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ALLIGATORING: AN INVESTIGATION INTO PAINT FAILURE AND LOSS OF IMAGE INTEGRITY IN 19TH CENTURY OIL PAINTINGS

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Master in Conservation and Restoration

DOCTORATE IN CONSERVATION AND RESTORATION OF CULTURAL HERITAGE

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To Avó Deolinda, Jeremie and Ema.

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ABSTRACT

"Alligatoring" or "Bitumen cracking" are terms used to describe extreme paint defects found in 19th century oil paintings. This paint failure in the form of severely disfiguring cracking and surface distortions often results in a loss of image integrity. This problem has been associated with the use of asphalt/bitumen paint, with no clear understanding of the materials and mechanisms which contribute to the phenomenon.

This thesis investigates this phenomenon from a multi-disciplinary approach that aims to contribute knowledge to the study of oil painting suffering from alligatoring.

Part 1 focuses on the perception of the problem through a literature survey, and introduces the 19th century painting used in the case study. A thorough review of the literature showed the existing bias created by the perceived connection between appearance and cause, resulting in an association of paint film defects in brown paint with the use of asphalt/bitumen. Because of this, the overall focus of previous research has been the detection of asphalt, considering it in isolation and as the primary factor in the paint defect. This singular view has had significant implications in the study and analyses of paintings with alligatoring. It inhibited wider investigations and overlooked other materials present in the paintings that may be acting in combination or be more predominant in the deterioration mechanism.

The visual and chemical study of the oil painting *O Cardeal D. Henrique recebendo a notícia da morte de D. Sebastião*, by Marciano Henriques da Silva (1831-1873), painted in Rome in 1861, which exibits extreme alligatoring, offered specific challenges due to its complex and highly disrupted paint layer stratigraphy coupled with the uncertainty introduced by analytical detection limits. For that reason, a multi-analytical approach was carried out using Optical Microscopy, micro Raman Spectroscopy, Scanning Electron Microscopy with Energy Dispersive X-ray Spectrometry, X-ray Fluorescence, micro Fourier Transform Infrared Spectroscopy, Fourier Transform Raman Spectroscopy, Attenuated Total Reflection Fourier Transform Infrared Spectroscopy Microscopy, Pyrolysis-Tetramethylammonium Hydroxide-Gas Chromatography/Mass Spectrometry and Time-of-Flight Secondary Ion Mass Spectrometry. This research indicates that the deterioration of the painting might be related to the oil binder which has a high degree of oxidation, rich in polar fatty acids and diacids, combined with a lack of the pigments that are capable of stabilizing the paint. The presence of the translucent lead azelate layer above the ground underlines the complexity of the paint layering, materials present, and possible mechanisms for degradation.

Part 2 reports on new research carried out using the British colourman Winsor & Newton's 19th-century Archive Database to analyse their production records for “Bitumen” brown for oil tube paints. While there are a substantial number of published recipes in 19th century artist’s manuals for the use of asphalt/bitumen brown, for the first time W&N’s records offer a unique source of detailed information on the commercially prepared product which differs substantially in ingredients used and method of preparation. The critical analysis of W&N's production records for "Bitumen" revealed that their formulation became standardised in the 1850s and that their product was prepared in two separate steps at two separate locations. Despite standarisation of the ingredients this research revealed that the company still found it necessary to make adjustments for each production run in order to achieve a uniform product.

A production record from 1858 was selected and reconstructed, using where possible, historically appropriate materials. W&N’s formulation for bitumen brown oil paint involved a complex mixture of ingredients, some of which were other proprietary products sold by the company (these were reconstructed individually using their production records and included drying oil, double mastic varnish, lead acetate, purple lake and the gelled painter's Medium, megilp).

The reconstructions were analysed using thermally assisted methylation with tetramethylammonium hydroxide, and pyrolysis comprehensive two-dimensional gas chromatography and compared with the starting material, Trinidad Lake asphalt, to determine how detectable this asphalt is after heat processing in lead treated linseed oil. Results show that asphalt markers identified in the Trinidad Lake asphalt disappear in the first stage of reconstructing W&N's "Bitumen" oil paint.

This important finding offers an explanation for the paucity of analytical evidence in previous attempts to identify asphalt/bitumen in paintings where this material was believed to have been used. In addition to clarifying the analytical results obtained from the investigation of the painting*, O Cardeal D. Henrique…*, the reference samples produced from the W&N reconstruction illustrate the strengths and weaknesses of organic analysis of highly processed complex mixtures.

Keywords: Alligatoring, Bitumen cracking, Asphalt, Oil painting, Marciano Henriques da Silva, Winsor & Newton, Bitumen brown oil paint, Multi-analytical characterisation

RESUMO

"Alligatoring" ou "Bitumen cracking" são termos utilizados para descrever defeitos extremos encontrados em pinturas a óleo do século XIX. Esta patologia sob a forma de fissuras e distorções severas da superfície pictórica resulta frequentemente numa perda de integridade da imagem. Este problema tem sido associado à utilização de tintas de asfalto/betume, sem no entanto existir uma compreensão clara dos materiais e mecanismos que contribuem para este fenómeno.

Esta tese investiga este fenómeno a partir de uma abordagem multidisciplinar que visa contribuir para o conhecimento de pinturas a óleo afetadas por este defeito extremo.

A parte 1 centra-se na perceção que existe sobre este problema através de uma pesquisa bibliográfica, e introduz a pintura do século XIX utilizada como caso de estudo. A revisão rigorosa da literatura revelou o preconceito existente criado pela perceção da ligação entre a aparência e a causa, resultando numa associação de defeitos em filmes de tinta castanha com a utilização de tintas de asfalto/betume. Devido a isto, o foco geral de estudos anteriores foi a deteção do asfalto, considerando-o isoladamente e como a principal causa nos defeitos de tinta. Esta visão simplista tem tido implicações significativas no estudo e análise de pinturas com “alligatoring” (efeito de pele de crocodilo), inibindo investigações mais abrangentes e subvalorizando outros materiais presentes nas pinturas que podem estar a atuar em combinação ou ser mais predominantes no mecanismo de deterioração.

O estudo visual e químico da pintura a óleo O Cardeal D. Henrique recebendo a notícia da morte de D. Sebastião, de Marciano Henriques da Silva (1831-1873), pintado em Roma em 1861, que exibe “alligatoring” extremo, ofereceu desafios específicos devido à sua estratigrafia complexa e muito alterada, aliada à incerteza introduzida pelos limites de deteção analítica. Por essa razão, foi realizada uma abordagem multi-analítica utilizando Microscopia Óptica, Micro-espectroscopia de Raman, Microscopia Electrónica de Varrimento com Espectrometria Dispersiva de Raios-X, Micro-espectrometria por Fluorescência de Raios X Dispersiva de Energias, Micro-espectroscopia de Infravermelho com Transformada de Fourier, Espectroscopia Raman com Transformada de Fourier, Espectroscopia de Infravermelho com Transformada de Fourier por Reflexão Total Atenuada acoplada a Microscopia Óptica, Pirólise-Cromatografia Gasosa acoplada à Espectrometria de Massa com derivatização usando Hidróxido de Tetrametilamónio e Espectrometria de Massa de iões secundários. Esta investigação indica que a

deterioração da pintura pode estar relacionada com o aglutinante de óleo altamente hidrolisado, rico em ácidos gordos polares e diácidos, combinado com a falta de pigmentos capazes de estabilizar a tinta. A presença da camada translúcida de azelato de chumbo sobre a camada de preparação sublinha a complexidade da estratigrafia, dos materiais presentes, e dos possíveis mecanismos de degradação.

A Parte 2 descreve a analise dos registos de produção de "Betume" castanho para tintas em tubos de óleo do arquivo e base de dados do século XIX da Winsor & Newton (fabricante de materiais para artistas britânico). Embora exista um número substancial de receitas de tintas castanhas de asfalto/betume publicadas em manuais para artistas do século XIX, os registos da W&N são uma fonte de informação detalhada e única sobre o produto preparado comercialmente que difere substancialmente nos ingredientes utilizados e no método de preparação. A análise crítica dos registos de produção da W&N para "Betume" revelou que a sua formulação foi normalizada na década de 1850 e que era preparado em duas etapas distintas e em dois locais distintos. Apesar da padronização dos ingredientes, esta investigação revelou que a empresa comsiderava necessário fazer ajustes em cada etapa de produção, a fim de obter um produto uniforme.

Um registo de produção de 1858 foi selecionado e reconstruído, utilizando, sempre que possível, materiais historicamente apropriados. A formulação da W&N para a tinta castanha de betume a óleo envolveu uma mistura complexa de ingredientes, alguns dos quais eram produtos produzidos e vendidos pela W&N. Estes foram reconstruídos individualmente, utilizando os seus próprios registos de produção, e incluíram óleo de secagem, verniz mástique duplo, acetato de chumbo, pigmento laca roxo, e o gel tixotrópico Megilp).

As reconstruções foram analisadas utilizando Pirólise-Cromatografia Gasosa acoplada à Espectrometria de Massa com derivatização usando Hidróxido de Tetrametilamónio, e Pirólise por Cromatografia Gasosa Bidimensional acoplada à Espectrometria de Massa. As reconstruções foram comparadas com a materia prima utilizada, o asfalto do Lago Trinidad, para determinar o grau de deteção deste asfalto após o processamento térmico em óleo de linhaça tratado com chumbo. Os resultados mostram que os marcadores asfálticos identificados no asfalto do Lago de Trinidad desaparecem na primeira fase da reconstrução da tinta a óleo "Betume" da W&N.

Esta descoberta importante oferece uma explicação para a escassez de provas analíticas em tentativas anteriores de identificação do asfalto/betume em pinturas em que se acreditava ter sido utilizado este material. Para além de clarificar os resultados analíticos obtidos a partir da investigação da pintura O Cardeal D. Henrique..., as amostras de referência produzidas a partir da reconstrução da W&N ilustram os pontos fortes e fracos da análise orgânica de misturas complexas altamente processadas.

Palavas chave: *Alligatoring* (efeito pele de crocodilo), *Bitumen cracking*, Asfalto, Pintura a óleo, Marciano Henriques da Silva, Winsor & Newton, Tinta a óleo castanha de betume, Caracterização Multi-analítica

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SYMBOLS AND ACRONYMS

μ	Micro
λ	Wavelength
ν	Stretching vibration. ν_{as}: asymmetric; ν_{s}: symmetric
δ	Bending vibration

AATA	Art and Archaeology Technical Abstracts
ATR-FTIR	Attenuated Total Reflection Fourier Transform Infrared Spectroscopy
BCIN	Bibliographic Database of the Conservation Information Network
C&R	Conservation and Restoration
C2RMF	Centre de Recherche et de Restauration des Musées de France
DCR FCT NOVA	Department of Conservation and Restoration of the NOVA School of Science and Technology
FT-Raman	Fourier Transform Raman Spectroscopy
HART	Historically Accurate Reconstruction Techniques
HCR	Highly Characterised Reconstructions
JAIC	Journal of the American Institute for Conservation
LAMS	*Laboratoire d'Archeologie Moléculaire et Structurale,* Paris
μ-EDXRF	Micro-Energy Dispersive X-Ray Fluorescence Spectrometry
μ-FTIR	Micro-Fourier Transform Infrared Spectroscopy

µ-Raman	Micro-Raman Spectroscopy
MNAC	National Museum of Contemporary Art - Museum of Chiado
OM	Optical Microscope
PLM	Polarized Light Microscopy
Py-TMAH-GC/MS	Pyrolysis-Tetramethylammonium Hydroxide-Gas Chromatography/Mass Spectrometry
Py-GCxGC/MS	Pyrolysis-comprehensive two-dimensional Gas Chromatography/Mass Spectrometry
RCE	Cultural Heritage Agency of the Netherlands
ROI	Region of Interest
SEM-EDX	Scanning Electron Microscopy-Energy dispersive X-ray Spectrometry
TIC	Total ion chromatogram
TLA	Trinidad Lake asphalt
TOF-SIMS	Time-of-Flight Secondary Ion Mass Spectrometry
UV	Ultraviolet
W&N	Winsor & Newton

GENERAL INTRODUCTION

The Problem - Alligatoring

A significant number of oil paintings produced during the mid-18th century and 19th century in Europe suffer from paint degradation that is so severe some of these paintings can no longer be displayed. Referred to as “Alligatoring” or “Bitumen cracking”, this problem is reported to develop some years after the work has been completed and has been associated with the use of asphalt/bitumen paint. The surfaces (thought to resemble alligator skin) are characterised by wide drying cracks, primarily in dark passages, leaving paint in isolated islands which themselves can have extremely wrinkled broken surfaces. It can ravage the whole painting or be confined to specific paint passages or colours, with a significant negative visual impact (e.g. Figures Figure 1-Figure 6). Paintings exhibiting this problem are found in collections in locations as far ranging as Europe, North America and Australia, with no clear understanding of the mechanism resulting in this phenomenon.

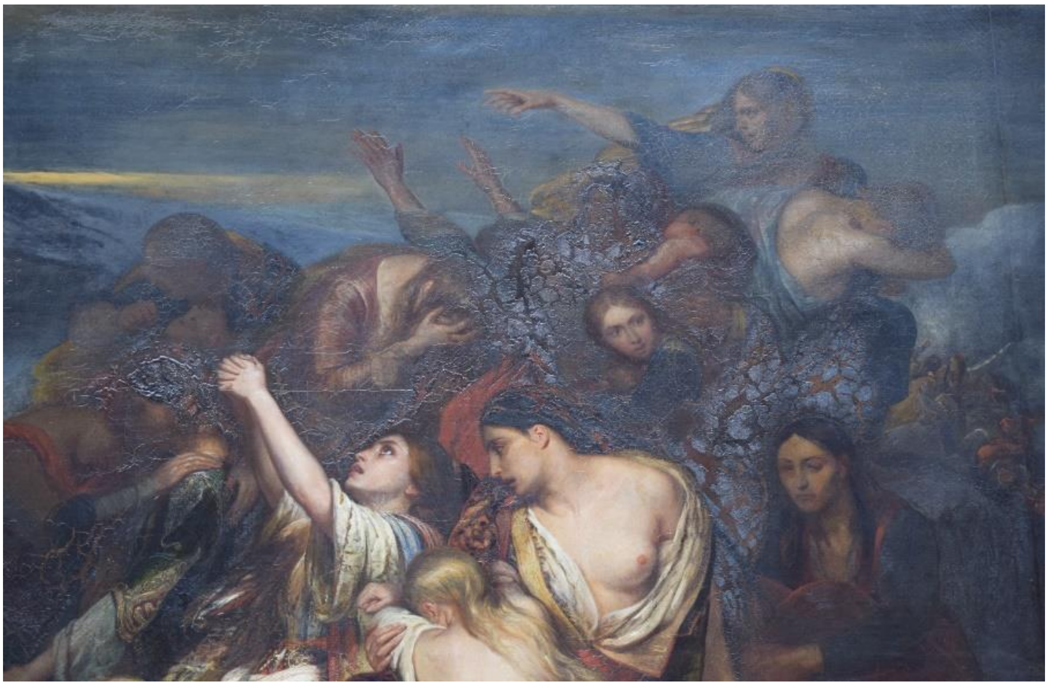

Figure 1: Alligatoring in a detail of the painting *The Souliot Women*, 1827-1828, by Ary Scheffer (1795-1858). Louvre. © Marques 2017.

Figure 2: Alligatoring in the background of the Portrait of *Marie-Marguerite Lagnier*, 1796, by Pierre-Paul Prud'hon (1758-1823) (left image). Detail marked in red of the wrinkled paint islands (right image). Louvre. © Marques 2017.

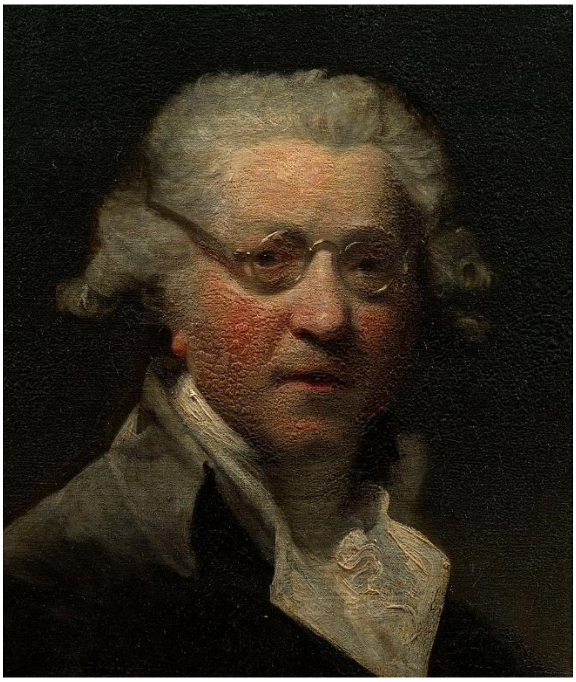

Figure 3: Alligatoring in the face of the portrait. Detail of the Self-portrait Wearing Spectacles, c.1788, by Sir Joshua Reynolds (1723-1792). Royal Collection Trust. © His Majesty King Charles III 2023.[1]

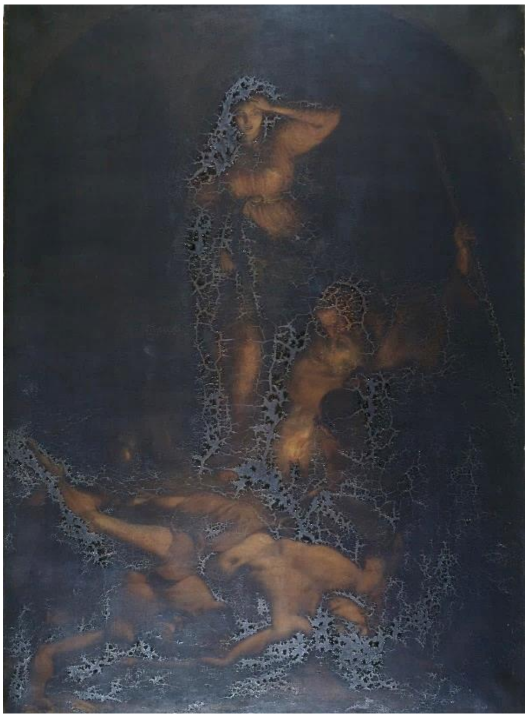

Figure 4: Alligatoring in the painting *Editha and the Monks Searching for the Body of Harold*, c.1834, by William Hilton the Younger (1786-1839). Tate, Presented by Robert Vernon 1847. Photo © Tate, CC-BY-NC-ND (3.0 Unported).[2]

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[1] Available in https://www.rct.uk/collection/400699/self-portrait. [online] (Accessed May 2020)

[2] Available at https://www.tate.org.uk/art/artworks/hilton-editha-and-the-monks-searching-for-the-body-of-harold-n00333. [online] (Accessed May 2020)

Figure 5: Case study painting: *O Cardeal D. Henrique recebendo a notícia da morte de D. Sebastião* (137.5 x 99.6 cm) by Marciano Henriques da Silva painted in 1861, MNAC, Lisbon (Inventory no. 337). ©Marques 2017.

