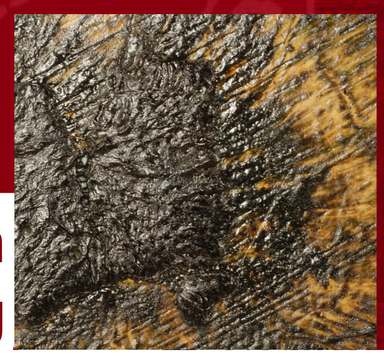
FACULDADE DE CIÊNCIAS E TECNOLOGIA UNIVERSIDADE NOVA DE LISBOA

LAMS Laboratoire d'archéologie moléculaire et structurale

DEPARTMENT OF CONSERVATION AND RESTORATION



A multi-analytical approach to investigate the mechanism of deterioration in an oil painting presenting severe asphaltum/bitumen cracking

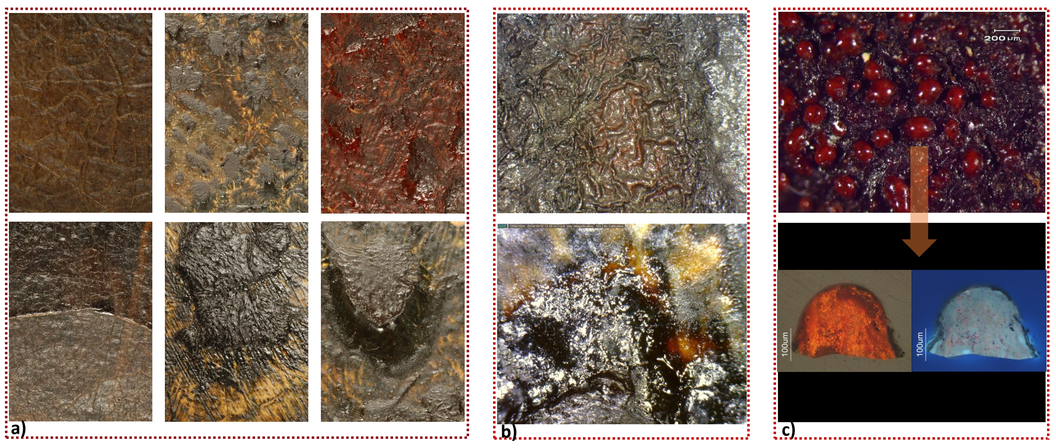
Raquel Marques,[1] Leslie Carlyle,[1] Isabel Pombo Cardoso,[1] Laurence De Viguerie[2]

[1] Department of Conservation and Restoration and LAQV-REQUIMTE, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal

[2] Laboratoire d'archéologie moléculaire et structurale, Sorbonne Universités, UPMC Univ. Paris 06, CNRS, UMR 8220, Paris, France

Introduction

A significant number of oil paintings produced during the mid-18th and 19th centuries in Europe suffer from a severe film-formation defect referred to as "Bitumen Cracking" or "Alligatoring" which develops some years after the work has been completed [1,2]. Paint surfaces are characterised by wide drying cracks and isolated islands of paint. In some cases the paint disruption is so severe the painting can no longer be on display. Such is the case for the painting *O Cardeal D. Henrique recebendo a notícia da morte de D. Sebastião* (dim.: 137.5 x 99.6 cm) painted in Rome, in 1861, by the Portuguese artist Marciano Henriques da Silva.



a) Macro-photography of paint surface (approx. 2x3 cm). Distorted paint islands and "exudates" (shinny paint) from and surrounding the paint islands.
b) Dino-Lite™ images, magnification 50x, showing wrinkled surfaces and softer exudates.
c) Stereomicroscope image of surface "beads" on top of a red island of paint. A cross-section of one bead (reflected light microscopy under cross-polarized light – left – and under UV light – right).

Multi-Analytical Approach

Considering the complexity of the paint surface and the different areas of interest, a multi-analytical approach for the investigation of the painting was developed making use of the following techniques:

