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Patination of historical stained windows lead cames from different European locations

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Abstract

Lead patination is a well-known phenomenon that occurs when lead is exposed to the atmosphere. A thin film mainly composed of insoluble lead salts is then formed on its surface, protecting lead against further corrosion. A study of the superficial patination of an ensemble of historical stained glass windows lead cames from different European locations (Belgium, Germany, Holland, Spain and Poland) and different chronologies (from 13th to 20th centuries) is reported in this paper. The main goals of the research were to characterise, both morphological and chemically, the patinas formed on their surfaces and to assess the weathering factors influencing the development of these patinas. Conventional optical microscopy (OM), scanning electron microscopy (SEM) with energy dispersive X-ray microanalysis (EDX) and micro-Raman spectroscopy were used to determine the composition of the patinas. The resulting data have proved to be very useful in establishing the degree of advance of the patination process, which seems to be directly influenced by the environmental conditions to which the lead cames were exposed rather than by chronology of the samples. The results have also provided outstanding data to make decisions in conservation/restoration issues of such historical materials.

Keywords: Lead cames; Stained glass windows; Patination; Raman spectroscopy; Cultural heritage

1. Introduction

In the production of historical stained glass windows, H-shaped or double-T lead cames were commonly used to assemble both coloured and colourless glass pieces into the different panels. Such lead cames were welded to each other using a melted tin–lead alloy [1]. In addition, putties made from calcium carbonate mixed with linseed oil or other organic compounds as binding media were also used to fix glass pieces into the lead came network.

Broadly speaking, studies on stained glass windows have been mainly focused on the analysis and deterioration of glasses [2–6] and the iconographic motifs painted on their surfaces using the so-called grisailles, a vitrifiable paint elaborated from transition metal oxides [7]. However, to date, either from a conservational or historical perspective, little attention has been paid to other materials, such as the own lead cames, which also form part of the whole stained glass windows but very often considered as secondary elements.

As the rest of materials forming the stained windows, lead is also subjected to weathering phenomena [8]. When exposed to the atmosphere, a protective thin film mainly composed of insoluble lead salts and known as patina is rapidly formed on its surface. This film gives lead the typical dark grey appearance and makes it resistant against later corrosion [9]. As a general rule, it has been common to remove the lead came network every time that the stained glass window panels were repaired in the past, mainly due to the physical deterioration: e.g., bulge and/or sagging caused by the pressure of wind. Nevertheless, in spite of having been considered a secondary element, this metallic item can be also a first-hand document, as the glass pieces or the rest of materials, for studying the technical and

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historical development of the stained glass windows in Europe. For this reason, the characterisation of the weathering effects that give rise to lead patination is an important task in preservation and restoration works of these historical materials, not only to know their current state of conservation but also to make decisions, based on this knowledge, on the convenience of removing or remaining lead cames in their original places, leaving as far as possible the original work of art unchanged or unaltered [10]. The importance of lead came conservation in stained glass windows has been also pointed out by the International Corpus Vitrearum through its guidelines [11].

This paper is focused on the study of the superficial patination of a wide ensemble (19 samples) of historical stained glass windows lead cames from different European locations, namely Belgium, Germany, Holland, Spain and Poland; and different chronologies, from 13th to 20th centuries. Additionally, three modern lead came samples were also selected for comparison. The main goals of the research were to morphological and chemically characterise the patinas formed on the lead came surfaces by conventional optical microscopy (OM), scanning electron microscopy (SEM) with energy dispersive X-ray microanalysis (EDX) and micro-Raman spectroscopy; as well as to assess the weathering factors influencing the development of the patinas. The research was also aimed at determining the current state of conservation and the corrosion degree of the different lead came samples analysed. The resulting data, especially those provided by micro-Raman spectroscopy, have proved to be very useful in establishing the degree of advance of the patination process, which seems to be directly influenced by the environmental conditions to which the lead cames were exposed rather than by the chronology of the samples.