Figure 6: Detail photographs in normal (a, b) and raking light (c) of the painting *O Cardeal D. Henrique…* (see Figure 5). © Marques 2017. The areas of the details are marked, in white, in the thumbnail of the full painting (image on the right).

Research and discussion have been devoted to the materials and techniques of paintings disfigured by these severe paint defects. However, as this research will show there has been a lack of comprehensive investigation into this form of paint deterioration. This is surprising considering how widespread alligatoring is and how its negative visual impact is so recognisable. It is undeniable that the degradation phenomenon responsible for the problematic drying and formation of paint film defects is inherently difficult to study due to the complex paint stratigraphys and nature of organic materials involved. A further complication is the correlation frequently made in the literature between effect: paintings with alligatoring, and cause: asphalt/bitumen being the material responsible. In previous research this has resulted in a bias with significant implications for the study and analyses of affected paintings. For example the search to identify a single component has neglected the role of the presence and influence of other materials, and has also led to a lack of questioning when results from chemical analyses fail to confirm the presence of asphalt.

In this context, this doctoral research was provided a unique opportunity to study the problem in a Portuguese context, with a painting by the Portuguese painter Marciano Henriques da Silva (1831-1873). Hailed in its time as a significant work by the artist, today the subject is barely recognisable due to the severe alligatoring of the paint. Results from research questions such as: who was the artist and where does this painting fit into his overall oeuvre? and what are the materials and techniques in this painting which may be associated with the problem? have produced a comprehensive study of the artist's life and work and have contributed new knowledge regarding the larger context of severe alligatoring found in many 19th century British and European paintings.

Access to the *Researcher's Edition of the Winsor & Newton 19th-century Archive Database* (Clarke and Carlyle 2005a; 2005b; Otero 2018; Carlyle 2020), allowed the analysis of production records for the colourman's *Bitumen* brown oil paint. These unique records of the commercial production of a bitumen/asphalt oil paint were compared with recipes for bitumen or asphalt brown published in British 19th century artist's manuals (Carlyle 2001). The study of Winsor & Newton's (W&N) production records provides detailed information on the raw materials, ingredients and preparation procedure used by the company to produce their 19th century paint containing asphalt/bitumen. A selected production record was reconstructed using historically appropriate materials to provide reference samples for the analytical detection of asphalt using chromatography techniques. Results have revealed a critical finding, and possible explanation for the paucity of evidence for the role of asphalt in previous studies.

Scope and outline of the thesis

The aim of this research was to investigate the severe paint defect associated with alligatoring through the following: a) a full characterization of the materials and paint stratigraphy of the painting *O Cardeal D. Henrique recebendo a notícia da morte de D. Sebastião,* painted in 1861 by Marciano Henriques da Silva (the case study). The extent of the paint defects in the painting can be seen in Figure 6 and 6; and b) a comprehensive documentary analysis of production records from the 19th century colourman, Winsor & Newton's *Bitumen* brown oil paint, with a reconstruction of a production record dated 1858 (the reconstruction). The samples produced from the reconstructions were used as reference samples to test the detection limits of analytical instrumentation.

The thesis is divided in two parts with three chapters each.

Part 1 explores the context of the problem and details the case study:

Chapter 1 gives an historical background of alligatoring/bitumen cracking based on a critical analysis of published sources. Asphalt is introduced with a description of its material properties and complex chemistry according to current knowledge. Evidence of its use in the 19th century is explored with regard to reports from artists and authors who associated the material with the disastrous problems seen in contemporary paintings.

Chapter 2 presents the case study of the painting *O Cardeal D. Henrique recebendo a notícia da morte de D. Sebastião*, introducing the artist Marciano Henriques da Silva, through a comprehensive study of his biography and oeuvre. The painting's history and condition are described.

Chapter 3 focusses on the characterization of materials and techniques of the painting *O Cardeal D. Henrique…* discussing for each layer of the painting the results from a multi-analytical approach. The results obtained provide a basis for the discussion of the possible degradation mechanisms. These results also highlight important analytical complications that illustrate the relevance of Part 2.

Part 2 concentrates on the reconstruction of W&N's *Bitumen* brown oil paint and is based on three articles which were published within the scope of the thesis.

Chapter 4 covers the critical analysis of W&N's production records and the rationale for choosing the "*Bitumen*" oil paint production record from 1858 as the basis for the reconstruction.

Chapter 5 describes the steps and outcomes in the reconstruction of the 1858 production record: its ingredients, their preparation and processing as well as the difficulties encountered during the reconstruction.

Chapter 6 covers the analyses of samples from the reconstructed paint using two highly sensitive techniques: Py-TMAH-GC/MS and Py-GCxGC/MS. Results detailed in Chapter 6 offer an explanation for the paucity of evidence found in past analyses to identify bitumen in 19th century oil paintings.

This is followed by the general discussion and conclusions from both parts, where the main findings are summarised and possible topics for future research are identified.

PART I

BACKGROUND AND CASE STUDY

1

BACKGROUND

This chapter presents a critical analysis of published sources on the subject of alligatoring, focusing on the perception of the problem: from how people view, identify and describe the problem to its perceived causes, exploring the role of asphalt/bitumen in the subjective narrative of this severe paint defect.

This section explores these points and discusses how confusing terminology, isolated case studies and ambiguous analytical results have led to a narrow view of the problem and fragmented literature on the subject.

Topics to be covered regarding alligatoring as a paint defect in 19th century oil paintings include: the terminology; descriptions in terms of appearance and mechanism of formation; statements and assumptions made by authors pertaining to its temporal and geographic distribution; and the time frame for the defect to occur. Asphalt itself is described with a discussion of its confusing terminology and its complex chemical and physical properties. Articles by the principal authors to devote attention to asphalt in the Conservation and Restoration (C&R) literature are covered with a close review of the published analyses performed on affected paintings. Particular attention is paid to the lack of results, the analytical problems encountered and "bitumen bias" which clearly results in this literature being inadequate on many levels. References to drying problems in Condition and Treatment Reports are investigated, and finally, ethical questions with regard to the appearance of affected paintings and past treatment decisions are explored.

1.1 The Problem - Alligatoring

Considering how widespread alligatoring is and its negative visual impact, it is surprising that a thorough review of the literature reveals a lack of comprehensive investigations into this form of paint deterioration. While painting techniques such as layering sequence and paint thickness, and choice of materials have been implicated in the historical documents both individually or in combination (eg. asphalt/bitumen pigment and gelled mediums), as will be seen reports on the scientific analyses of these materials and their role in the context of drying problems are scarce.

It would also appear that the descriptor *Bitumen Cracking* has created a confirmation bias, and as a result the possibility that other materials may be acting in combination or be more predominant in the deterioration mechanism has largely been overlooked. This shows that focusing on visual perception alone (the association of paint film defects in brown paint with the use of asphalt/bitumen) can lead to the assumption of a connection between appearance and cause that is not necessarily underpinned by consistent material evidence (as demonstrated in subsection 1.4, page 52). Rowan Frame in her recent exploration of this topic emphasizes this by stating that "the assertion that bitumen causes defects was repeated so regularly that a type of reverse argument also became accepted: any brown paint passage with defects *must* contain bitumen. The start of this somewhat circular reasoning can be traced to the nineteenth century and followed through the twentieth-century literature." (Frame 2022).

1.1.1 Sources and Methodology

The literature review initially focused on Conservation and Restoration (C&R) publications in order to gather and systematize the information available from the point of view of researchers dealing with artworks. A thorough review of published work in the C&R field on the subject of drying cracks and alligatoring was carried out, comprising 106 bibliographic references, which range from contemporary reports[3] of degraded surfaces to scientific articles on artists' materials and techniques. Additionally, books from the Paint and Coating Industry were consulted as well as references from different fields such as Chemistry, Art History and Archaeology, selected for being referenced in the C&R literature or cross-referenced in the same subject. An overview of the selected bibliography divided by number and source type is given in Appendix A, Table A.1 (page 235).

Conservation Databases such as AATA, BCIN and JAIC online were consulted and followed by cross-checking in specific internet domains such as the IIC website, ICOM-CC Publications Online and Taylor & Francis Online with particular emphasis on content from the Conservation Journals: *Studies in Conservation* and *The Conservator*.

The Centre de Recherche et de Restauration des Musées de France (C2RMF) archives for both the analytical documentation (Louvre) and the Conservation documentation (Versailles) were

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[3] For example, in Portugal, reports of such material failures were made by Manuel de Macedo, published in 1885, and in Britain, paintings affected were described by Richard and Samuel Redgrave, in their two-volume publication in 1866 (M. de Macedo 1885; Redgrave and Redgrave 1866).

consulted in person. Concerning French sources, Gallica (the digital library of Bibliothèque Nationale de France - BnF) provided access to important 19th century French literature, manuscripts, books and images as well as more recent studies on the live and oeuvre of 19th century artists.

This research concentrated primarily on British, Portuguese and French literature. German researchers which are important to the topic are included, for example Gaby Theurer (1998), Catarina Bothe (1999) and Bettina Grober (2006).

1.1.2 Terminology

According to Sheldon Keck "possibly the earliest author to discuss crack formation in paintings" was Von Frimmel in 1904, followed by Eibner and Laurie, who established "two categories of cracks" in paintings – Drying cracks and Age cracks – with numerous variation on the terminology (Keck 1969).

The nomenclature for age cracks is quite straight forward with a few variations, such as, mechanical or brittle cracks (e.g., Keck 1969; Hodge 1987, 39; Jones 1990; Bucklow 2021), however the terms used to describe drying cracks can range from premature, modern, early, immature, shrinkage, traction, contraction or ductile cracks (e.g., Keck 1969; Hodge 1987, 39; Jones 1990; Jones, Townsend, and Boon 1999).

In 1999 De Willigen summarised the "Types of Craquelure" proposed by different authors such as Keck, Boers, Stout and Bucklow, presenting their drawings and proposed nomenclature for the crack patterns and depth profile in an attempt to define features that could be used for classification of the cracks. Concluding that although the "descriptive framework" given by Stout would likely account for all features, because of the "enormous amount of different crack features" in a painting, creating "good standardization" is very hard even with a smaller set like the one proposed by Bucklow (de Willigen 1999, 16–23). Bucklow had already discussed these issues in his PhD and related articles explaining that "The apparently random nature of the craquelure pattern helps it elude formal description. Consequently, those systems for explicitly describing cracks which have been proposed have not been widely adopted" (Bucklow 1996). Adding to this difficulty Bucklow expresses the fact that "Analysis of craquelure - by whatever means - will always produce a more equivocal result, this is a consequence of the nature of craquelure as a 'holistic' phenomenon; it is the visible product of the response of the whole painting to its whole history" (Bucklow 1999).

The terminology for describing extreme drying problems varies in the C&R literature and numerous terms have been used to illustrate severe paint film failure, the most common of which are divided into two categories. The first category refers to the appearance of the paint in relation to the skin of animals: "alligatoring" (e.g., van der Loeff and Groen 1993), "crocodiling" (White 1986; White and Kirby 1994) or "alligator cracks or crackle" (Stout 1950, 41; Shimazu 2015, 121); while the second category evokes the presumed material that caused the problem and is referred to as “Bitumen cracking, craquelure or shrinkage” (e.g., Jones 1990), “Bituminous cracks”, “bituminous-like craquelure” (Massing 1988) or “Asphaltum cracks” (e.g. Redgrave and Redgrave 1866, 597)[4]. Additionally, there is also the term Englisches craquelée” (Theurer 1998) or “craquelure anglaise” (Carlyle 2001, 480) which makes the correlation between the problem and artists in the United Kingdom, an idea summarised by Bucklow who quoted from Kirby Talley (1986), “It must be admitted that England produced some spectacularly cracking paintings in the eighteenth and nineteenth centuries” (Bucklow 2021, 297).

This literature survey shows a predominance for English trained conservators to use terms such as “Bitumen cracking” while authors from other countries tend to adopt the term “alligatoring” when writing about severe drying defects.

In this dissertation, the broad term “drying cracks” (DC) and the more specific “alligatoring” will be preferred when referring to these paint defects.

1.1.2.1 Alligatoring

The term alligatoring, refers to a severe paint surface defect where the paint develops a pattern resembling the skin of an alligator, this happens by contraction of the paint into islands that are separated by wide apertures often exposing the layer below.

Historically, the term can be found in the Paint and Coating Industry literature. It can be inferred that its incorporation into the conservation lexicon happened through this industrial literature, for example Sheldon Keck’s article (1969) cites the second edition of a book from the Paint and Coating Industry “Hess's Paint Film Defects Their Causes and Cure”[5] from 1965.

During this research the earliest reference found to “alligatoring” was by Alvah Sabin in 1904 (Sabin 1927, 455)[6] in the Paint Industry literature, while in the C&R literature the earliest was from 1950 by George Stout (Stout 1950, 41), in both cases no specific reference for the term is given which prevents tracing its prior use.

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[4] The terms "asphalt (or asphaltum)" and "bitumen" were used interchangeably. See section 1.3 Asphalt, page 37, for information on asphalt terminology.

[5] This book is frequently cited in the C&R literature and has become an important source of information with its first German edition published in 1939 and the English edition in 1951. The English edition was reprinted twice, the second edition in 1965 and the third edition, revised by H. R. Hamburg and W. M. Morgans, in 1979 (Hess and Hamburg 1979). Rica Jones described Hess's book as "an industrial paint manual" (Jones 1990).

[6] Although the word “alligatoring” is not used in the 1st edition (Sabin 1904), it appears written in the Index for the 3rd edition (Sabin 1927) referring to the exact description presented in the 1st edition.

From an etymological point of view, it makes sense that the term would have been coined by North American authors since Alligators are a native species, however the only author suggesting this is Cruikshank Smith in his witty description of the term:

> "The term alligatoring as applied to paint is an American one and has crept into use in popular paint literature. It is a descriptive term used to describe the appearance presented by a paint, varnish or enamel film when it has become cracked in such a way as to resemble the markings on an alligator's back. Unfortunately, the same term is also used to describe a particular variety of wrinkling or ridging, and as there is a sufficiency of English words available to describe either phenomenon it would appear to be desirable to eliminate the term "alligatoring," which is by no means a suggestive term to people who rarely see alligators."
> (Cruickshank Smith 1912, 27)

To track and categorise the available information, descriptions pertaining to the term "alligatoring" were gathered from 24 published sources: 16 from the C&R literature and 9 from the Paint and Coating's Industry[7] (see Table A.2, Appendix A, page 236). The criteria for selection were references to the term "alligatoring" which gave further information, for example the visual appearance of the surface or possible causes for the defect. Six sources were included where the actual term "alligatoring" is not used, instead the word "alligator" is followed by "cracks" (R. Mayer 1991a, 714; Pey 1998, 499; Doherty and Woollett 2009, 24; Shimazu 2015, 121) or "skin" (Carlyle and Southall 1993, 23; Southall 1996, 118–19). Also included are 2 references in articles from Raymond White which present a description of the phenomenon and possible causes but use the term "crocodiling" (White 1986, 66; White and Kirby 1994, 71), because the terms can be considered direct synonyms.

No mention of the term "alligatoring" was found in the 19th century sources consulted (e.g. Redgrave and Redgrave 1866).

1.1.2.2 Bitumen Cracking

The same criteria were used for the selection of sources that refer to the term "bitumen cracking" or any of its variants which included for example, the visual appearance of the surface or possible causes for the defect. Only four results were obtained (see Table A.3, Appendix A, page 241).

The lack of references to bitumen cracking cited in this study may be a reflection of the criteria defined for the selection of sources, since the term can be used informally (without a full description

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[7] The 9 published sources consulted from the vast field of Paint and Coatings Industry literature were selected as they are cited in the Conservation literature or a cross-reference from those sources.

of its meaning), for example, while describing the painting defects in *Dr. Samuel Johnson* by Sir Joshua Reynolds, paintings conservator Bettina Jesseli simply states "(…) there was serious bitumen cracking in the background (…)" (Jesseli 1981).

1.1.3 Description of the problem

As the literature survey shows, when describing drying defects on a painting the terms “alligatoring” and “bitumen cracking” are used in combination with information on:

- the aperture of the drying cracks (narrow, average or wide),
- the impact of the colour visible from the paint below,
- the appearance/shape and size of the paint islands,
- the wrinkling of the paint layer,
- the affected colour areas,
- the presence of specific cracks patterns (i.e. crow’s foot), and
- the darkening of the colours.

The following paragraphs illustrate these points and discuss the information present in the sources.

Contrary to mechanical cracks, drying cracks (DC) have characteristic wide apertures, which are a feature noted by various authors, "A wide aperture is a characteristic of all cracks caused by the inability of a paint film to hold together while it dries." (Stout 1950, 42) and "The aperture of the drying crack varies in width even in an individual rupture and is invariably greater than the apertures of age cracks" (Keck 1969). With edges "sometimes rounded in profile due to plastic elongation and flow before and after rupture" (Keck 1969) they have been visually compared with a riverscape “The edge of the crack has a fluid appearance like the bank of a muddy river." (Stout 1950, 42) or a "whimsical river landscape formed by the cracks" (van der Loeff and Groen 1993).

Stout noted that “the paint between the cracks is apt to be lumpy, pulled up in a kind of blob" (Stout 1950, 42). This evidence of the movement of the paint into agglomerates has more recently been described as paint “islands”; a good summary is given by Shimazu, "The upper paints have become islands of paint resulting from contraction of surface paint layers" (Shimazu 2015, 122). The movement of the top layers is associated with the exposure of underlying paint as Van Zuien wrote, "The top layer of paint has formed islands and the underlying layers are revealed in the cracks between them" (van Zuien 2012). In the fifth edition of Ralph Mayer's *The Artist's Handbook of Materials and Techniques*, revised and updated by Steven Sheehan, this was noted and described as "fissures in which the separation of the "islands" of paint are wide and ragged, exposing the underpainting or ground.” (R. Mayer 1991a, 473). Carlyle and Southall describe an extreme drying defect on a painting as "shiny islands of one colour floating meaninglessly on paint of quite another colour." (Carlyle and Southall 1993).

The visual impact of different coloured paint layers being exposed by the wide crack apertures has a profound influence on the perception of the overall image. As Shimazu observed "The large cracks in particularly(sic) expose the colors of underlying paints, and seriously change the tonality, the color harmony and the composition…" (Shimazu 2015, 122). This is true regardless of whether the colour shown below is lighter or darker since the problem lies in the colour contrast. In this sense, the higher the contrast between the colours of the upper and lower paint layers, the more disturbing the effect produced.