Cross-sections
- ✓ Optical Microscopy
- ✓ µ-Raman
- ✓ SEM-EDX

Micro-samples
- ✓ µ-FTIR & FTIR-ATR
- ✓ GC/MS
- ✓ Py-TMAH-GC/MS

Complementary techniques
- FTIR-Imaging
- TOF-SIMS
- HPLC-DAD

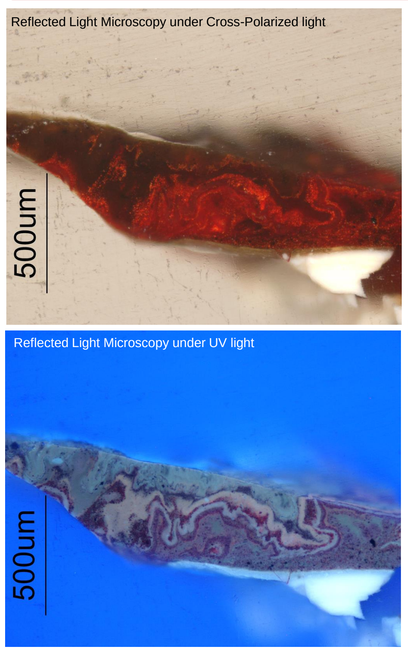
Pigments Characterisation

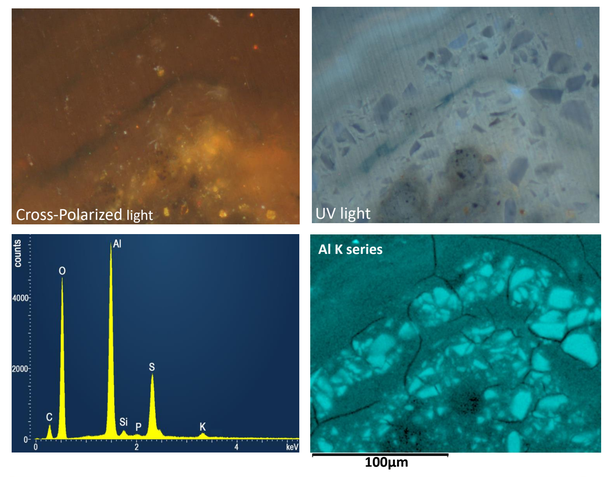
By focussing in-depth on the characterisation of *O Cardeal D. Henrique*, ongoing research aims to clarify how Marciano's choice of materials and technique may have influenced the development of the extreme paint defects, and whether the problems can be related to the larger context of severe *Alligatoring* found in many 19th century European paintings.

➢ Cross-sections show a complex stratigraphy with distorted and disrupted paint layering, best distinguished under UV light.

Cross-sections

✓ Optical Microscopy ✓ µ-Raman ✓ SEM-EDX

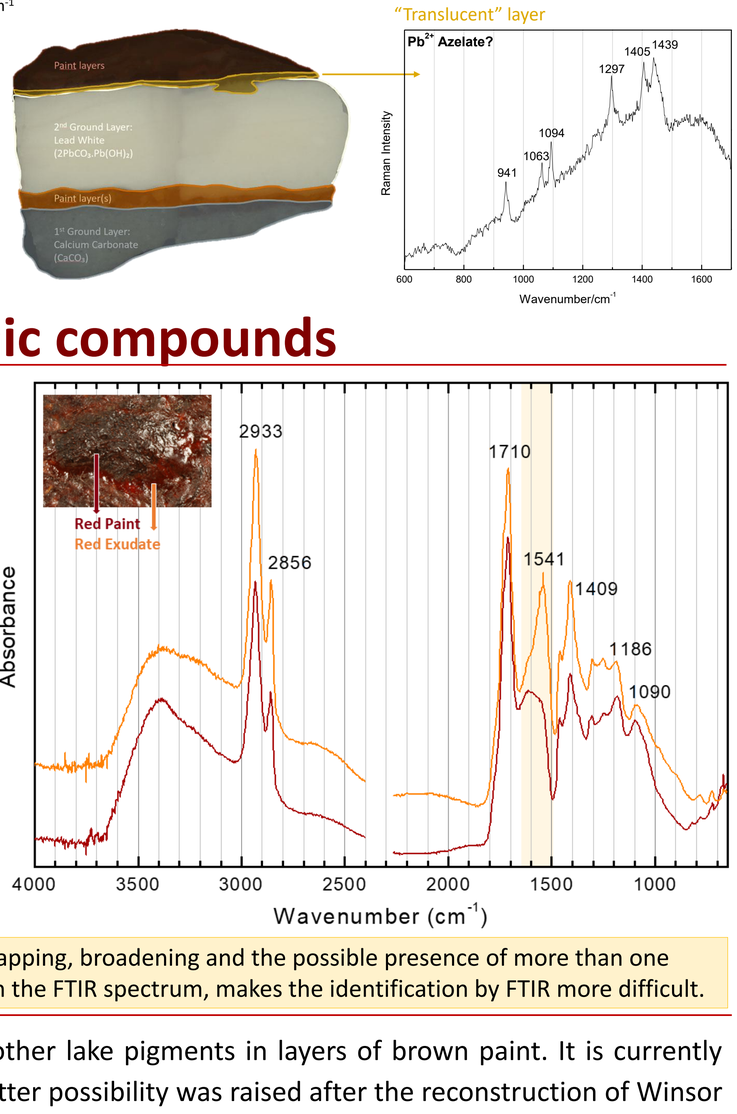




➢ Significant quantity of lake pigments: red, but possibly also brown or yellow in the brown glaze-like paint layers (identified by SEM-EDX showing particles composed of Al, S and K).

➢ "Translucent" layer containing lead azelate [3].

➢ Limited palette of inorganic pigments characterised by µ-Raman and SEM-EDS.



Characterization of Organic compounds

➢ So far, only highly hydrolysed drying oil has been identified (FTIR and GC/MS data) [4,5],

➢ The main differences amongst paint layer micro samples, are in the range of 1655 – 1480 cm^{-1} - metal carboxylate soaps region [6,7].

  ➢ These are most likely due to the presence of lead soaps, but considering the detection of Zn in the matrix and Al and K from the pigment particles, further discrimination is necessary.

➢ Data interpretation of the organic components and possible identification of bitumen/ asphaltum remains challenging. Further imaging techniques will be pursued.

Shifting, overlapping, broadening and the possible presence of more than one type of soap in the FTIR spectrum, makes the identification by FTIR more difficult.

Conclusions and Future Work

While red lakes were evident visually in cross-section, an unexpected finding during elemental analysis was the significant presence of other lake pigments in layers of brown paint. It is currently unclear whether lake pigments were used as the sole colouring agent or represent just one ingredient of a more complex paint mixture. This latter possibility was raised after the reconstruction of Winsor & Newton's "Bitumen for Oil Tubes" from production records in their 19th century archive. Asphaltum is dissolved in drying oil at high heat and along with other ingredients is the addition of Purple Lake. The role of the notoriously poor drying lake pigments remains to be examined but could also be eclipsed by the complex mixtures used to formulate Bitumen/Asphaltum brown oil paint.

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