1.1. Lead patination process

In the literature [9,12], the atmospheric patination of lead is described in two different ways:

$$Pb \rightarrow PbO \rightarrow 2PbCO_3 \cdot Pb(OH)_2 \rightarrow PbCO_3 \rightarrow PbSO_3 \rightarrow PbSO_4 \quad \text{(I)}$$

$$Pb \rightarrow PbO \rightarrow 2PbCO_3 \cdot Pb(OH)_2 \rightarrow 4PbO \cdot PbSO_4 \rightarrow PbSO_4 \quad \text{(II)}$$

In the first corrosion mechanism, metallic lead is quickly oxidised by atmospheric oxygen forming lead oxide, which then forms the basic lead carbonate hydrocerussite by reaction with atmospheric CO_2 and humidity. Higher exposure to CO_2 turns hydrocerussite into the common lead carbonate cerussite. Finally, with the presence of SO_2, cerussite converts into lead sulphite, which forms lead sulphate when the former is oxidised. A second route of reactions points out, with the presence of SO_2, the formation of a tetrabasic lead sulphate from the basic lead carbonate hydrocerussite. Such tetrabasic lead sulphate turns later into normal lead sulphate, which is the final phase of both sequences of reactions. Furthermore, lead surfaces exposed to marine environments may form also patinas with some compounds containing chlorine. As a result, lead oxide reacts with humidity and the anion Cl^- to form the basic lead chloride laurionite [Pb(OH)Cl], while the phase formed in the presence of CO_2 and Cl^- is phosgenite ($Pb_2CO_3Cl_2$) [13]. In addition, other insoluble lead mixed compounds can be formed, as well as non-stoichiometric lead oxides (PbO_x). In the present paper, most of the lead phases here mentioned were identified in the lead cames analysed through micro-Raman spectroscopy.

Table 1
Description of the lead came samples analysed in this study

Historical period	Sample	Date (A.D.)	Location
Gothic	A-10	Beginning of 13th century ?	Triphorium, Cathedral of Brussels (Belgium)
	P-3	Beginning of 14th century ?	Royal Windows, Cathedral of Köln (Germany)
	Ped-1	Beginning of 14th century	Monastery of Pedralbes (Barcelona, Spain)
	R-1	End of 15th century	Gruuthuse Castle (Middelburg, Belgium). Archaeological
	C-1	End of 15th century	Cartuja de Miraflores Monastery (Burgos, Spain)
Renaissance	A-8	16th century	St. Lenaarts Church (province of Antwerpen, Belgium)
Neogothic	A-1	End of 19th century	St. Barbara Church (Leuven, Belgium). J.B. Capronnier Workshop (Brussels, Belgium)
	A-2	End of 19th century	Cathedral of Antwerpen (Belgium). J.B. Béthune Workshop (Gent, Belgium)
	A-3	End of 19th century	Cathedral of Antwerpen (Belgium). Dobbelaere Workshop (Brugge, Belgium)
	A-4	End of 19th century	Cathedral of Antwerpen (Belgium). Stalins-Janssens Workshop (Antwerpen, Belgium)
	A-5	End of 19th century	Cathedral of Antwerpen (Belgium). E. Didron Workshop (Paris, France)
	P-1	End of 19th century	Ludwigshafen Church (Germany). Koob Workshop
	P-2	End of 19th century	Warenfridus Church (Workun, The Netherlands). De Vos Workshop (Utrecht, The Netherlands)
	P-5	End of 19th century	St. Laurentius Church (Warendorf, Germany). V. Von Der Forst Workshop (Münster, Germany)
	J-1	End of 19th century ?	Jagellonian University Museum (Cracow, Poland)
	P-4	Beginning of 20th century ?	Restoration of a 15th century stained window made by Enrique Alemán, Cathedral of Seville (Spain)
	A-6 A-7	Beginning of 20th century	St. John Church (Antwerpen, Belgium). Stalins-Janssens Workshop (Antwerpen, Belgium)
Neorenaissance	M-1	Beginning of 20th century	Goyeneche House (Madrid, Spain). Maumejean Frères Workshop (Madrid, Spain)
Modern	A-9 N-1	21st century	Stillemans Company (Asse, Belgium)
	Z-1	21st century	Zelenski Workshop (Cracow, Poland)

The sign "?" means that there is uncertainty in the proposed chronology since it has been common to remove lead cames every time that the stained windows were previously repaired.