While darker colours are reported to be more affected and therefore lighter colours appearing from below are more noticeable, the opposite can also happen as observed by Carlyle and Southall when describing the DC of *The First Interview between the Spaniards and the Peruvians* by Henry Perronet Briggs: "(…) the sky is scarred with cracks through the upper layers of paint, revealing the darker colours beneath" (Carlyle and Southall 1993).

Information on the shape and size of the paint islands is rarely given which is understandable considering the heterogeneity of the islands within the same painting and the subjectivity of the words used, such as, small, medium or large which are concepts applied in relation to the painting's overall measurements and are difficult to standardize[8]. More precise measurements are unrealistic since a severely affected painting would have an enormous amount of paint islands to measure and in the end an average of those values would not be meaningful. The use of photographs or "Maps of Damage" often included in Conservation Condition and Treatment Reports are visual solutions that present better results when describing the problem, however, these damage maps are not normally included in in published articles, therefore perpetuating the lack of detail given for paint island characteristics.

Despite this, there are descriptions of the appearance and properties of the paint islands, for example Carlyle and Southall describe paint which has : "crept and shrunk into glistening globular islands of soft and soluble paint." (Carlyle and Southall 1993), and a French Conservation report on Ary Sheffer's *Bataille de Tolbiac.496* notes the propensity for dust accumulation, “Le retrait de la couche picturale a formé des îlots de matière propices aux accumulations de poussière.”[9].

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[8] This assumption is made for single reports of affected paintings. An attempt to create standard measures for defining the size of paint islands (likely a range or percentage) could be made within a collection/group of affected paintings.

[9] "The retraction of the paint layer has formed islands of material that are conducive to dust accumulation." (transl. by Marques).

One feature which is mentioned extensively in the descriptions of paint film defects is the term wrinkling. Hess defines wrinkling as "the development of wrinkles in a film during drying, usually due to the formation of a surface skin." He adds that it "occurs if the upper film layer dries quicker and expands more than the lower layer" (Hess and Hamburg 1979, 80).

Carl Grimm provides two examples of wrinkled surfaces associated with Albert Pinkham Ryder paintings and forgeries. He describes the appearance of the surfaces in authentic works as having a "(…) faintly wrinkled, somewhat lumpy, undulating surface texture and a frequently observed soft, oily sheen, [which] often imparts a leather-like appearance." (Grimm 1999, 52) whereas the surface of *Storm Rock*, a forgery, "looks like a thick film of drying oil, has shrunk, wrinkled, and pulled apart throughout the surface, exposing the brightly colored wash beneath through the network of cracks." (Grimm 1999, 363).

Concerning the colour areas affected by drying cracks Keck explains that:

> "Drying cracks often appear more frequently in areas of pure color or dark tones without admixture of white. It appears that, in these cases, the pigment volume concentration is low, and that the contractile forces in the medium meet less restraint than when the paint is bulked by a high concentration of pigment." (Keck 1969).

Keck's observation is supported by other more recent publications, "The most severe cracks lie in dark passages of paint" (Grimm 1999, 238), and "This phenomenon can be observed particularly in areas of darker colour" (van Zuien 2012), or simply “especially in the dark painted areas” (Shimazu 2015, 121–22).

An important crack pattern which can be present but which is rarely described is called "crow's foot". According to Hess this term is used "to describe shallow breaks in a paint film (…) [which] do not penetrate to the substrate" that are characterised by "a definite 3-prong pattern with the breaks running from the centre and forming an angle of about 120º between prongs" (Hess and Hamburg 1979, 262).

This term is used by Van der Loeff and Groen when describing the drying cracks in Gerard Dou's *The Young Mother*, writing that a "finer crow's foot crack pattern" is visible in the girl's face and some "dark-coloured objects" and further stating that "The wrinkling, alligatoring and crow's foot cracks are clear signs of problems with the drying of the paint." (van der Loeff and Groen 1993).

The darkening of oil paintings was also reported in association with the paint defects. Van den Berg et al. stated that "Darkening and paint deformations are disfiguring phenomena frequently encountered in oil paintings. They are particularly widespread in the 19th century." The affected paint associated with darkening in the set of paintings studied by the authors is described as having "surface deformations, especially the various forms of alligatoring and premature cracks" (K. J. van den Berg et al. 2002) which suggests a correlation between both phenomena. This parameter is hard to define because even if the yellowing of the varnish and possible darkening of linseed oil (Carlyle 2001, 215; Carlyle et al. 2002) are ignored as a source of colour alteration, an important consideration is the commonly darker palette of the affected oil paintings of this period, which combined with the textural alteration of the surface, could possibly result in what was perceived as the darkening of the painting. A more precise confirmation or assessment of the level of darkening without a reference point of how the painting initially looked is extremely difficult, yet some overall darkening may have been reported for the painting *O Cardeal D. Henrique*… within a few years after its completion. The painter Francisco José Resende (1835-1893) wrote in a letter in 1867 that "O Cardeal D. Henrique parece estar ás escuras; ou as tintas alteraram ou o local é mau."[10] (Mourato 2000, 249) while describing the paintings in the Portuguese section of the "Exposition Universelle" in Paris. In this case the painting would not have been more than 6 years old and its growing darker is already being questioned (discussed in section 2.2).

Finally, it should be noted that the description of the problem is often preceded by the overall impact that the defect has on the reading of the painting. As Van Zuien stated "This phenomenon, known as 'drying cracks' reduces the legibility of the composition because shapes are interrupted and areas of colour are less uniform than the artist had intended." (van Zuien 2012). In a similar focus on the disruption of the composition, Shimazu wrote "Presently, the defects seriously hamper observation of the composition" (Shimazu 2015, 121). Interestingly, legibility is also the word chosen in sources from other languages, such as French "Un important réseau de craquelures prématurées très ouvert lié à la technique de l'artiste gêne la lisibilité."[11] and Portuguese "desagregou-se em aglomerados de empastamentos grosseiros, como de tapete gasto e ilegível"[12] (D. de Macedo 1951, 21).

1.2 Assumptions & statements about the problem

During the literature review an attempt was made to distinguish between what were actual descriptions of the problem versus information that consisted of statements or assumptions made by the authors concerning the problem's appearance and causes.

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[10] "The Cardinal D. Henrique seems to be in the dark; either the paints have changed or the location is bad."

[11] "An important network of premature cracks, very open due to the artist's technique, hinders legibility.". Conservation report on Ary Sheffer's *Bataille de Tolbiac.496,* consulted in the C2RMF archive in Versailles, France.

[12] This can only be very loosely translated into "[the paint] disintegrated into clumps of coarse impasto, as of a worn and illegible carpet."

1.2.1 Temporal and geographic distribution

One of the first generalizations observed relates to the time period for the paintings affected with the 19th century being consistently evoked as a problematic period. Some reports mention both 18th and 19th century (e.g. Izat 2001; Bothe 2007) and some sources detail this further "from the last three decades of the eighteenth century and a good part of the nineteenth" (Jones 1990).

This information is often accompanied by the words "British" or "English" to establish the location of the artists and paintings affected. For Izat the "So-called bituminous cracks have almost mythological status as being the cause of disastrous cracking in British 18th and 19th century paintings" (Izat 2001, 1) while for Bothe the geographic location is broader, "Such defects are found on numerous paintings, primarily by English and continental artists of the eighteenth and nineteenth centuries" (Bothe 2007, 111).

As the survey of paintings affected by film forming defects demonstrates (see Table A.5, Appendix A, page 245), the problem was certainly not restricted to British paintings. Zuien remarks that "In the nineteenth century the phenomenon took on a more extreme form, and it is associated with works by artists like Prud'hon, his contemporaries and later nineteenth-century French painters such as François Gérard (1770-1837) and Théodore Géricault (1791-1824)." (van Zuien 2012).

Southall argued that "the defects seen on British paintings after circa 1755 are uncommon (but not unseen) on French and other European paintings in the eighteenth century, but are found more often during the following century in Europe, Canada, and Australia, for example, where direct links can be made between a painter or a school, and Britain, or a British master" (Southall 1996).

From this research a line of reasoning emerged concerning three cities: Paris, Rome and London that were at the centre of the artistic expression of the time and will be shown to have connections to a significant number of painters whose works are associated with severe drying problems. It is important to note that Rome was the destination for winners of the French "Prix de Rome"[13] and the English "Grand Tour" which had Rome "at the centre of their cursus honorum or honours course in culture" (Izat 2001, 6). This will be further explored in Chapter 2, section 2.1.1, when discussing the Portuguese painter Marciano Henriques da Silva who lived in all three cities.

1.2.2 Time frame

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[13] Scholarship awarded to study at the "Académie de France in Rome". For more information see: https://www.larousse.fr/encyclopedie/peinture/prix_de_Rome/154163 (accessed February 2022).

Recommendations are found in British 19th century artist's manuals and handbooks to wait at least a year (or as long as three years) before varnishing to ensure that "the paint was fully dry" otherwise "the varnish would contract and cause cracking in the underlying paint" (Carlyle 2001, 239). This implies that oil paint could take at least a year if not longer to be considered fully dry, and also suggests that such cracks associated with a ductile paint would occur within this reasonably "short" period.

According to Keck, drying cracks "occur while the paint, even though it may have become touch-dry, is still soft enough to be subject to plastic deformation" (Keck 1969).

Probably due to this preconceived idea that drying cracks have to occur within the "drying" time of the oil paint, while the paint is still ductile, very little attention is given to the actual time elapsed from the execution of the painting to the actual appearance of the defect.

However, in more than one example alligatoring has happened many years after the completion of the paintings. As will be seen (section 2.2) the painting *O Cardeal D. Henrique…* executed in 1861 appears to have remained in good condition for at least 7 years before alligatoring was reported. Interestingly in another artist's work 7 years is also given for this phenomenon to become apparent. Mayer and Myers write that the artist Thomas Sully (1783-1872) "was seeing noticeable problems on West's picture only seven years after it was painted, although he did not specify whether the defect was a change of tone or another problem, such as cracking." (L. Mayer and Myers 2011, 19).[14]

Another example is the dramatic case of the *Curfew Hour* painted in 1882 by Albert Pinkham Ryder where at least 27 years passed before alligatoring ravaged the painting's surface (Figure 1.1). In Ryder's case it has been reported that "In addition to looking wet, it seems that some of the paintings were not dry decades after creation" and "Museum condition reports indicate that materials remained plastic, sometimes even creeping to the lower edges" (Svoboda and van Vooren 1989).

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[14] It might be of relevance to mention another problem encountered in 20th century paintings, known as "Dripping paints", which also has a particular characteristic time frame of 7 years prior to happening (Boon and Hoogland 2014).

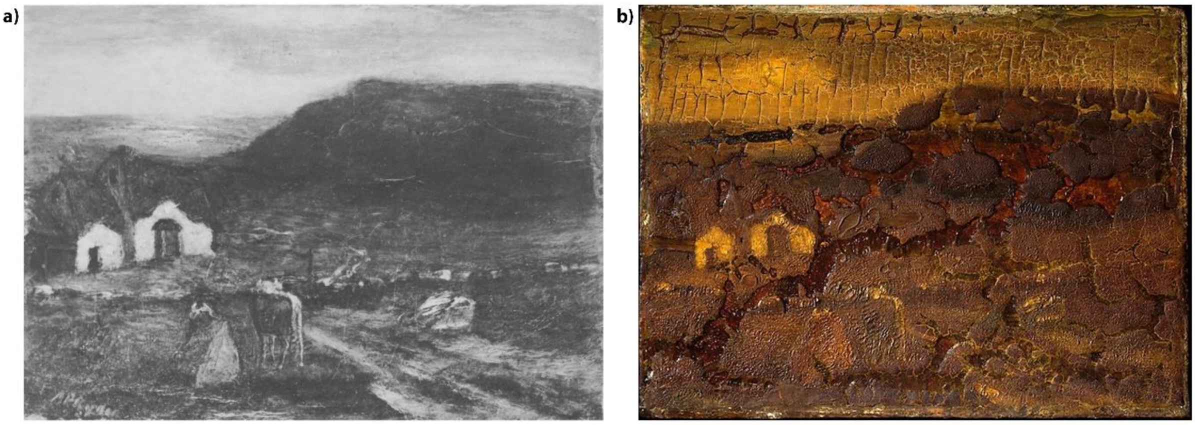

Figure 1.1 - Albert Pinkham Ryder, *Curfew Hour*, 1882, The Metropolitan Museum of Art (19.1 x 25.4 cm). a) Condition when acquired in 1909, image reproduced from (Hill Stoner 1990); and b) Current condition (undated image from The MET, CC0).

The most comprehensive explanation was given by the Redgrave brothers writing in 1866. They account for this time delay by citing possible alterations to the painting's storage/exhibition and the act of varnishing,

> “It is a misfortune to pictures painted with preparations of bitumen, that the evil does not always display itself at once: indeed, under favourable circumstances, they will remain very many years without disruption; but a change in hanging, or in the temperature of the room or gallery, an exposure to the sun's rays, and above all varnishing, will, though heretofore free from harm, crack them in a few weeks." (Redgrave and Redgrave 1866, 593)

Zuien suggests a different time frame for two paintings by Prud'hon (1758-1823), "This phenomenon was visible soon after the paintings were made; it was remarked upon at the time." She then notes however that "According to Mérimée[15], the cracks [in Prud'hon's paintings[16]] were caused by applying varnish at too early a stage, on a paint layer which had not completely dried." (van Zuien 2012).

The Redgraves went even further and stated that "from this cause [bitumen and all the “pitchy colours”] many of the pictures of our greatest portrait painter [Sir Joshua Reynolds] have failed terribly in the darks, and every fresh varnishing increases the evil." (Redgrave and Redgrave 1866, 593) which once again specifies the use of bitumen and implies that the paint defect problem would be aggravated by each campaign of varnishing and not only after the first varnishing. This idea is reinforced by the

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[15] Zuien cites the 1830 French edition of M.J.F.L. Mérimée "De la peinture à l'huile ou des procédés matériels employés dans ce genre de peinture depuis Hubert et Jean van Eyck jusqu'a nos jours".

[16] "the 1808 *Justice and Divine Vengeance Pursuing Crime* in the Louvre and *Venus and Adonis* of 1810 in the Wallace Collection in London"

Redgraves recounting a description by the painter William Mulready (1786-1863) of David Wilkie's (1785-1841) *Duncan Gray.* Mulready stated that "when nearly finished, Wilkie became enamoured of tone, and went all over the picture with asphaltum, painting into it, and repeating this process even a second time." with a "fatal" outcome to the picture which had "cracked and went into a very sad state" only to be restored and later on have the problem reappearing "it is now again slowly parting either in the old cracks, or probably new ones are forming." (Redgrave and Redgrave 1866, 268).

1.2.3 Opinions regarding the cause of Alligatoring/Bitumen cracking

As stated in the beginning of section 1.2, the information gathered from the literature and discussed here, consists of statements or assumptions made by the authors concerning the possible causes for the problem. These opinions clearly show that the phenomenon is recognised, which is why there is an attempt from the authors to determine possible causes even in the absence of studies to demonstrate or prove them (as will be discussed in section 1.4).

1.2.3.1 **Painting Technique**

Painting techniques described as poor, experimental or unorthodox have been associated with alligatoring and drying defects found on works by famous artists such as Sir Joshua Reynolds (1723-1792) (Boon, Townsend, and Jones 1999) or Albert Pinkham Ryder (1847-1917) (Erhardt, von Endt, and Tsang 1990). Although specific materials such as asphalt and megilp are still mentioned as possible culprits, Erhardt, von Endt, and Tsang (1990) argue that it is not the selection of materials but rather the way in which they were employed that has resulted in drying defects. Reports of poor technique are discussed below in relation to the layers in a painting.

The preparatory layers (grounds)

The Redgraves state that paintings from the English school up to 1835 "have suffered more from the use of improper pigments than from bad grounds" (Redgrave and Redgrave 1866, 593). The problem with pigments will be discussed in section 1.2.3.2. Regarding the preparation layers or grounds, the Redgraves explain that "The subject of grounds is of the greatest importance to the future of the picture" and "If too hard and impervious, the picture is apt to divide from it and blister off" citing Turner's paintings. They also blame Reynolds for being "careless in overloading his pictures, repeating his work over and over again when dissatisfied with his previous labours, thus losing the benefit of a pure ground" and making him "liable to suffer from this cause" (Redgrave and Redgrave 1866, 592). Two important factors should be highlighted here, the absorbency of the ground and possible negative effect of "re-using" a canvas (which includes the additional issue of continuous re-working of a painting).

More recently, Keck also noted the importance of the ground by stating that "Drying crack formation may be simultaneously promoted by other factors such as an insufficiently matured ground, still plastic when the paint is applied, or a ground excessively rich in medium and glossy which permits shrinkage forces in the paint to overcome both the paint's cohesive energy and the adhesive bond between paint and ground" (Keck 1969).

The paint layers

The application of multiple layers, working wet in wet, or painting "lean over fat" instead of "fat over lean"[17] were given as possible causes for drying cracks. Such features of the artist's painting technique were thought to have a significant impact on the physical properties of the paint film.

In the fifth edition of Ralph Mayer's *The Artist's Handbook of Materials and Techniques*, revised and updated by Steven Sheehan, it appears that the following could lead to cracking with an "alligator design": "Coats of paint less flexible than underlying coats (…) when the underpainting contains considerably more oil than the overpainting, when it contains a vehicle of entirely different and less brittle composition, or when the top layer of paint was overdiluted with turpentine." (R. Mayer 1991a, 209). The same information is referred by Keck "conditions for crack formation also prevail when upper layers are brushed over undercoats of paint which are plastic, too rich, or glossy" who further describes that "a quick-drying material, aqueous, oleaginous, emulsive, or resinous, applied too soon over a slow-drying one will tend to develop drying or traction cracks" (Keck 1969).

These practices have been described in the work of artists such as Reynolds or the American painter Ryder. Buckley states that "the manner in which Reynolds mixed and interlayered them [experimental painting media] created differences in drying times for the various layers. This set up an unstable matrix liable to form strong cracking patterns or wrinkling in the paint layers" (Buckley 1986).

Erhardt et al. also see Ryder's technique as a root cause for the degradation of his paintings:

> "Much of the blame for the condition of Ryder's paintings, therefore, must be put on the way he used his materials rather than what he used. For instance, the darkening of his paintings is most likely due to the application of numerous layers of oil glazes. Working wet into wet, layering paints which contain different proportions of pigment, using layers of fast-drying materials, and overpainting paint layers which have not properly dried are other practices which are discouraged

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[17] expressions that relate to the ratio of binder to pigment (a fat paint will have a higher binder to pigment ratio than a lean paint, see Ralph Mayer, *A Dictionary of Art Terms and Techniques*, 1981 edition p. 141). Originally published in 1969 by Thomas Y. Crowell Company. Barnes and Noble edition, 1981 ISBN: 0-06-463531-7.

