and of some of its underlying glass in the more severely affected areas. This study investigates the deterioration mechanisms involved and demonstrates that cracking was probably brought about by different levels of expansion and contraction experienced by the paint layer constituents in response to fluctuations in temperature. Differences between the thermal expansion coefficients in the enamel paint and glass are thought to induce the formation of microcracks within the enamel. Certain physical properties of the blue enamel were expected to increase these thermal expansion coefficient differences, making this colour more susceptible to deterioration, resulting in the selective detachment observed in these painted fragments.

1. Introduction

In a routine clear out of a coal hole beneath Tom Quad in Christ Church, one of the colleges of the University of Oxford, over 9000 enamel painted window fragments were recovered. It was obvious that the fragments were part of an early scheme for the windows of Christ Church Cathedral, which doubles both as college chapel as well as cathedral church for the diocese of Oxford. Stylistic analysis and comparison with existing windows elsewhere in the Cathedral and in other colleges indicated that the majority of the fragments were remains of a 17th century scheme of windows carried out by the van Linge brothers [1,2]. Records from college archives show that the van Linges had been commissioned to execute an entire scheme of perhaps as many as 19 windows for Christ Church Cathedral between 1631 and 1641, as well as for other college chapels and individual windows in Oxford [2–4]. Most of the Christ Church windows probably portrayed a single scene depicting an event in either the Old or New Testaments, and would have been one of the largest in the country installed at this time [2]. Despite the cost of the scheme, all windows were quickly removed from the Cathedral during the English Civil War after 10 years [5–8]. They then had a complex history: some were lost and others returned to windows, moving several times before being stored and eventually re-discovered in the coal bunker [4,9]. Only two of these van Linge windows still remain as windows in Christ Church; namely 'Jonah before Nineveh', and the heraldic representation of 'Bishop King'.

The palette employed on these fragments consisted of opaque black contours with various shades of red, blue, green, purple and brown enamels, and a yellow stain. In general, the glass itself and the majority of the surface enamel of these discovered fragments appeared to be in a very good state of preservation. An exception to this was the blue enamel, which in places showed considerable cracking, flaking and detachment. This deterioration was also presented in the two surviving van Linge windows in the cathedral.

Similar degradation of paintwork and enamel on window glass has previously been documented in 16th, 17th and 19th century enamels, with the most commonly occurring loss also reported in blue enamels [10–12]. Nevertheless, though glass corrosion has been an intensely studied problem, little research has looked at this loss of paintwork. Relevant studies by Verita (2003) and Becherini (2008) have both explored expansion coefficient differences as the main cause for grisaille detachment on prepared physical glass models [13,14]. The impact of thermal stresses resulting from direct solar radiation are also measured with respect to paint colours, and it is indicated that blue and purple grisaille present a maximum thermal difference when exposed to thermal stresses [13]. Work specifically focusing on expansion coefficients of blue enamel reports slightly different crack patterns in the glass support when

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http://dx.doi.org/10.1016/j.culher.2014.06.011
1296-2074/