> precisely because they can result in the types of cracking and degradation seen in Ryder's paintings. Ryder was obsessive at these practices, often overpainting and reworking paintings over periods of years." (Erhardt, von Endt, and Tsang 1990)

In a study carried out by van den Berg and colleagues where nine paintings with "extensive surface degradation" from Dutch collections were analysed, a correlation was found between the number of paint layers and surface defects, with problems such as alligatoring being "most obvious in the paintings with the most paint layers.". They also note that defects were "most dramatic in the darker, relatively medium-rich areas" and therefore concluded that "the painting technique of application of layer after layer without proper drying of the previous layers, which will happen especially with medium-rich, slow-drying layers, was responsible for the presence of the surface deformations." (K. J. van den Berg et al. 2002).

Repeated painting had also been seen as a problem by the Redgrave brothers who note "how much better pictures stand which are painted with freshness and facility and with little or no repetition, than those in which the dissatisfied or fastidious artist repeats his painting many times, over work perhaps already too loaded and not sufficiently dry to receive the new layer of colour." (Redgrave and Redgrave 1866, 596–97).

Their observation is in keeping with van Zuien's account of Delacroix maintaining that drying problems in Prud'hon's work was due to "elaborate working methods". Delacroix "believed that the paintings the artist worked on the longest were the most degraded" (van Zuien 2012). This could explain the alligatoring seen in the outline of the figures or in pentimenti areas in his paintings (see identified paintings by Prud'hon in Table A.5, Appendix A, page 245).

Mayer and Myers also emphasize the importance of painting technique in their excerpt of John Neagle's (1796-1865) experience with cracking in one of his paintings,

> "After glazing it repeatedly with asphaltum, he applied a layer of paint containing Japan drier and placed it in the sun, only to find '*it cracked in deep long gashes down into the body of the work underneath, in the short space of a few hours*'[italics original]. Neagle believed that if he had allowed his underlayers to dry more completely, he would not have had this problem; like many other painters of this time, including Sully, he apparently did not think that asphaltum itself was at fault. But he added - correctly, according to modern authorities - that the proper sequence of layers for a painting would consist of lean paint first, followed by more "elastic" (medium-rich) layers." (L. Mayer and Myers 2011, 121–22)

This is an interesting remark because not only points to the artist's perception on the technical aspects but also to the author's impression on the role of asphalt as a problematic material.

Varnishing

Although not necessarily associated with the artist technique[18], varnishing, as previously discussed in section 1.2.2., has also been attributed to drying problems if performed before the proper drying of the oil painting or by acting as the initiator for degradation in paint layers.

Other issues

Ann Massing observed two situations in Gentileschi's *Joseph and Potiphar's Wife* from ca. 1633 in which drying cracks did not occur "where the paint surface was protected by the frame" and where "highlights of lead-tin yellow" were applied, which "seem to have prevented the formation of drying cracks in the paint layers underneath" (Massing 1988). The first statement points to the formation of film defects being somewhat hindered in areas where the frame is protecting the surface, which in turn relates the problem to external environmental factors.

A similar observation was reported by Wolbers of a painting "where the rabbet of the frame had protected some of the dark background along the painting's edge, no signs of deterioration or cracking were evident". Interestingly he reports that samples from both "the protected edge and the badly cracked face were virtually identical" in terms of FTIR results (Wolbers 1983).

Nicola Costaras (2007) addresses the perception of drying problems in the 19th century at the South Kensington Museum (SKM)[19], and the role of environmental factors through a discussion surrounding the museum's heating and artificial lighting[20]. Costaras presents the arguments of "key figures" speaking to "the controversy over the heating and lighting" which for some "were causing or exacerbating the cracking of paint films" while others, such as Richard Redgrave (1804-1888) "believed the problems were inherent". This debate prompted documentation of the painting's condition through photographs (as early as 1860) as well as a more careful monitoring of the environment (Costaras 2017, 15, 22).

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[18] Due to the time required for the painting to dry before varnishing, which could take a year long, this final varnish layer was not necessarily applied by the artist. It could be for example done by picture dealers, artists' colourman (at vernissage) or the paintings subsequent owners (e.g. Swicklik 1993; Carlyle 1996).

[19] Currently Victoria and Albert Museum (V&A), London.

[20] Through "burning of coal gas" (Costaras 2017, 17).

Materials

> "There is undoubtedly a connection between materials and condition, and to some extent one can guess what materials might have caused what defects." (Southall 1996)

Carlyle and Southall note that by the mid-19th century, two main materials were held to be responsible for drying defects, both individually and in combination: the transparent brown paint made with asphalt (also called bitumen) and the various gelled Mediums known as Megilp or Gumtions (Carlyle and Southall 1993). Carlyle, in her PhD thesis (1991) and later work (Carlyle 1993; Townsend et al. 1995) provides more background and points to contemporary accounts of industrial processing or material substitutes introduced during this period which were thought to have played a role: coal-tar derivatives as substitutes for traditional sources of asphalt/bitumen, drying oil processing using sulphuric acid, and adulterated oils (a high proportion of non-drying oil seeds mixed with drying oil seeds, and/or the addition of inferior or non-drying oils). The adulteration or substitution of traditional mastic resin with substances such as colophony (rosin) or sandarac was also reported at the time and was thought to have played a role in the paint defects observed (Carlyle 1993).

Concerns about the role of adulterants and the artists' ignorance regarding their materials were expressed by the brothers Redgrave:

> "the artist is now too often ignorant of the commonest facts relating to the pigments and vehicles he uses, and so long as they are brilliant in themselves, dry rapidly, and mix well in tints with other pigments, makes little inquiry into their durability or permanency, and uses indifferently those which have received the sanction of the past, with those yet untested, because newly brought into use and notice." (Redgrave and Redgrave 1866, 590)

Costaras gives a summary of the Redgrave's opinion on the causes for drying cracks which focus mainly on materials but also, as mentioned above, on the artist's technique:

> "It was Redgrave's opinion from his(sic) observations and experience of his own paintings as well as those of others that the drying cracks that affected the paintings were due to a number of causes, the principal ones being poor choice of pigment and medium, such as bitumen and megilp, and poor execution (i.e. making too many changes to the composition) compounded by varnishing, resulting in a rapid contraction of the surface."[21] (Costaras 2017)

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[21] In this quote Costaras is referring to Richard Redgrave (1804-1888) who was an artist, his brother and co-author, Samuel (1802-1876), was in the civil service and wrote on English artists (Carlyle 2001, 320).

Scheme 1.1: Scheme of the materials mention in the literature as possible causes for Alligatoring.

Scheme 1.1 shows the materials that are mentioned in the literature in association to alligatoring. It is important to consider these materials but also the myriad of variables reported that could contribute to drying problems, such as the material's origin, quality/purity, method of preparation (which will certainly vary depending on whether it is made by individual artists or by the colourmen, see Part II Chapters 4 and 5), and additions by the artist of materials which may also have influenced stability, and of course the application techniques.

The following explores the materials associated with alligatoring as they appear reported in the literature.

Asphalt/Bitumen

Out of 61 literature sources consulted for severe drying problems in oil paintings, 55 refer the terms asphalt and/or bitumen (often used interchangeably)[22] associating it with paint defects. Given its prevalence in the literature and possible importance for the problem a more detailed discussion of this material is given separately (see section 1.3 Asphalt, page 37).

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[22] See the discussion on the definition of both terms and their indiscriminate use in the literature in section 1.3.2 (page 45).

Coal-Tar

Referred to as a possible asphalt substitute (e.g. Carlyle 1991; 1993; 2001; Townsend et al. 1995; Languri 2004; Bothe 2007), coal-tar is produced from the distillation of coal, a by-product of coke production. The process is described in recent literature, "Bituminous coal, a very complex chemical mixture, decomposes into simpler components when heated in retorts without air above 700°C (1292°F). Gas, aqueous vapor, and coal tar are driven off, leaving coke as residue. The coal tar is dehydrated and heated in stills to yield oil and coal tar pitch" (Stoner 2006, 9–1). In a 1995 review of coal-tar chemistry the material was defined as "viscous, black liquid at room temperature" with the following properties, "density of about 1.20 g cm^{-3} (20ºC) and an elemental composition of C 90-93%, H 5-6%, N 0.6-1.2%, O 1.5-2% and S 0.6-1%" with more emphasis being given to the chemical composition which "consists predominantly of polycyclic aromatic compounds" (Zander 1995). *The Pigment Compendium*, referring to the *Oxford English Dictionary* (2002) states that "out of its [coal-tar] constituents are obtained paraffin, naphtha, benzene creosote, the aniline or coal-tar colours, etc" (Eastaugh et al. 2008, 111).[23]

Carlyle identifies coal-tar as being mentioned in the 19th century by authors such as: Neil (in 1833) who noted that the asphalt made from “gas tar” was “unfit”; Field (in 1841) commenting on the “excessive abundance” of this “product of the distillation of coal at the gas manufactories”; Osborn (in 1845) pointing out it was the available option at the time, "the only kind that we have ever been able to procure in this country", and how cheap it was to acquire this material”; Martel (in 1859) who summarizes the concerns for the use of this material that was “a factitious kind [of bitumen], a produce obtained from the gas-works” which was “not fit for artist’s use, as it never dries”; and finally Church (in 1890) who remarks on coal-tar being lower quality despite being “largely sold in lieu of the original and genuine product” (Carlyle 2001, 479–80).

Similarly, in 1904 Sabin warns that “Much cheaper than asphaltum is coal-tar pitch, and a great deal of asphaltum varnish is made of this, which is inferior to asphaltum in every respect, even, unfortunately, in price” (Sabin 1904, 110).

White describes coal-tar properties and how it can be similar in appearance to asphaltum, "Though liquid when freshly exposed to the air, it dries by loss of the more volatile components to form a substance that ranges from a semi-solid to a brittle pitch. In the latter state, it is indistinguishable as far as physical appearance and properties from some forms of asphaltum". He continues to explain that although asphalt and coal-tar "suffer from the same paint defects and slow down the drying of oil media, the former [does] more so than the latter for coal tar contains a far greater amount of phenolic fragments, which act as anti-oxidants and delay free radical formation and subsequent cross-linking in the drying oil" (White 1986, 70). Previously in that article, pertaining to softwood

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[23] Outside the scope of this work are “Coal Tar Colours”, often referred to as “aniline colours”, both terms are nowadays “superseded by the use of the chemical nomenclature of the azo and polycyclic pigment groups” (Eastaugh et al. 2008, 111).

pitches, White had clarified the chemical mechanism of the phenolic fragments as inhibitors of the oil drying: "This effectively means that assuming the tar component is evenly distributed throughout the paint film, the phenolics in the top layers will be used up first and the cross-linking of the glycerides will proceed first. The lower levels of the film where oxygen availability is somewhat lower, will be protected against radical chain formation for a longer period. As a result, the surface skin will dry and contract during hardening pulling the lower, softer layers into characteristic 'islands' - that is, crocodiling and wrinkling will occur" (White 1986, 66).

Hodge, in her Masters project on cracking in oil paintings, also points to the use of coal-tar, "the worst cases of crawling are probably due to Coal tar which was first produced in the 18th century and contains the most phenolic fragments." noting that "At their worst bituminous layers may never form a dry film but continue to flow plastically, crawling (…) and even forming 'droplets' (…). This can happen because the bitumen or tar is thermoplastic with a fairly low melting point. It also dissolves in the oil medium forming a very plastic composite" (Hodge 1987, 50).

Carlyle and Southall, propose that the “differences between the brittle fracture of paint or glazes containing natural asphaltum, and the rents or tears in the paint, called drying cracks, associated with artificial asphaltum” can be seen in detail photographs of two different paintings. They base this position on George Hurst's observation that asphaltum from natural sources was brittle and prone to cracking and it was the artificial variety which was the poor dryer (Hurst 1892, 404, as cited in Carlyle and Southall 1993). They further emphasise the paint's appearance, “The more extreme drying defects, perhaps caused by the tarry bitumen derived from the distillation of coal, can result in wrinkled and torn paint that looks like an alligator skin… " (Carlyle and Southall 1993). According to Carlyle, it is possible that some problems “associated with the use of bitumen or asphaltum on paintings from the 18th and 19th century resulted from the use of a substituted bitumen” reasoning that “By the late 18th century there were reports of substitutions with pitch or other balsamic materials. Then, in the first decades of the 19th century, coal-tar sources were used” (Carlyle 1993).

In Hess's book, concerning the coating of metals, the following information can be found, “As a binder for coatings, coal tar pitch is preferred to natural asphalt for several technical reasons, particularly with respect to resistance to petroleum crudes which will dissolve the natural asphalt”, clarifying with its chemical composition that “the polar nature of coal-tar confers properties of improved adhesion to the system” while “sensitivity to light is aggravated by the presence of large amounts of free carbon and naphthalene”. The later leading to a “Breakdown in light can be either by 'black' chalking or by alligatoring (…) which may not for some time extend through to the substrate, and which are caused by oxidation of the surface layer while the layers below still remain thermoplastic. Results vary considerably” (Hess and Hamburg 1979, 266).

Currently coal-tar is still an important material for the Paint and Coating Industry because "it exhibits excellent water resistance, and good resistance to acids, alkalies, and mineral, animal, and vegetable oils." (Schweitzer 2006, 105). The complexity and variety of factors that influence the final product is recognised: "Depending on the source of the coal tar and the amount of heat applied, pitches of different characteristics are obtained. When used as bases for superior coatings, coal tar pitches are reprocessed, and any corrosion-accelerating substances are removed. Various types of coal tar pitches are then blended together", producing Coal-tar paints with "outstanding" qualities such as "their extremely low permeability, their high electrolytic resistance, and their remarkable resistance to the disintegrating action of water" (Stoner 2006, 9–1).

Interestingly, Stoner[24] speaks to the tendency of these coatings with coal-tar to "alligator", "All coal tar paints “alligator,” more or less, in the sun. This alligatoring is a surface defect. It is brought about by the hardening of the upper layer of the film, stimulated by the sun’s rays. This causes the upper layer to contract, crack, and slip over the lower stratum which is still soft. If not enough coats are applied, these alligator marks can go right down to metal, opening the path for atmospheric corrosion." (Stoner 2006, 9–2). The authors compared "asphaltic paints" who "dry by evaporation only" as "more weather resistant than corresponding coal tar paints because they do not alligator, but they are inferior in water resistance.” (Stoner 2006, 9–3). Other recent articles still describe the propensity of coal-tar coatings to "alligator" and crack (Schweitzer 2006, 105; Koleske 2012, 710).

Megilp

The artist's Medium, Megilp, is described as a thixotropic gel produced by mixing "a lead-treated drying oil with a mastic varnish", to be added to the paint on the palette (see Carlyle 2001 for a description of its history and use[25] and Carlyle and Southall 1993; Townsend et al. 1998). The material is reported to increase the paint's transparency which made it valuable for glazes, and it improved the "spreading quality (brushability)" of oil paints (Carlyle 2001, 101).

By the late 18th century Megilp already had a bad reputation for darkening, discolouring and cracking. Nevertheless, Megilp appears as "the most frequently described medium in the artists handbooks of the nineteenth century" (Carlyle and Southall 1993), and the Redgraves emphasise its use by writing that "Most of the works of the early part of the century are painted with a magylp composed of half mastic varnish and half boiled oil" (Redgrave and Redgrave 1866, 597).

This literature review demonstrates that sources blamed both Megilp and asphalt/bitumen individually or in combination "for the disfiguring disruptions in the paint film which have come to characterise eighteenth and nineteenth century paintings" (Carlyle and Southall 1993). In fact, both ingredients were reported to be used together: historical accounts and recipes show that megilp was amongst the principal materials that were added to brown asphalt/bitumen paint (Carlyle 2001

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[24] Henry R. Stoner is the author of a book chapter entitled "Coal Tar and Asphalt Coatings" in *Coatings Materials and Surface Coatings, ed.* Arthur A. Tracton, 2006. At the time the author worked at *Henry R. Stoner Associates, Inc. - Industrial Coating & Paint Consultant, North Plainfield, USA.*

[25] Information on megilp's spelling variations, ingredient ratios and recipes as well as its presence in British colourmen's sales catalogues, can be found in Carlyle (2001, 391-402).

Appendix 14 Megilp and Gumtion recipes, 391). An example of a complex mixture of ingredients is given by Hill Stoner as she describes the American painter Washington Allston medium called "Titian's Dirt" that involved "asphaltum, Indian red, ultramarine and megilp" in some instances with the addition of "Japan gold size (…) to make it dry faster" (Hill Stoner 1990).

Megilp alone, as promotor of drying cracks or film-forming defects, was particularly associated with Sir Joshua Reynolds. For example, Talley reported on Reynolds's use of "the disastrous painting medium megilp" (Kirby Talley 1986). Townsend describes Reynolds painting The Death of Dido as "particularly rich in megilplike layers" with "very striking surface defects" which "arise when a modified oil layer is applied to fairly pure oil, whereupon microwrinkles form in the previously stable film, and the surface later exhibits a rough texture with drying cracks cutting in deeply" (Townsend 1995). For Morrison "The use of complicated applications of paint and the combination of oil and resin in certain passages, possibly formulated into the gelled megilp medium, appears to be responsible for the drying defects, which are so characteristic of many paintings by Reynolds" (Morrison 2010).

Despite the warnings, it seems that the material possessed qualities that were hard to resist: "artists continued to be seduced by the marvellous thixotropy which megilp imparted to their paints because the negative effects were not immediately apparent. Sometimes years would go by before darkening and cracking occurred." (Townsend et al. 1998).

Regarding the chemical properties of artist's gelled Mediums, recent studies by Pasco (2019) and Pasco et al. (2002) show that "the gelation process is based on the interaction of the acidic part of the terpenoids of the resin with the lead compound, forming lead-resin soap species" (Pasco et al. 2022). Pasco reports that colophony could replace the mastic resin on the formation of a successful gel, unlike "dammar or sandarac resin", and only the lead compounds[26] formed "homogeneous gels" (Pasco et al. 2022). Pasco also notes that "the oil and the polymer [part of the resin] probably only have a role in the overall texture of the material, which is a crucial question for the painters, but are not directly involved in the gelation mechanism" (Pasco 2019, 126).

Drying Oil (& Driers)

Both oil and driers have been associated with drying problems such as wrinkling and alligatoring. The following passages show the type of information that has been perpetuated in the C&R literature without much authoritative references to support those arguments with evidence.

The excessive amount of driers that appears reported as a problem. According to Field "too much drier 'is inimical to drying' (1835, 56)" (as referenced in Carlyle 2001, 43). While Mayer's 1991 edition states that cracking can be cause by "Too much drier" and will result in wider alligatoring cracks

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[26] Other metallic compounds such as copper, manganese and zinc were also tested (Pasco et al. 2022).

(R. Mayer 1991a, 210). Southall and Rae specify these concerns for lead driers: "Used in excess, lead could certainly cause wrinkling, cracking and probably darkening of the paint." justifying that it is because "excessive or inappropriate use of driers could result in a very rapid surface contraction and the formation of a wrinkled skin to the paint." that could "then tear, resulting in a random pattern of wide appertured rents in the paint" with worst results in thicker paint (Southall 1996). While Rae reports that "too many lead driers" would "result in retardation of the polymeric ageing processes of the paint film causing cracking" this sentence is accompanied by an end note that attributes this information to Joyce Townsend unpublished research but also remarks on contradictory findings from Carlyle who "found that adding excess lead driers to paint caused it to become dry and brittle, and therefore was not a likely cause for drying cracks and ductile behaviour" (Rae 2010, 48, 66).

Another consideration is the type of oil, the fifth edition of Mayer's book (edited by Steven Sheehan) states that "Poppy oil will crack in the same manner as linseed (…) it is generally agreed, however, that its cracking will be more exaggerated and that it will begin to crack under less extreme conditions that will linseed oil. The typical poppy oil crackle under normal painting conditions is likely to result in an elongated alligator pattern with ragged edges along the short sides of the pattern; the fissures are usually wide enough to reveal the ground underneath." (R. Mayer 1991a, 210). No further studies were found that could prove this statement. There is however extensive literature on the artist's use of poppy oil and how it has worse drying qualities that linseed oil (e.g. Sabin 1904, 141; Carlyle 2001, 25).

Interestingly, in a production record from Winsor & Newton is the note: "Poppy caused the Bitumen not to dry so well" (Production Record V2P150, from 1852, concerning the preparation of Sugar Lead for Bitumen oil paint) (see Chapter 4). This information confirms Vibert statement that poppy oil was used for griding commercially prepared paints "except for some dark colours, where the use of linseed oil is extolled" (Vibert 1892 as cited in Carlyle 2001, 152).

Wax, Balsams & Resins

> "Artists' notebooks reveal the use of many mediums and other additives, often more than one at a time, which produced very complex mixtures, and make assessment of the causes of drying problems far from simple." (Southall 1996)

As Carlyle has shown, wax, balsams and resins are mentioned in the British 19th century artist's manuals as additives to the oil in order to produce artist's mediums (Carlyle 2001, 111). These mediums, as mentioned above for megilp, imparted specific characteristics to the oil paint such as increasing brushing qualities, transparency of glazes, and for thinning opaque colours for scumbles (Carlyle 2001, 101).

Closely associated to the use of these materials is Sir Joshua Reynolds, whose experimentation with materials and mediums has been considered the cause of cracking and wrinkling in his works. The Redgrave brothers describe his pursuit for "new vehicles to give his pigments increased body" by "using not only the various siccative oils and resinous varnishes, simple and compounded; but the essential oils, wax, and asphaltum, were also pressed into his service, to give brilliancy, impasto, depth, or richness" (Redgrave and Redgrave 1866, 591). The consequences of this experimentation was marked by "the decay of his works" (Redgrave and Redgrave 1866, 8).

Hélène Dubois emphasises Reynolds problematic technique by stating that "Unfortunately, when materials such as wax and oily glazes are used in excess, neglecting sound principles such as drying time and incompatibility, they discolour, darken, crack and can cause paint loss." (Dubois 2000).

Regarding wax, Carlyle states that in medium recipes, mixtures of oil and resins were reported to be "added to alter the texture of the paint, to keep it firm and prevent its running" (Carlyle 2001, 111)[27]. Aside from the variety of recipes and preparations[28], there were also different kinds of wax, such as "beeswax" and "white wax" (also known as spermaceti wax) (Southall 1996; Carlyle 2001, 111). As noted in Carlyle one 19th century author warned, "all preparations of wax should be avoided, as wax prevents freedom of handling, and ultimately injures the picture, by its tendency to crack and separate" (Cawse 1840, 27, as cited in Carlyle 2001, 114). According to Dubois who studied Reynolds's technique and materials "From the late 1760s on, Reynolds used wax in his paintings in many forms and this was often at the cost of durability." Dubois provides extremely relevant information on the use and problems with wax, referring to Reynolds's note books, contemporary sources and paint analysis (Dubois 2000). Recent studies have also identified wax and mixtures of wax with resins, balsams or oils in Reynolds's pocket books (Gent 2019; von Aderkas, Gent, and Peggie 2021).

As well as Reynolds, artists whose work shows evidence of alligatoring and who have also been reported to have used wax are: Turner "beeswax and spermaceti wax" (Townsend 1995), Ryder "wax" and "candle wax" (Svoboda and van Vooren 1989; Grimm 1999, 38), Fuseli (Rae 2010, 55), and Prud'hon "pure wax" (van Zuien 2012).

In terms of Balsams, Mills and White (1897) report on the properties of a selection of these natural resins. The authors mention for example how Venice turpentine "dries very slowly to a rather yellow film and when dry the film is quite brittle" (Mills and White 1987, 89). Other authors have made the association between the brittleness and difficulty in drying of balsams with crack formation (interestingly in the same sentences as asphaltum). For example, Carlyle relates the 19th century artist Cawse's observation that "attempts to find a colourless substitute for oil by using Canada balsam and balsam copaivi [Copaiba balsam] made drying with sugar of lead, were unsuccessful" as he reports,

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[27] Not to be confused with its use as an "important ingredient in copal vehicles and in emulsion and encaustic-emulsion mediums" (Carlyle 2001, 111).

[28] An example is the medium called "Italian Varnish" involving "wax with resin and oil" described by Mérimée which also features as an ingredient in a Bitumen recipe (Carlyle 2011, 112, 404).

"these materials were 'liable to crack when dry' and were 'glutinous'" (Cawse 1822, as cited in Carlyle 2001, 27). The role of copaiba balsam is also cited in Mayer and Myers who state, "West's method for glazing with asphaltum at one time included mixing it with copaiva balsam, another unstable material that may have exacerbated the problem"[29] (L. Mayer and Myers 2011, 20).

Recent studies have focused on Copaiba balsam, in its use in the "Pettenkofer method" (Schmitt 1990; 2012), and on its molecular characterization (van der Werf et al. 2000), analytical detection and its impact on paintings (Gent, Morrison, and von Aderkas 2015).

Pigments

> "the prevailing viewpoint has been that pigments like asphalt, mummy containing asphalt and Kassel earth are the causes of poor drying in black-brown oil paintings from the 19th century" (Languri 2004, 165)

The colours most frequently associated with alligatoring, besides asphalt, are similarly complex brown pigments with relatable properties, such as Vandyke brown[30] and Mummy[31] brown. Since ample research exists on both pigments and can be found elsewhere (e.g., Harley 1982; Woodcock 1996; Languri 2004), this section will focus on reports of drying problems associated with these pigments.

Regarding Mummy brown, Harley reports that "Mummy, or Egyptian brown (…) was more durable and less liable to crack than asphaltum" adding that "Field suggested (…) it could usefully be employed as a substitute for that colour [asphaltum]" (Harley 1982, 153). Harley also comments on the pigment Prussian Brown[32] that was "sometimes mentioned in conjunction with mummy in late eighteenth-century books" (Harley 1982, 153).

Sally Woodcock found more divergent opinions regarding "the drying qualities of mummy in the late nineteenth century", with some sources finding it to be "absolutely unsuitable for artists' use", while others stated that the "combination with bitumen would improve its drying" and others thought that even though problematic was "more durable than pure asphalt" (Woodcock 1996).

Cruikshank asserts that Vandyke brown "possesses poor drying properties and in many cases actually retards the drying of linseed oil" alerting to the adulteration of the material "A good deal of

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[29] Benjamin West (1738-1820), American-born painter moved to London in 1763.

[30] Also referred to as Cassel/Kassel earth or Cologne earth. According to Harley it "was called an earth because it was dug out of the ground, but it is organic since it is derived from deposits of lignite or peat, and it is of a bituminous nature which means that it is a slow drier in oil"(Harley 1982, 149–50).

[31] Made from powdered body parts of Egyptian mummies, ground with drying oil. Mummy brown consists of "an extremely complex and diverse composition" due to the actual human body parts and "variety of materials used for embalming, for example asphalt" (Languri 2004, 15).

[32] Eastlake states that burning Prussian blue produced "a very fine and durable brown" but "required much filtering to free it from salts" (Eastlake 1960, 465).

the Vandyke brown now sold in the colour trade is by no means identical with the original Vandyke brown which was a species of brown bituminous earth" (Cruickshank Smith 1912, 165). In the same note, without referencing sources to corroborate this description, Mayer describes Vandyke brown as a "Native earth, composed of clay, iron oxide, decomposed vegetation (humus), and bitumen. Fairly transparent" cautioning to the fact that in oil it is "one of the worst driers" and "always turns dark, cracks, and causes wrinkling, exhibiting the same defects as asphaltum, but to a somewhat lesser degree" (R. Mayer 1991a, 60).

A brief remark to lake pigments, mixtures and additionss will be made. The inclusion of lake pigments in this discussion, despite not being a pigment associated with drying defects in the literature, will be further explored in section 1.4 Analysis (page 52) and throughout this dissertation because of the overall material characterizations made of affected paintings in the literature and in particular the characterization of materials and techniques of the case study *O Cardeal D. Henrique recebendo a notícia da morte de D. Sebastião* by Marciano Henriques da Silva (see Chapter 3).

Adulterations and additions to brown and red paints and substitutions

According to Eastlake, Williams alludes to "the practice of enriching browns with transparent yellows" advising that practice over the use of brown pinks (Eastlake 1960, 465). Townsend et al. provide similar information listed in tables that show "asphaltum" being adulterated with "yellow lake and aniline black" (Townsend et al. 1995). Another pigment recommended, by Vibert, as a possible substitute for bitumen (since it did not present "its defects") was "Vibert brown" quoted by Carlyle as "a mixture of lithanthrax and oxide of iron on aluminium basis" (Carlyle 2001, 480).

According to Carlyle "Madder reds, vermilion and Aureolin were among the pigments most often reported to be adulterated" and "Brown ochres, the madders and Mars colours were all reported to have been assisted by aniline dyes." This association to aniline dyes, which initially were derived from coal-tar should not be overlooked and is further explored by Carlyle who describes authors such as Holman Hunt (in 1875) and Vibert (1892) stating that lakes (in particular madder) could be made of coal tar and in that case they would be soluble in alcohol and would be light sensitive. Adding to this Muckley (1882) warns that vermilion was adulterated with cheap lakes which "may also have referred to the use of aniline dyes" (Carlyle 2001, 158). Detailed lists with the substitutions and additives for these pigments can be seen in Townsend et al. (1995). The authors also point to likelihood of mixtures of vermilion and rose madder found in a painting by Holman Hunt and "Whistler's oils of 1865-75 in the Tate's collection" being commercially prepared which "implies that vermilion tube paint was supplied to the artist mixed with the lake to enhance its colour". With the inverse being also true "red organics were augmented with colourless extenders in some cases, and brightened with vermilion in the case of scarlet madder" (Townsend et al. 1995).

1.3 Asphalt

> "Of the materials used by artists, few present a puzzle like that of asphalt."
>
> (Bothe 2007)

The idea of this section is to present how the material is associated with alligatoring, the main authorities on the subject publishing in C&R literature and discuss what are considered the most relevant topics for the scope of the present dissertation. However, sources from Petroleum Geochemistry were also consulted in order to better understand the terminology, and the material's chemical and physical properties.

1.3.1 C&R literature

Reports on its use as an artist material in association with alligatoring

This material, when associated with severe drying problems, is described in two ways: either through a generalization of its consequences when used as a paint material; or specifically associated with an artist or a painting that presents drying defects regardless of analytical results.

As noted in the introduction, references to this material have become descriptive of the appearance of a specific type of paint defect, for example Ann Massing states, “To the restorer, a deep brown-black paint layer with pronounced drying cracks, which is soluble in relatively weak solvent mixtures, is considered 'bituminous'” (Massing 1988). Massing's statement is particularly important because it demonstrates a direct correlation between the appearance and behaviour (solubility) of the paint and the assumption that it contains bitumen/asphaltum. She also uses the term "bituminous" as a descriptor in use by conservator/restorers. Other authors, also make this material association in terms of appearance, for example Bothe states that "a host of severe paint film defects are attributed to the use of asphalt: extreme cracking and wrinkling as well as darkened, discolored, or creeping picture surfaces" (Bothe 2007). Languri reinforces this association: "the prevailing viewpoint has been that pigments like asphalt, mummy containing asphalt and Kassel earth are the causes of poor drying in black-brown oil paintings from the 19th century. This belief was based on the information available in the literature about the materials and pigments used in the 19th century" (Languri 2004, 165).

Harley states that in the 17th and 18th century asphalt was "recommended" for "glazing and inserting shadows in the final stages of a painting" mainly for flesh tones, however its "popularity during the second half of the eighteenth century led to indiscriminate use, and the poor condition of some paintings from that period may be attributed to the presence of excessive quantities of asphaltum"

(Harley 1982, 152). Harley also notes that it was "likely that fashion, not technical considerations, dictate whether or not a painter used the colour" (Harley 1982, 152).

Of the 19th century sources consulted, the Redgraves present information on the largest number of artists whose works were compromised by drying defects thought to be associated with bitumen/asphalt, "The works of some of the contemporaries (…), as well as those of the pupils and followers of Sir Joshua, have suffered from the like cause, and many of the pictures of Northcote, Opie, and Fuseli have, as to their finer qualities, perished from the use of asphaltum." continuing "Notwithstanding that the evils arising from the use of bituminous pigments must have already made great progress in destroying the works of Reynolds and his immediate followers, the artists who succeeded them employed these pigments still more unreservedly. Wilkie and Hilton are notable examples, as their decaying works painfully testify." (Redgrave and Redgrave 1866, 593–94). They illustrate this information by providing the example of two paintings by both artists. One of the paintings is *Duncan Gray* by David Wilkie (1785-1841) who according to the Redgraves "became enamoured of tone, and went all over the picture with asphaltum, painting into it, and repeating this process even a second time. The result was fatal to the picture" and the second is *Edith and the Monks Searching for the body of Harold* by William Hilton the Younger (1786-1839) (Figure 4, page 2) which had "twice nearly slipped from the canvas" (Redgrave and Redgrave 1866, 171).

The Redgraves place bitumen under "improper pigments", "the worst is bitumen in all its varied forms of asphaltum, mummy, bitumen, &c. These pitchy colours never thoroughly harden; they are readily affected by heat and change of temperature, and as they remain soft beneath the surface, any harder dryer imposed over them, either as a vehicle for the last glazings of the picture, or as a securing varnish, is certain to draw the work together, and to result in deep separation of the parts." (Redgrave and Redgrave 1866, 593). According to Melissa R. Katz who wrote "Holman Hunt on Himself: Textual Evidence in Aid of Technical Analysis", the British artist Holman Hunt (1827-1910) also warned against its use, "Hunt also devoted attention to the evils inherent in binding media, vehemently denouncing the 'ruinous' use of asphaltum (also known as bitumen), source of the sunken patches and wide craquelure that disfigured so many British paintings" (Katz 1998, 429).

Even in more specific reports that link asphalt to an artist or painting, generalizations are still made as well as assumptions based on the visual appearance of the paint surface: “Ryder is commonly thought to have used bitumen in his painting. This is because many of his paintings have darkened, flowed, or contain extremely thick areas which consist of a cracked upper surface over a much softer lower layer” (Erhardt, von Endt, and Tsang 1990).

There are also reports that relate the preparation of the colour to its poor drying properties and consequent cracking. Massing states that "When prepared with a drying oil bitumen can absorb any amount of oil and the result is a rich transparent brown paint pleasing to use but which never dries completely, and the paint layer forms drying cracks which may continue to develop into abnormally wide cracks” (Massing 1988). By the 1991 edition of Ralph Mayer (edited by Steven Sheehan), asphaltum is described, as "not a true pigment color" but consists of "A blackish brown solution of an asphalt in oil or turpentine. At one period it was extensively used as a glazing color. Dries badly, causes wrinkling and cracking, and develops almost every fault of oil colors” (R. Mayer 1991a, 37).

Some 20th century authors consider the problem in terms of the artist's technique. For example Keck specifies that "Where bituminous oil paints are employed under those which dry at normal rate, the upper layer tears apart with the same kind of cracks as it dries" (Keck 1969). And Ineke Pey notes that "The non-drying and thermoplastic properties of asphaltum (…), had disastrous effects on the paint layer if it was used in the underlying layer of a quick-drying layer. The result was 'alligator cracks', shrinkage and wrinkling" (Pey 1998, 476–77). The thickness of the paint layer is referred in multiple studies, for example Joyce Hill Stoner writes "Art historian William Gerdts notes that many artists used asphaltum unwisely which he says 'gradually ruined many paintings.' and she remarks, "This would be true especially where it was used thickly." (Hill Stoner 1990), van Zuien writes of Prud'hon (1758-1823) that "Clément [33] claimed that in Prud'hon's case, too, bitumen was the reason for the development of cracks in the paint layer: 'Like most of the artists at the beginning of the century, he used a lot of bitumen and, besides, the thick paint of his manner, which caused his painting to darken and crack, particularly in the shadows.'" (van Zuien 2012).

Bothe, however, argued based on her own experiments on the deteriorative effect of asphalt/bitumen, that "next to the composition of the ground and the painting technique, the most important factor is the amount of oil in the asphalt color, whether derived from the binding medium, the paint medium, or the bitumen" and concluded "the pigment itself, provided that it is genuine asphalt, does not necessarily cause damage". In her work Bothe pointed to technical considerations in use, for example she observed the formation of wrinkling and cracking when "asphalt color was applied very thickly as an underpaint" covering either an oil paint layer or a tempera layer. She also noted that "wrinkle formation was encouraged by a smooth and glossy oil ground as well as by a high proportion of oily material in the asphalt color" (Bothe 2007, 124).

Main authorities on the subject publishing in C&R literature

The most comprehensive source of information in terms of the history of use and characteristics of asphalt/bitumen for artists, is Catarina Bothe's chapter in volume 4 of Artists' Pigments 2007 (Bothe 2007). For the 19th century use of asphalt/bitumen it is Leslie Carlyle who provides context for this material in terms of its use and reputation. She provides artist's recipes as well as colourman's product information and possible adulterations (Carlyle 1991; 2001). Regarding the analyses of this material

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[33] Charles Clément author of the book "Prud'hon sa vie, ses oeuvres et sa correspondance" 1st ed. 1872. Paris.

in artist's works, as will be seen below, Raymond White introduced the tracking of hopanes using GC/MS for the characterization of bitumen in paint samples (White 1986; Mills and White 1987), and Georgiana Languri developed an analytical methodology based on mass spectrometric techniques for the characterization of a large number of biomarkers and marker compounds in asphalt with the aim of detecting these markers in 19th century reference materials, model systems and paintings suffering from film-forming defects (Languri 2004).

In her chapter on Asphalt in the Artists' Pigments series, Bothe, compiles a detailed state of the art for asphalt, with information not only on its use as an artist's pigment but also its physical and chemical properties, some of which highlighted and discussed in this dissertation given its relevance. It should be noted that this article is a summary of Bothe's thesis (German diploma in 1997) and susequent book (Bothe 1999). Her information is supported with references to treatises and recipes for preparing asphalt as an oil paint or a varnish.