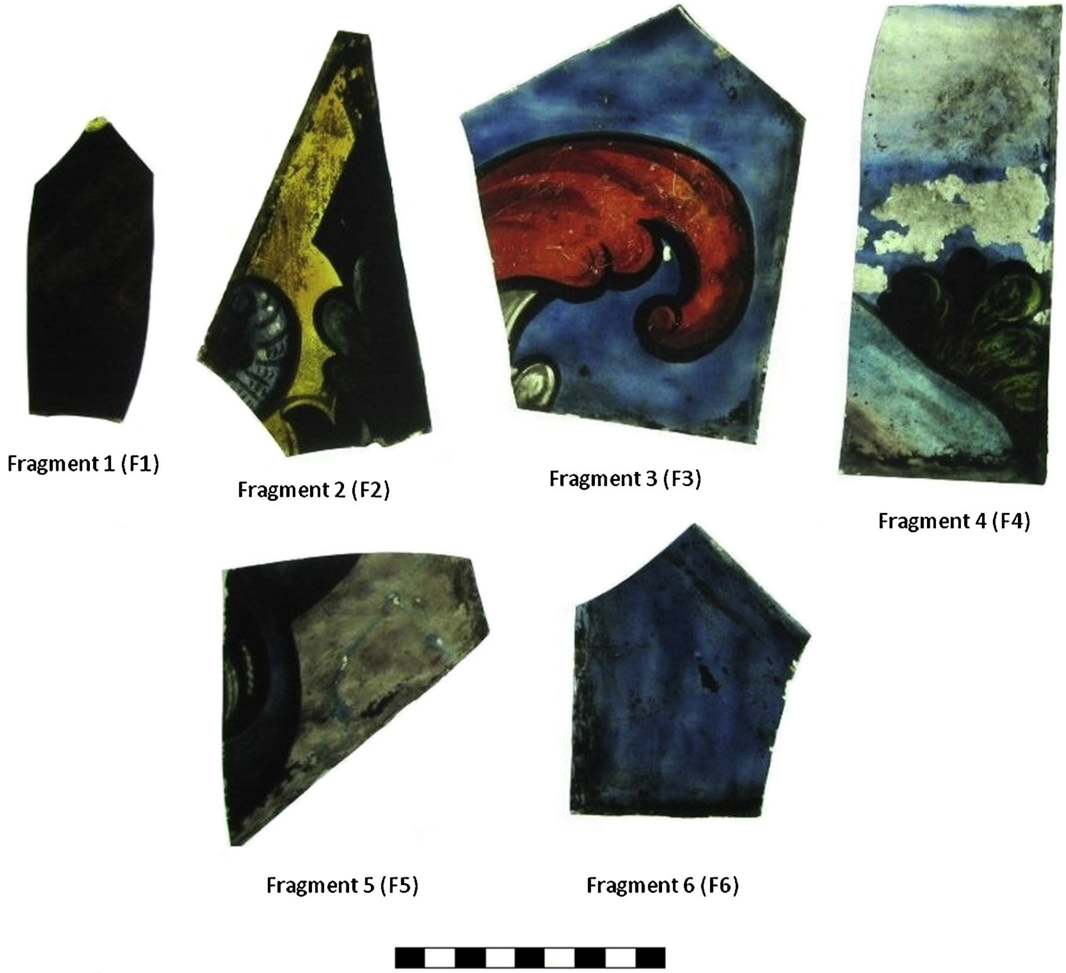

Fig. 1. Photographs of the selected fragments collected from the coalhole.

compared to those observed in van Linge glasses [12]. The present work complements previous research on the deterioration of grisaille and enamels painted on glass, exposed to environmental weathering. It is the first study in its kind that looks at such well-preserved glass fragments, potentially from one of the largest schemes of painted glass windows commissioned and installed during the 17th century in Britain. This study also investigates theoretical calculations for expansion coefficient based on compositional and physical measurements from the painted glasses.

2. Research aims

The detachment of blue enamel in these van Linge fragments indicated a problem inherent to structure and composition of the enamelled window glass, rather than simply relating to its location and associated history. The aims of this research were to characterise the materials and identify the physical processes experienced by the glass and enamel in these fragments. This paper focuses on the blue enamels and discusses possible deterioration processes that led to their particular vulnerability and selective detachment.

3. Experimental

Visual observations of fragments collected from the coal hole were carried out under direct, transmitted and raking light at Christ Church in Oxford. From the many fragments, six representative fragments were selected for further analysis based on the period of history they were assigned to, their good range of colours, as well as the presence of blue enamel with varying degrees of deterioration (Fig. 1). All samples were firmly stylistically identified as 17th century van Linge fragments.

Twenty-three subsamples were taken from the six fragments and were initially examined visually under an optical microscope. These were then mounted on aluminium stubs using a carbon-loaded pressure sensitive adhesive and observed in a CamScan MaXim 2040 VP electron microscope (SEM-EDS) operated in EnVac (VP) mode at 20 kV. Samples were further prepared in cross-section by mounting the fragment perpendicular to the glass surface for backscattered electron imaging and EDS analysis of stratigraphies. Samples were also carbon coated to prevent electron charge build-up. SEM-EDS examination of these sections was executed using a Cambridge Instruments Zeiss SMT S360 SEM, operated in HV also at 20 kV. Quantitative oxide concentrations in weight percent (wt%) were calculated by stoichiometry from element concentrations as detected by the attached Oxford Instruments INCA energy analyser. Readings were collected using EDS factory settings at 90 s live time from 3–5 areas through the glass, and 5–8 areas in the enamel per sample during analysis of cross-sections. Regular runs against a cobalt standard were executed at every 20–30 minutes of analysis time to check for machine drift and calibrate the instrument. Accuracy was monitored against Brill's Corning standard D and analyses normalised to 100% for comparability [15]. Backscattered electron images (BSE) and elemental maps were obtained in the CamScan electron microscope at scanning times of 500–2000 minutes.