Bothe begins her chapter by explaining that asphalt "is neither a pigment nor a dye but rather a color preparation that, in contrast to most other pigments, which are of either organic or inorganic origin, consists of a mixture of organic and inorganic materials" (Bothe 2007, 111). She then explores the complex definitions and terminology and contextualizes the material's history exploring its use from antiquity up to the 20th century, with the earliest reference for asphalt as a colour being from Italian treatises, the first dated 1584 (Bothe 2007, 113). Bothe concludes that, in terms of "dates of use", given "the difficulty of proving the presence of asphalt in a painting (…) our knowledge of its use as an artists' pigment relies almost exclusively on the study of written sources" (Bothe 2007, 120). Clarifying that it was "used in easel paintings from at least the sixteenth century on" achieving "its greatest popularity in the late eighteenth and throughout the nineteenth centuries" (Bothe 2007, 111).

Regarding asphalt properties, Bothe summarizes the main characteristics that can be relevant when studying pigments: “Color and Spectral Reflectance”, “Optical Properties: Transparency and Tinting Strength” and “Permanence” in terms of “Resistance to Light”, “Migration” and “Wrinkling and Cracking”, with the latter being particularly relevant in this dissertation and therefore previously discussed in section 1.1.3 - Description of the problem, along with the chemical composition discussed below.

Bothe also discusses the "adulteration and sophistication" of asphalt mainly with distilled materials and resins, which were cheaper and could pass as natural asphalt because of their similar aspect and physical properties (despite having much worse drying properties). She notes that in the beginning of the 20th century authors were still complaining about "the adulteration of asphalt with vegetable resins and with tars and tar-pitches from wood and resin" (Bothe 2007, 137, and see in Carlyle below).

Bothe provides an overview of previous analyses focussing on the identification and characterization of asphalt in artworks and culminates in a section entitled "Occurrences" where the author presents an exhaustive list of paintings which have been analysed and whether or not asphalt has been convincingly detected (this topic will be further detailed in section 1.4 Analyses).

Finally, a particularly relevant issue discussed by Bothe which is explored in this thesis, is the conflation of the term "bituminous" with the material, remarking that bitumen was "used not just for substances that actually contain bitumen but also for those that simply possess characteristics ascribed to a material containing bitumen, whether or not the presence of bitumen can be demonstrated." Bothe further states that "the use of this word is extremely misleading, particularly since *bituminous* so clearly has a negative connotation in paintings" and suggests replacing this term with "the unambiguous phrase *containing bitumen*" solely in cases where bitumen is present and not "for substances alleged to contain bitumen by transmitted opinions or assumed to contain bitumen based on subjective, visual impressions or physical condition." (Bothe 2007, 112). The last sentence is a clear criticism of the path, also discussed by Frame (2022), that led to the generalized interpretation of defects in brown paint passages being related to the use of bitumen without direct evidence. It should be noted however, that Bothe's recommendation for clarifying the terminology overlooks the fact that there may well be occasions where the observations are a valid clue to the material's presence in certain paintings since as this research will demonstrate, its detection is extremely hard to achieve even with modern analytical techniques.

In her doctoral thesis (1991) and subsequent book (2001) Leslie Carlyle explored the use and perception of asphalt/bitumen by 19th century artists. She provides a comprehensive study of British 19th century artist's manuals, and points to references where asphalt/bitumen is associated with poor drying, "Authors variously described the deteriorative effects of asphaltum as blackening, never drying and causing cracks" (Carlyle 2001, 481). Carlyle details the use of asphalt by 19th century artists through recipes, descriptions and remarks in their contemporary manuals and handbooks, which is supported by its prevalence in British colourmen's product catalogues (Carlyle 2001). She also described references to the adulteration and substitution of asphalt in this period which could account for the discrepancies in negative effects found amongst the artists and draws attention to the artists' colourmen responsibility (Carlyle 1993; 2001).

Reconstructions based on Historical Recipes

The importance of Carlyle's work pertaining to paintings suffering from alligatoring and the use of asphalt/bitumen brown as an oil colour, is demonstrated by the many citations to it found during this literature review. Another aspect of her work has been the development and application of the HART research model which begins with extensive documentary research on historical artist’s materials. This is followed by the production of reconstructions, underpinned by the documentary research, and prepared with historically appropriate materials and methods. Detailed documentation of the materials used, the method of preparation, and behaviour during and after application results in highly characterised reconstructions (HCRs). These in turn act as reference materials which are then investigated and compared with actual historical oil paintings using visual and micro-analytical techniques (Carlyle et al. 2006; Carlyle et al. 2008; Carlyle 2020).

The "Asphaltum Recipes" summarized and transcribed in *The Artist's Assistant…* (Carlyle 2001, 403–7) provided a basis for the following studies: reconstructions made by René Boitelle in 1999; and the project carried out by Adelaide Izat in 2001 where she made reconstructions of a selection of six of these recipes using TLA and Coal-Tar for a comparison of the handling and aesthetic properties of both paints. Observations made in 2001 on the paints' short-term behaviour (shortly after painting them) showed that cracking only occurred where TLA or Coal-Tar were thickly applied as underpaint layers (not as top paint layers). In, recipes containing "turpentine rather than drying oil" cracking of the upper paint layer was more severe. And wrinkling only happened in recipes with drying oil and in all recipes "the coal tar shows fewer signs of wrinkling than the asphalt" which was unexpected for Izat since "due to the antioxidant nature of coal tar, which delays the formation of free radicals and cross linking, one would anticipate more signs of contraction of its skin than with the asphalt". Another observation was regarding recipes where mastic varnish was used, it "formed a skin very quickly, whilst remaining soft beneath the surface of the film". Izat concludes that "the recipes have largely been found to produce viable painting materials, both in aesthetic and handling terms" (Izat 2001, 32, 35).

Another similar experiment was performed by Bettina Grober (2006) with the aim of exploring the alleged substitutes of asphalt in deteriorated paintings, mainly coal tars and pitches. The methodology employed was similar to the one used previously by Bothe (Bothe 1999) who made reconstructions using two sources of asphalt to explore the behaviour and aging of these asphalt-based paints. A summary of these reconstructions in terms of recipes followed, sources of "asphalt" for producing the paint, and variations in the paint application (grounds, layer sequence, paint thickness, etc.) and samples for aging can be found in Appendix A, Table A.4 (page 242).

Earlier analytical approaches for the identification of asphalt in oil paintings

Raymond White, a senior conservation scientist in the Scientific Department of the National Gallery of London, explored “geologically modified organic material” such as Bitumen and Asphaltum pointing to their “very complex” chemistry, noting that these materials were also reputed to be substituted by coal-tar derivatives (White 1986, 63, 70). After stating that "successful characterization of asphaltum in actual paint samples requires very sensitive techniques of high resolving power" he concluded that "GC-MS appears reasonably well-suited for this purpose." (White 1986, 63). In his book, co-authored with John Mills (then head of the Scientific Department), White devoted a chapter to "Bituminous Materials" addressing the biological markers for "Asphalt and Bitumen" and "Tars and Pitches". And another chapter in the book focussed on the identification of bituminous materials in an ancient sarcophagus and as a sculpture adhesive, using GLC-MS (gas-liquid chromatography-mass spectrometry). This identification was based on the presence of "triterpanes together with minor polyaromatic hydrocarbons, both characteristic for bitumen" and "hopanoid compounds which are invariable components of bitumens and serve as their most characteristic identifier" scanned in the chromatogram using the mass-to-charge ratio (*m/z*) 191 (Mills and White 1987, 48–59, 152).

This work with GC-MS led White to become the first person to positively identify bitumen in oil paintings suffering from film-forming defects such as alligatoring (see section 1.4 Analyses). He focussed on the distribution of hopanes as markers for asphalt compounds in artworks (White 1986; White and Kirby 1994). As will be seen in Chapter 6, this methodology did not prove reliable when analysing processed paints prepared with asphalt.

In the early 2000s Georgiana Languri, investigated the presence and influence of brown colours, such as asphalt for her PhD research, “Molecular studies of Asphalt, Mummy and Kassel earth pigments: their characterization, identification and effect on drying of traditional oil paint” which was published in 2004. For this work, under the supervision of Professor Dr Jaap Boon, she developed an analytical methodology based on mass spectrometric techniques, such as Py-GC/MS (with and without TMAH) and DTMS[34], for the characterization of a large number of biomarkers and marker compounds in asphalt (Scheme 6.1, page 190). The objective was to detect these markers in 19th century reference materials, model systems and paintings suffering from film-forming defects. Her work focused on the traditional sources for the pigments, and did not cover materials reported to be used as substitutes and adulterants nor the use of gelled Mediums. Her investigation did not explore the effect of paint layering sequences. However she did investigate the effects of asphalt and Kassel earth on the drying of linseed oil.

Languri emphasized the complex issue of determining cause for film formation breakdown: “The pretreatments of the pigments (roasting, melting, dewaxing) and restoration procedures (solvent cleaning and relining) certainly have an effect on the chemistry of the paint and the mobility of the paint layers” (Languri 2004, 166). She noted that there is an inherent difficulty in detecting asphalt markers in oil paintings since many characteristic markers “can be evaporated or released by pyrolysis” which she recognised could have already occurred during paint manufacturing processes involving heat-treatments (such as roasting) which can result in the “extensive or even complete loss of the marker compounds identified” in the original reference samples. In addition, she noted that strongly oxidizing conditions during ageing of the paintings and possible restoration treatments involving solvents, could induce the extraction of solvent sensitive materials such as the maltene fraction. In a personal communication to Bothe, Languri explained that the marker compounds from the asphaltene fraction (which include alkylbenzenes, alkylnaphthalenes, alkylbenzothiophenes, etc.) are also present

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[34] Pyrolysis Gas Chromatography Mass Spectrometry (Py-GC/MS), with/without tetramethylammonium hydroxide (TMAH) and Direct Temperature resolved Mass Spectrometry (DTMS).

in "diverse other fossilized hydrocarbons, such as those contained in mineral coal tars" and so although their presence may "serve as a further indication" they "do not represent definite proof of the use of asphalt" (Bothe 2007, 140).

Despite questioning the use of hopanes as markers to track in paintings since these are sensitive “solvent extractable biomarker compounds” and arguing that the asphaltene fractions would likely be a better source for tracking asphalt in paintings, Languri nevertheless concluded that “Only hopanes seem to be reliable for the identification of asphalt in the aged oil paint reconstructions” when aged to the calculated equivalent of c. 40 years in museum conditions.

However in her 19th century samples after 150 years of natural aging she reported that, "no trace of hopanoids could be found" and proposed two hypotheses: either "the absence of asphalt" or, "its presence in such a form (degraded and cross-linked to the paint matrix) that makes it 'invisible' for the mass spectrometer". She concluded that “the determination of asphalt in painting samples is surely difficult and the data will be hard to interpret” (Languri 2004, 25, 45, 144, 166).

Her results from the analysis of three 19th century paintings which suffered from film-forming defects, showed "very little proof for the presence of geomaterials" which led her to posit that rather than the presence of asphalt paint, “The chemical and physical behaviour of these paints is highly related to their complex composition rich in other non-drying components like vermilion, beeswax or megilps.” (Languri 2004, 166). This statement was reinforced in a later article which discussed the analyses of Boitelle’s asphalt-oil paint reconstructions (see Table A.4, Appendix A), where she concluded, "The asphalt-oil paints prepared according to 19th century recipes do not result in poorly drying paints as expected. This suggests that the poor drying of black–brown 19th century paints must have other causes than the presence of asphalt." (Languri, Boon, and Boitelle 2005).

Concerning the effect of asphalt on the drying of linseed oil, her experimental reconstructions showed that "Asphalt has a strong antioxidant activity and retards the oxidation of oil paint" with "The formation of a network via cross-linking reactions" this "preference for cross-linking of triglycerides instead of oxidation is opposed to the situation observed for normal (linseed) oil paint.". It was still noted that "the overall drying effect of the oil paint is dependent on the composition of the paint including chemical modification due to heating of the pigments or solvent cleaning procedures" as well as "Other ingredients than oil and asphalt like driers, resins or wax, [which] when present completely change the drying behaviour of an 'asphaltic paint'." (Languri 2004, 166).

Whilst inconclusive in some regards, particularly when approaching the detection of asphalt markers and biomarkers in 19th century oil paintings, Languri’s research and publications are a landmark for her use of the analytical methodology applied to the analysis of paintings where asphalt is suspected to be present. Her comprehensive characterization of markers and biomarkers in reference samples (for e.g., a sample of asphalt from the Hafkenscheid Collection and a sample of type I Dead Sea asphalt) provided lists of identified compounds, showed their distribution in mass chromatograms and highlighted characteristic fragment ions that can be used to scan the mass chromatograms in search of those feature markers (Languri, van der Horst, and Boon 2002; Languri 2004; Languri and Boon 2005).

1.3.2 Terminology

The survey of the artist's and C&R literature above, as well as the literature covering petroleum geochemistry which follows, reveals complexity surrounding the terminology for asphalt/bitumen. Despite its common usage the word asphalt can have different meanings depending on several factors, which can range from common terminology to its precise chemical characterization. As a consequence, which was already present in the 19th century as pointed by Carlyle (2001, 479)[35], terms such as “bitumen”, “asphalt” and “tar” are still used interchangeably to describe “certain black, semi-solid mixtures of hydrocarbons” (Hsu and Robinson 2019, 6). In the USA bitumen produced by crude oil refining is known as “asphalt” or “asphalt binder” while outside the US it is called “bitumen” or “refined bitumen” (Hsu and Robinson 2019, 6; Hunter, Self, and Read 2015, 4). In Europe “asphalt” refers to a mixture of “bitumen and aggregate[36]”(Hunter, Self, and Read 2015, 6).

Shell’s *Bitumen Handbook* offers greater precision, referring to “bitumen” as a “refined bitumen, a hydrocarbon product produced by removing the lighter fractions (such as liquid petroleum gas, petrol and diesel) from crude oil during the refining process.” The handbook notes that the hydrocarbon product “should not be confused with natural or lake asphalt such as Trinidad Lake Asphalt, Gilsonite, rock asphalt and Selenice”, because “these products are unrefined and not produced by refining of crude oil” and often contain “a high proportion of mineral matter (up to 37% by weight) and light components, leading to a higher loss of mass when heated.” (Hunter, Self, and Read 2015, 4).

Asphalt has been divided into two categories: *natural asphalts* which are the rock/sediments of bitumen/asphalt from natural deposits such as the Trinidad Lake or the Gilsonite variety, which are completely soluble in carbon disulfide (see Figure 1.2) (Yen 2000, 12; Asphalt Institute 1989, 6); and the *artificial asphalts*, distilled products made by pyrolysis, which encompasses petroleum-derived asphalts, pitches and tars, including coal-tar (Yen 1990; Mills and White 1987, 48; Languri 2004, 24).

When consulting publications that focus on asphalt alone (not including plant sources such as pitches) these categories shift to *natural* and *refined asphalts,* the latter of which constitutes residues of crude oil distillations (Peters, Walters, and Moldowan 2005a, 358; Bothe 2007). According to a report from the World Health Organization, *natural asphalts* or *"natural bitumens"* are "naturally occurring deposits of asphalt-like material (…) [that] occur in various parts of the world, mainly as a result of mineral oil seepage from the ground" with the best known location being Trinidad's Pitch Lake,

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[35] With the added term "asphaltum" which is an old spelling for "asphalt".

[36] Frequently referred to as "mineral matter".

amongst others found in the Dead Sea, Venezuela, Switzerland or the Athabasca oil sands in Alberta. The report continues, "While these deposits have physical properties that are similar to those of petroleum-derived asphalt, the composition is different" (Wess, Olsen, and Haring Sweeney 2004), this information also appears in the Conservation field literature (see Bothe (2007, 112) for a more complete discussion on these terminological issues) and is crucial when researching the chemical composition of "asphalt" because the information found is often pertaining to the refined asphalt[37] and not the natural source.

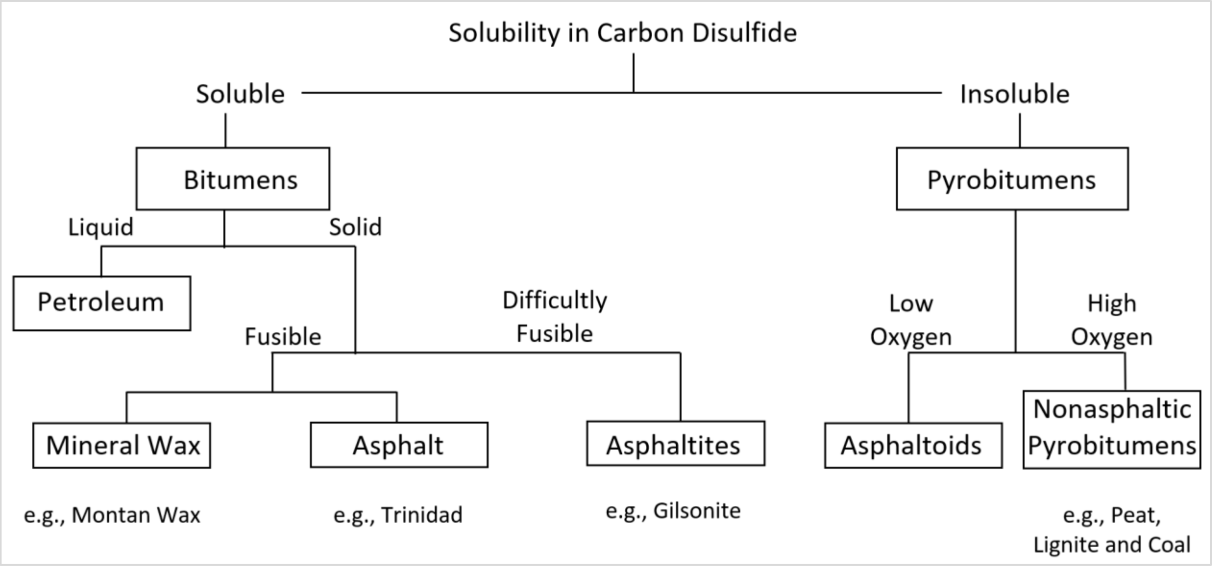

Figure 1.2: Simplified scheme based on the diagram published by Yen for the "designation and classification of natural asphalts, according to Abraham (1960)" (Yen 2000, 12).

Considering the previous definitions and the scope of this work, in this dissertation the term asphalt will be used to describe natural asphalt, which was most likely the source used by artist's and colourmens when they were not dealing with adulterated versions.

1.3.3 Chemical and Physical Properties of asphalt

As an organic material, asphalt varies in terms of its composition and properties. These chemical and physical variations are dependent on geological sources (for natural asphalts) and the means of production (for refined asphalts). In addition, when considering asphalt used as an artist's colour, factors

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[37] According to Languri and Bothe the production of refined asphalts through distillation of petroleum by "large-scale petrochemical industry" dates to the 1850s and 1860s in the USA (Bothe 2007, 135), which implies that "asphalt in earlier paintings must have relied on open pit sources or floating blocks" (Languri 2004, 25).

such as the preparation/processing of the asphalt for paint as well as age of the paint film can also affect its properties and consequent characteristics (Bothe 2007).

Even though “asphalt is not composed of a single chemical species, but is rather a complex mixture of organic molecules that vary widely in composition from nonpolar saturated hydrocarbons to highly polar, highly condensed aromatic ring systems” (Petersen 2000, 364–65), there are chemical and physical properties that are characteristic for all asphalts.

Chemically, asphalt is predominantly composed of carbon and hydrogen, with significant quantities of nitrogen, sulphur, and oxygen (NSO) compounds[38] and trace amounts of complexed metals, such as vanadium and nickel, in the form of heteroatoms. Asphalt can be separated into various fractions based on the reactivity and/or polarity of the various molecular types present (Petersen 2000, 366). These fractions are designated as: asphaltenes, resins and maltenes (the latter is also known as *gas oil*, which more specifically comprises: saturated hydrocarbons and aromatic hydrocarbons) (Yen 1990; Bothe 2007, 128), Peters et al. also point to the presence of heavy waxes (Peters, Walters, and Moldowan 2005a, 358).

Bothe summarizes the colloidal nature of asphalt, it is, "a colloidally dispersed system, with the asphaltenes as a solid phase dispersed in the gas oil/maltene fraction and the whole system stabilized by the resins" (Bothe 2007, 128). Petersen remarks on the solvent-soluble fraction (maltenes) and the insoluble fraction (asphaltenes), stating that "the most nonpolar or oily fraction, in the absence of the resinous components, is so unlike the asphaltene fraction that the two fractions are not mutually soluble. Yet, these extremes in molecular types must coexist in neat asphalt as a microscopically homogeneous mixture. This is made possible by the interaction of various components of asphalt with each other to form a balanced or compatible system" (Petersen 2000, 371). Yen explains that the resins are "considered part of the oily medium but have a polarity higher than the gas oil itself." Yen explains that this higher polarity "allows easy absorption of the resin molecules onto the asphaltene micelles, where they act as the peptizing agent of the colloid stabilizer by charge neutralization" and concludes that "the physical properties of the asphalt are directly related to the quantity of dispersed phase (asphaltenes); the size of the micellar structures, which is dependent on the degree of adsorption of resins; and the nature of the dispersion medium, oils, and resins (maltenes)." (Yen 1990, 6–7).

In addition, according to Petersen, the role of the heteroatoms should not be overlooked, since they "impart functionality and polarity to the molecules, their presence may make a disproportionately large contribution to the differences in chemical and physical properties among asphalts from different sources” (Petersen 2000, 365). He also notes that in natural asphalts sulphur can be a particularly characteristic element and "is usually found in a large percentage of the individual asphalt molecules;

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[38] According to the glossary of The Biomarker Guide, Vol. II "NSO compounds (resins) (…) are sometimes called heterocompounds or non-hydrocarbons." (Peters, Walters, and Moldowan 2005, 2:1013).

but in unoxidized asphalt, it is rather nonpolar and is found distributed among all the component fractions" (Petersen 2000, 369).

Extensive research has been devoted to the fractions of asphalt, particularly the asphaltenes, which are considered a macromolecule (Yen 2000, 17). A summary of the chemical characteristics of each fraction can be found in Bothe's article, along with a description for the "mineral matter". According to Bothe the mineral matter includes an "entire range of natural minerals and rocks" being the "most common mineral compounds (…) aluminum silicates and the carbonates and oxides of silicon, aluminum, iron, calcium, magnesium, sodium, potassium, and sulfur" (Bothe 2007, 131).

Bothe explains that, "asphalts form a large group of raw materials with a bitumen content of over 30% and a melting point of up to 150ºC" and notes that with "varying amounts of mineral matter and water, they are relatively soft". With surface deposits throughout the globe, these are "assumed to have provided the main sources of supply from antiquity until well into the eighteenth century (…) as they were easy to find and collect and relatively rich in bitumen." Bothe reports that, with the exception of "deposits in Trinidad and Venezuela", during the 19th century "the exploitation of most natural asphalt deposits became too expensive" in relation to the increased availability of less costly refined asphalts, The exception, Trinidad and Venezuelan deposits, "although known since the sixteenth century, were not industrially exploited until the end of the nineteenth century". Bothe states that today (2007) these deposits "meet nearly all of the world's need for natural asphalt (…), even though they are less pure than those from the Dead Sea and thus have to be further processed"[39] (Bothe 2007, 132).

As a way of illustration, Table 1.1 shows chemical and physical properties of natural asphalts from the Dead Sea and Trinidad.

Table 1.1: Extracted from Bothe's table for the "major elemental composition and softening points" (Bothe 2007, 129) of selected natural asphalts.

Asphalt	Bitumen (%)	Mineral Matter (%)	Water (%)	Sulfur (%)	Softening Point (ºC)
Asphalts					
Dead Sea, Israel	98-99	1-2	-	6-7	130-135
Trinidad, natural	39	27	34	6	106
Trinidad, refined (Epure)	53-55	36-37	-	6-8	84-97

As noted previously, due to its geological origins and various sources, there is no exact chemical structure or chemical composition of "asphalt" as a singular material. There are, however, ranges

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[39] In *The Pigment Compedium* Eastaugh et al. also remark on the purity of the Dead Sea source, "'High purity' asphalt sources are considered to be the 'Egyptian' occurrences, including those in the Dead Sea, and these were most suitable as pigments" (Eastaugh et al. 2008, 28).

defined through elemental analyses that mark the percentage of carbon, hydrogen, trace nitrogen, sulphur, and oxygen compounds. In addition elemental analysis can identify trace amounts of metals such as vanadium and nickel, as well as the presence of other elements that comprise the mineral matter of natural asphalts.

A general example of these ranges for refined asphalt is given by Speight (1992) as reported by the World Health Organization[40]: "elemental analyses indicate that most asphalts contain 79-88 wt% carbon, 7-13 wt% hydrogen, traces to 3 wt% nitrogen, traces to 8 wt% sulfur, and traces to 8 wt% oxygen" (Wess, Olsen, and Haring Sweeney 2004, 8). Petersen (2000) reported on the elemental analysis of four "representative petroleum asphalts" with results within these ranges, however he notes that "elemental analyses are average values and reveal little information about how the atoms are incorporated into the molecules or what type of molecular structures are present” information that is crucial when trying to understand physical properties and “chemical reactivity” (Petersen 2000, 365).

To shed light on the molecular structures researches rely on models and equations to unpack specific fractions. For example, the Yen-Mullins model illustrates the molecular and colloidal structure of asphaltenes in crude oils and laboratory solvents (Mullins et al. 2012).[41]

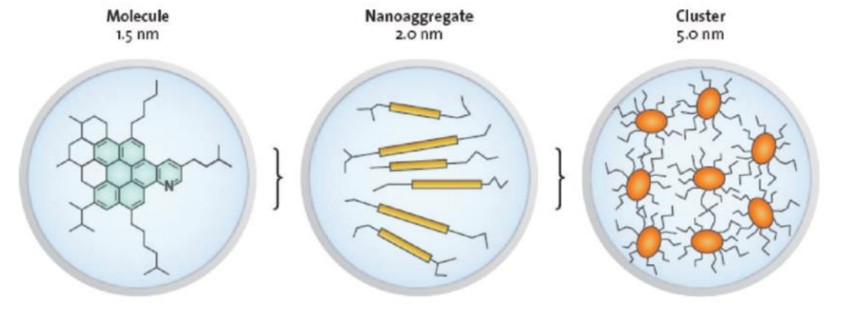

Figure 1. Yen–Mullins model.[1,2,10,11] This model shows the dominant molecular and colloidal structures for asphaltenes in laboratory solvents and crude oils. The most probable asphaltene molecular weight is ~750 g/mol (Da), and the “island” molecular architecture dominates with one aromatic ring system per molecule. With sufficient concentration, asphaltene molecules form nanoaggregates with small (<10) aggregation numbers and with one disordered stack of aromatics. At higher concentrations, nanoaggregates form clusters, again with small (<10) aggregation numbers.

Figure 1.2: Reproduction of the "Yen-Mullins model" and respective caption from Mullins et al. 2012.

An earlier version, referred to as the "Yen model" was adopted by Languri (2004) in her illustration of the markers and biomarker molecules present in asphalt (see Scheme 6.1, Chapter 6).

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[40] On the Concise International Chemical Assessment Document 59 - Asphalt (Bitumen). The CICADs "provide summaries of the relevant scientific information concerning the potential effects of chemicals upon human health and/or environment" (Wess, Olsen, and Haring Sweeney 2004).

[41] This model shows the complex structuration of asphaltenes at different length scales, which certainly influence the structuration and self organisation of the material at the microscopic and macroscopic levels. An interesting theory to consider for the role and behaviour of asphalt in a paint film.

Biological markers, commonly known as biomarkers, are "complex molecular fossils derived from biochemicals, particularly lipids, in once-living organisms. (…) they can provide information on the organic matter in the source rock (source), environmental conditions during its deposition and burial (diagenesis), the thermal maturity experienced by rock or oil (catagenesis), the degree of biodegradation, some aspects of source rock mineralogy (lithology), and age" (Peters, Walters, and Moldowan 2005a, xi). Biomarkers are seen as "powerful geochemical tools because many are highly resistant to biodegradation. For example, biodegraded seep oils and asphalts commonly contain unaltered biomarkers that can be used for comparisons with non-biodegraded oils" (Peters, Walters, and Moldowan 2005a, 9).

The importance of these biomarkers for the analytical identification of asphalt in oil paintings will be discussed below (see Chapter 6).

Trinidad Lake Asphalt

Given the relevance of Trinidad Lake Asphalt (TLA) as a possible source in use by 19th century artists, and its use in the reconstructions (see Table A.4 and Chapters 5 and 6), this material will be further detailed here.

The material safety data sheet (MSDS), dated 2009, from the company Lake Asphalt of Trinidad and Tobago (1978) Limited, reports that Trinidad Refined Asphalt (Epure) is a "naturally occurring" "stable colloidal mix of bituminous compounds and mineral matter" with a "black or dull grey (solid appearance)." While it is considered a thermoplastic material, at room temperature, "it is actually a semi-solid or can be classified as a gel-sol but appears solid at first glance" (‘Lake Asphalt of Trinidad and Tobago (1978) Limited’ 2009). The MSDS notes that it is also known as "Dried Asphalt (DA)", and the information on its chemical composition is compiled in Table 1.2. In the company's MSDS from 2012 (‘Lake Asphalt of Trinidad and Tobago (1978) Limited’ 2012), there is a variation in terms of percentage in the bitumen content and mineral matter, with 52-62% and 33-38% respectively.

Table 1.2: Chemical composition of TLA according to the information provided in“Lake Asphalt of Trinidad and Tobago (1978) Limited” 2009.

Components	Approx. Percentage	Chemical Data
Bitumen Content	53-55% (2012: 52-62%)	"a) Saturated polycyclic compounds containing oxygen, sulphur and clay minerals of general chemical formula - $\mathbf{C_nH_{2n+2}}$. [42]

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[42] Saturated hydrocarbons with this formula are known as Alkanes or Paraffins (Peters, Walters, and Moldowan 2005a, 21).

		b) Polar aromatic and nap[h]thenic compounds of general chemical formula -$\mathbf{C_nH_{2n-2}}$. Also contained are aromatic compounds of formula $\mathbf{C_nH_{2n}}$ [43] and aliphatic compounds."
Mineral Matter	35-37.5% (2012: 33-38%)	"Silica, Alumina, Ferric Oxide and other trace compounds"
Water of Hydration of Minerals	4.3%	-
Other organic matter*	3.2%	

* Described by Charles and Grimaldi (1996) as "Insoluble in Carbon Disulphide".

These results are consistent with what had been previously reported (Table 1.1) and in publications pertaining to TLA (e.g. Charles and Grimaldi 1996; Maharaj 2009). A comprehensive description of TLA is provided by Charles and Grimaldi[44] (1996) who report that it is a "naturally occurring, semi-solid asphalt found in an emulsified form in an asphalt lake to the south of the island of Trinidad. The lake is commonly referred to as the "Pitch Lake"" further explaining that the "Refined TLA [or Epure] is produced by ripping the lake surface with light tractor machinery and transporting the crude material to refining stills" where "it is heated by steam coils to a constant temperature of 160ºC to remove excessive water and volatiles and then screened to remove traces of extraneous and deleterious material." They stress that this is not a distillation process but rather a process of "dehydration with relatively low temperature and impurity removal" (Charles and Grimaldi 1996).

In terms of composition, Charles and Grimaldi report that the water of hydration is in the range of 9-10% (higher than in the 2009 and 2012 MSDS described in Table 1.2). Regarding the mineral matter they state that it is "extremely fine" and "mainly quartz and clay minerals (Kaolinite and Ilite)". Furthermore, the authors report that the bitumen fraction in Epure is composed of 82.3% carbon, 10.7% hydrogen, 6.2% sulphur and 0.8% nitrogen and fractionally constituted of "36% malthenes and 18% asphaltenes" with a range of "67%-70% malthenes and 30-33% asphaltenes" in the soluble bitumen; while, the asphaltenes composition is defined with the approximate percentages of "Carbon - 82%, Hydrogen - 7.8%, and Sulphur - 10.2%" while in the maltenes "around 39% prove to be unsaturated hydrocarbons" and "yield 6.3% of Fixed Carbon" on ignition. This fraction is described as being "soft and exceedingly sticky, like "*maltha*"" (Charles and Grimaldi 1996).

Information on "Trinidad asphaltum" was found in a book on "The Industrial and Artistic Technology of Paint and Varnish" by Alvah Horton Sabin published in 1927. Sabin states that it contains "so

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[43] Known as monocyclic alkanes they are formed "when two ends of an acyclic alkane join" to "form a single ring" and "those with combinations of five (cyclopentyl) or six (cyclohexyl) carbon atoms are common in petroleum", finally, "Alkanes containing rings are sometimes called naphthenes" (Peters, Walters, and Moldowan 2005a, 23).

[44] The authors affiliations in the article describe R. Charles as a "Senior Lecturer from the Department of Civil Engineering, Faculty of Engineering, The University of the West Indies (UWI)" and F. Grimaldi as a "Specialist Consultant in Pavement Engineering, USA".

much mineral oily matter that pieces which are pressed together readily though slowly unite, and if a barrel of it is laid on its side with the head removed the asphalt will in time flow out of the barrel. He reports that it "has about the consistency of soft rosin" (Sabin 1927, 139) and continues, "some of the solid asphalts, such as Trinidad, while hard enough to be brittle when struck are soft enough to be viscous and flow under long-continued pressure; the more fluid of these cannot be made to unite freely with linseed-oil" (Sabin 1927, 341).

1.4 Analyses of paintings with alligatoring

This section intends to give an overview of the existing literature on the analysis of paintings with alligatoring. As will be seen this review of the literature points to the importance of systematically investigating the paint defects from a more objective view since previous studies involving paintings with alligatoring have reported inconclusive results and have focussed almost exclusively on the presence or absence of asphalt/bitumen. For this reason, in this section, attention was primarily drawn to the detection of asphalt since the expectation of this material being responsible appears to be resulting in a bias which has significant implications in the study and analyses of paintings with alligatoring as will be discussed.

From 61 published sources that address or mention drying problems, there were 20 articles[45] which refered analytical results. The 18 sources considered represented a total of 50 paintings with film-forming defects.

In an attempt to understand the scarcity of analytical information three main areas will be discussed: the presence or absence of asphalt in the paintings analysed; the additional information provided for the paintings stratigraphy or other analytical results such as binder or pigments; and the analytical techniques used.

Asphalt identification

Out of the 50 paintings with drying defects where asphalt was suspected to have been used, only in 5 paintings were "asphaltic or bituminous materials" clearly identified and linked to the problem, whereas analysis carried out on 39 paintings did not reveal its presence (Figure 1.3). Interestingly,

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[45] Two articles reported the detection of asphalt/bitumen (Carlyle and Southall 1993; Townsend 1995, 179) however the method of analysis was not described, which leaves a total of 18 sources that included analytical information.

this latter result did not call into question the analytical methodology used, instead the presence of asphalt was simply dismissed. This appears to have been a consequence of an absolute belief in the validity of the analytical results. For example, Grimm completely discounts the existence of bitumen in Albert Pinkham Ryder's paintings which "were long thought to contain bitumen" because he asserts, this was "an untrue assumption that became accepted as fact"; he bases this on a scientific study by Erhardt et al. (1990) which did not find bitumen in the paintings analysed (Grimm 1999, 38). In later years these negative findings are questioned, for example Rae cautions that "due to the difficulty of identification (and the possibility of artists using a bitumen created from a coal tar derivative) the presence of bitumen should not be ruled [out] even when it is not identified in scientific analysis" (Rae 2010, 48).

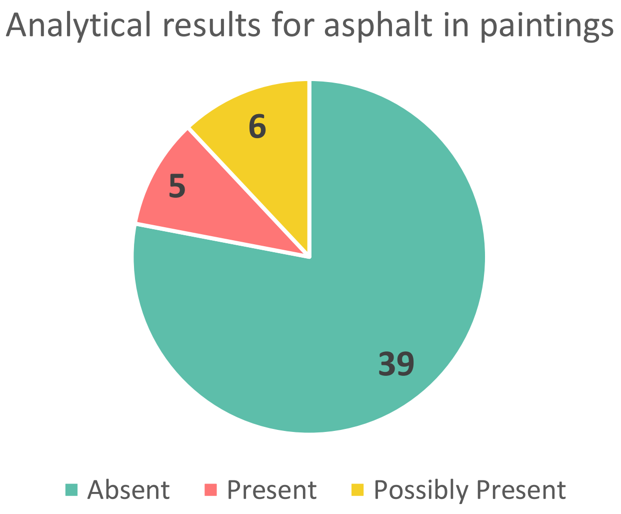

Figure 1.3: Asphalt identification on a total of 50 analysed paintings. Divided by whether asphalt is absent (39 paintings), present (5 paintings) or possibly present (6 paintings).

For this literature study, a category of "possibly present" (Figure 1.3) was created to allow for uncertainty presented by the authors and/or because the analytical technique gave inconclusive results. From the 6 paintings in this category, 5 authors expressed uncertainty with words such as "possibly", "perhaps" or "suggesting" the presence of bitumen (Shank 1984; White and Kirby 1994; Jones, Townsend, and Boon 1999; White 1999) and 1 had an identification "based on Richard Wolber's experience and observation of bituminous layers" with fluorescent staining (Buckley 1986) which, without further confirmation must necessarily remain subjective. This resonates with the opinion of other authors, for example Bothe states that “since microscopic and chemical analyses are unreliable, only instrumental methods of analysis are worth considering” (Bothe 2007, 140).

In 3 of the 5 paintings where asphalt was reported to be present (Figure 1.3 and Table 1.3) the identification was made by Raymond White at the National Gallery, London, using gas chromatography-mass spectrometry (GC-MS) (White 1986; van der Loeff and Groen 1993; Groen 1994). Two things should be noted: GC-MS is normally used to identify markers from the maltene fraction[46]; and all three paintings are from the 17th century, which could raise questions about the processing of the pigment. According to Bothe 17th century recipes show that, the main processing involved heating the asphalt with drying oil (Bothe 2007, 116–18). Later on, in the 19th century the recipes collected by Carlyle involve heat treatment but with the further addition of a range of different materials such as balsam, resins, waxes, siccatives and megilp (Carlyle 2001, 403–7). And as will be shown (see Chapter 6) at least some of these additional ingredients complicate the clear identification of asphalt.

The remaining 2 paintings where asphalt was identified are from the 18th and 19th century. The late 18th century painting, by Henry Fuseli was analysed by Henk van Keulen at the ICN[47], and results were reported by Rae (2010): "GC/MS analysis revealed the presence of hopanes and alkanes (…) considered two of the characteristic markers of traditional bitumen." However Rae notes that this data should be "treated with some caution due to the great difficulty in identifying bitumen" (Rae 2010, 54).

Erhardt and his co-authors have made the definitive claim that "the analysis for bitumen is not simple, but is possible" since "despite the differences" all bitumens "have in common a number of compounds in the region labelled 'Hopanes' (…) [which] is in fact diagnostic for bitumen. If bitumen is present in a paint sample in any reasonable quantity, such as a pigment would be, then these peaks should appear in the analysis of an extract of the paint sample" (Erhardt, von Endt, and Tsang 1990). Such certainty fails to acknowledge the role of other factors such as the impact of paint preparation processes on the asphalt (bio)markers (see Chapter 6 for further discussion on this point). They also fail to account for artists knowingly or unknowingly using substituted materials in place of asphalt/bitumen, according to White "The presence of a range of hopane homologues is an excellent indication of the asphaltic nature of a sample. They are not found in the tar and pitch of wood and resin" (White 1986).

The last of the paintings with a positive result for asphalt/bitumen was analysed with Fourier transform infrared spectroscopy (FTIR) by Richard Wolbers at Winterthur, Delaware in 1983. The identification of asphalt in the 19th century painting was made based on the presence of a 810 cm^{-1} peak and a 1600 cm^{-1} peak. As Wolbers explained, the “weak bands around 800 cm^{-1} “ could be used as “diagnostic for asphalt-type” since they do not have “counterpart or interfering bands contributed from linseed or the other drying oils, or the varnishes for that matter” (Wolbers 1983). This detail might

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[46] While Py-GC-MS provides information on markers and biomarkers from the asphaltene fraction.

[47] Currently the Cultural Heritage Agency of the Netherlands (RCE).

explain the need for the multi-step extraction[48] which Wolbers carried out on the paint sample, since a typical oil paint could have pigments or fillers with IR absorption bands in that area.

Table 1.3: Paintings where asphalt was reportedly identified, with information on the artist, painting and respective dates, as well as source reference.

Artist	Artist's dates	Painting	Date	Article
Gerard Dou	(1613-1675)	*The Young Mother*	1658	(van der Loeff and Groen 1993)
Orazio Gentileschi	(1563-1639)	*Joseph and Potiphar's Wife*	c.1633	(Groen 1994)
van Dyck	(1599-1641)	*Portrait of a Man* (from the Royal Collection)	n.d.	(White 1986)
Henry Fuseli	(1741-1825)	*The Three Witches appear to Macbeth and Banquo*	1793/94	(Rae 2010)
Jane Stuart	(1812*-1888)	*Martha Washington*	n.d.	(Wolbers 1983)

As will be shown, the overwhelming absence of positive analytical results for the presence of asphalt/bitumen does not indicate a lack of use or an absence of cause and effect (asphalt/bitumen = drying problems), but rather an indication of a systemic problem related to the analytical methodology available.

There is a multitude of reasons to support this later hypothesis, starting with the chemical complexity of asphalt, the way the pigment was processed to form an oil paint (heating, addition of other organic and inorganic materials), the possible adulteration of asphalt with other materials, the whole history of the painting in terms of environmental conditions during aging and conservation treatments; and of course the analytical methodology applied, from the sampling stage (area, size, separation of layers) to the analyses with possible extraction stages prior the use of different instrumental methods. All of these factors will have a profound impact on the detection of markers or biomarkers from asphalt; yet they are often neglected since the researchers appear to assume that they should be finding the same markers in the paint as they find in their reference samples of “raw” asphalt or other substitutes such as coal-tar.

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[48] The samples went through a complex preparation: extraction with CS_2 and acetone, "clarification by centrifugation from associated inerts", spotting "onto NaCl plates", evaporation "to near dryness as thin films", vacuum drying to "drive off residual solvent" and the use of dry N_2 flow during analysis to "eliminate CO_2 and H_2O from contributing to background spectra" (Wolbers 1983).

This hypothesis will be further demonstrated and discussed in Chapter 6 with the analysis performed to the W&N "bitumen" oil paint reconstructions.

Reference samples

From the 61 sources reviewed, only 7 describe analyses of reference samples. For example, White (1986) presents the results from a multi-analytical approach to the study of "geologically modified organic material" such as bitumen/asphalt and pyrobitumens, and "artificial products formed by pyrolysis" like resin, softwood tars, pitches and smoke condensates (coal-tar is included in this section); while Erhardt (1990) used GC to analyse "historical commercial bitumen pigments" from the colourmen Weber, Roberson and Winsor & Newton. Another example is Languri (2004; Languri and Boon 2005) who characterized an asphalt sample from an historical collection, *Hafkenscheid*, and compared it to a "representative sample" from Shell that would "match the chemical properties of the Dead Sea asphalt".

These can be extremely valuable in establishing markers for analysis, but should not be interpreted as direct comparison for the results obtained from 19th century oil paintings.

Characterization of materials and techniques

As noted above, previous studies have reported inconclusive results and have focussed almost exclusively on the presence or absence of asphalt. By relating the problem specifically to asphalt, due consideration has not been given to other materials known to have been used in combination with this brown colourant and their presence and influence has not been comprehensively explored. Therefore, previous research has overlooked the importance of documenting the organic or inorganic materials present which could help find correlations amongst different paintings, solely focusing on the presence or absence of bitumen in detriment of a more complete characterization of the painting's materials.

For this reason, this review also considered additional analytical information present in the 18 sources[49], which was divided into 3 categories: Binder, Pigments and Stratigraphy.

The category with the most data is the binder with 14 sources referring to it; followed by pigments and stratigraphy featuring in 10 sources each. Note that there is no direct correlation between these numbers, for example only 5 sources gave information on both pigments and stratigraphy and 7 sources includeeed pigments and binder or binder and stratigraphy.

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[49] From these only 3 sources relate to paintings where asphalt was identified (3 paintings) and 4 sources where asphalt was "possibly present" (5 paintings).

From an analytical point of view it is understandable that binder analysis is more consistently present in studies of paintings with alligatoring since the search for asphalt or other complex medium involves using instrumentation that gives information on the organic fraction of the sample, therefore even if asphalt is not found, the data produced often identifies drying oils, resins or waxes.

The pigment category is a complicated one, since even when pigments are mentioned they relate to a single colour or layer (e.g. ground or brown layer) and do not represent a complete characterization of the pigments present in the painting or even in the affected areas. As well, in some cases the pigments are inferred from elemental analysis, which is often the case with lake pigments. In this review 6 sources mentioned lake pigments, mainly red lake, one of them was from a painting where asphalt was identified and 3 from paintings where asphalt was "possibly present" (see Table 1.4).

For the stratigraphy (see Table 1.4), preference was given to sources that had images, drawings or some sort of schematic of the cross-sections over simple written descriptions of layers observed.

Table 1.4: Additional analytical information of paintings where asphalt was present (above dotted orange line) or "possibly present" (below doted orange line).

Source	Artist	Painting	Binder	Pigments		Stratigraphy
				Any	Lakes	
(van der Loeff and Groen 1993)	Gerard Dou (1613-1675)	*The Young Mother*	✓	✓	-	✓
(Massing 1988) (Groen 1994)	Orazio Gentileschi (1563-1639)	*Joseph and Potiphar's Wife*	- ✓	✓ -	✓ -	✓ -
(Rae 2010)	Henry Fuseli (1741-1825)	*The Three Witches appear to Macbeth and Banquo*	✓	-	-	✓
(Jones, Townsend, and Boon 1999)	Sir Joshua Reynolds (1723-1792)	*Self-portrait as a doctor*	✓	✓	-	-
		Self-portrait as a deaf man	✓	-	-	-
(White 1999)	Van Dyck (1599-1641)	*Portrait of George Gage with Two Attendants*	✓	✓	✓	-
(Shank 1984)	John Singleton Copley (1738-1815)	*Mrs. Daniel Denison Rogers*	✓	✓	✓	-
(Buckley 1986)	Sir Joshua Reynolds (1723-1792)	*The Ladies Amabel and Mary Jemima Yorke*	✓	✓	✓	✓

Analytical techniques

Another aspect worth noting is the variety of analytical techniques applied. As can be seen in Figure 1.4, GC-MS is the predominant technique reported (14 sources), followed by optical microscopy

(OM). The section "Others" encompasses 12 different techniques from 13 sources. The majority of these techniques were used for the characterization of the paintings and are quite standard for paintings conservation, for example IR-Reflectography and X-radiography, as well as FTIR and scanning electron microscopy (SEM). Curiously no mention of Raman spectroscopy was found in this literature review.

Within the OM analysis specific approaches are mentioned such as polarized light microscopy (PLM) or fluorescent staining. Although not scientifically conclusive, some OM results pertaining specifically to the identification of asphalt appear, e.g., "under the microscope, brown translucent particles of low refractive index, characteristic of asphaltum, were indeed found to be present in a sample of the paint mixed with bone black." (White and Kirby 1994). In this regard, Rae wisely stated that "Reasoned suggestions regarding the cause of drying defects can be made using analytical microscopy however scientific analysis is needed in order to conclusively characterise the media used" (Rae 2010, 47).

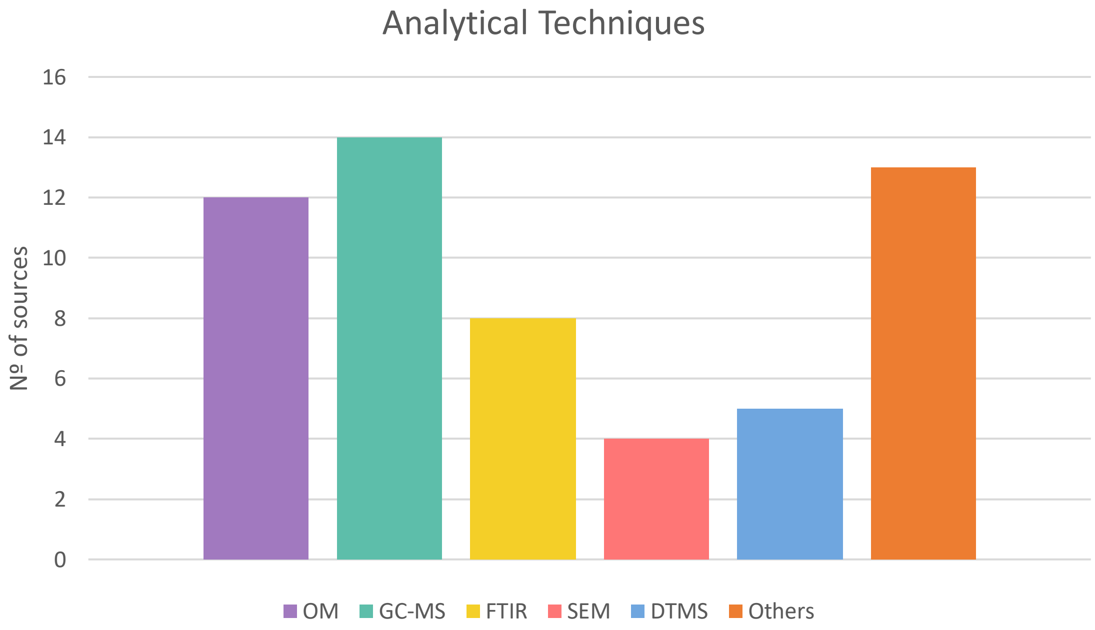

Figure 1.4: Identification of the main analytical techniques mention in the sources for the analyses of affected paintings.

Also in the "Other" column are chromatographic techniques such as GC, High performance liquid chromatography (HPLC) or high pressure size exclusion chromatography (HPSEC) and mass spectrometry techniques such as Py-GC-MS with and without derivatisations, and electrospray ionisation Fourier transform ion cyclotron resonance mass spectrometry (ESI-FTICR-MS). More sparsely mentioned are techniques such as Nuclear magnetic resonance (NMR) or Electron Microprobe.

Discussion

The overall focus of previous research has been the detection of asphalt due to an informal correlation of this material as responsible for drying defects. Both Bothe (2007) and Frame (2022) discuss the bias which results from this thinking. This bias has significant implications in the study and analyses of paintings with alligatoring as discussed above.

Ann Massing, explains that a paint layer is described as “bituminous” when it displays specific characteristics: pronounced drying cracks and solubility in relatively weak solvents. Massing avoids making a causal connection since she recognises that analysis has not confirmed the relationship: “In this article, we have referred to bitumen although a definite identification of bitumen has not been made” (Massing 1988). However her use of the term bituminous to describe the paint's appearance is quoted as evidence for the confirmation bias that descriptors such as “bitumen cracking” create. In this case, ironically, bitumen ended up being detected in the painting[50] a few years later.

Conclusion

Nevertheless, it is undeniable that the search for a single component has obscured the presence and influence of other materials that may play a role in the deterioration mechanism. The second conclusion that can be taken is the lack of critical thinking applied to the analytical techniques; whilst it is possible that asphalt is not present in the paintings there is also a strong possibility that the material cannot be detected by the instrumentation used, since as Gent points out "although the presence of marker compounds can positively identify its inclusion, their absence in results cannot rule out its presence in a paint layer" (Gent 2019, 31). This later point has also been stressed by Frame noting that "the lack of analytical detection only calls into question the assumptions about bitumen to a certain extent, since whenever using such analytical techniques, and particularly when sampling from larger paint passages, absence of evidence of a material’s presence is not necessarily evidence of absence." (Frame 2022).

1.5 Conservation and Restoration Reports

In the literature consulted, only 2 articles and 4 C&R reports (covering a total of 6 paintings) describe the restoration process of paintings with alligatoring where the decisions concerning the approach to the reintegration of the image are discussed. Reintegration of such severely disrupted paint

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[50] Orazio Gentileschi’s *Joseph and Potiphar's Wife* (c.1633), analyses described by Groen (1994).

surfaces is a complex and challenging issue. The problem is to balance improving the legibility of the image by minimizing the impact of drying cracks or extreme defects while maintaining the ethical principal of minimal intervention which respects the original painting (e.g. does not simply paint over the defects).

Van Zuien describes this dilemma for the retouching process of *Rutger Jan Schimmelpenninck with his Wife and Children* of 1801-02 by Pierre-Paul Prud'hon, stating "On the one hand the introduction of a lot of new material was not desirable, but on the other improving the legibility of the family portrait so that it would regain its impact was of the highest priority." And concluding that in this particular case the option was to inpaint the light-coloured cracks without filling them prior, so that "the texture of the contracted paint has remained visible, but this is not disturbing. Because of their matching colour the cracks are lost in the larger form of the composition." (van Zuien 2012).

An earlier reference from 1993 by Van der Loeff and Groen presents a similar approach when discussing the restoration of *The Young Mother* (1658) by Gerard Dou (1613-1675). The history of restoration for this painting showed that in 1815 "cracks (…) were referred to with the recommendation of filling and retouching them." The recommended filling had been carried out since the condition summary in 1986/7 described the current state of the painting: "The putty had been applied so as to level out the whimsical river landscape formed by the cracks, in order to match the other intact and smooth areas of the painting" however it also covered "the inward sloping original topmost paint along the cracks, making the cracks appear even broader than they actually were.". The treatment approach chosen by the authors writing in 1986/7 is clearly stated "Contrary to the earlier restoration, the slopes of the wide alligatoring craquelure were not filled, leaving the misformed relief of the original paint visible." (van der Loeff and Groen 1993). Despite the inpainting of the drying cracks which "were found to be too disturbing and attracted too much attention" an important remark is made by the authors: "We are usually tempted to accept this type of drying craquelure and make no attempt to hide it." Justifying that "Apart from the ethical reason for this, there is the possibility of discolouration of new retouches, which subsequently might have to be removed again someday" (van der Loeff and Groen 1993). While the latter reason could be improved using appropriate archival quality materials the first reason still remains true and relevant for current painting conservation practice.

The minimal approach adopted in later treatments clearly showcases the development of conservation and restoration as a profession, with its higher standards and ethical guidelines.

Another approach, to accept the problem without attempting any treatment is also discussed in the literature. Rica Jones argues that "bitumen shrinkage" "is recognised by restorers and art historians alike as an inbuilt, irreversible problem for which mental compensation has to be made when viewing the picture." (Jones 1990). Rather than presenting the work and leaving it to the viewers to re-image, Grimm concludes that "Nothing can be done to restore the original appearance of The Curfew Hour (…) Because of its present condition, the painting has little aesthetic value as a work by Ryder and is no longer on view." (Grimm 1999, 95) (see the painting in Figure 1.1).

Interestingly, according to the Redgraves' both approaches - invasive treatment or no treatment - were already considered in the 19th century:

> "What is best to be done with pictures cracked and flowing from the use of asphaltum? No doubt many repairers will readily undertake to bring the parts together with the pressure of a heavy iron over a strong glue, and then with a little repainting, and not a little varnishing, the picture for a short time will appear perfectly renovated; yet it is but a fallacious cure. New rents will soon open, all the sooner for the strong varnishing; and the little repainting will be mixed up with the original, to be again cured by the same process. Far better is it to abstain from any attempt at repair, to cleanse the surface with fastidious care by means of cotton wool, and then to preserve the picture from dust (which sticks so readily to the pitchy surface) by means of glass, and from damp and change of atmosphere by covering up the canvas behind." (Redgrave and Redgrave 1866, 596–97)

Their opinion comes after a graphic description of paintings from William Hilton the Younger (1786-1739) in the National Gallery which "have had to be removed from time to time, in order to reverse them, [so] that eyes and limbs may float back again to the places from which they had slipped whilst hanging on the walls!". This is exemplified by his painting *Editha and the Monks Searching for the body of Harold* (Figure 4, page 2) that had "twice nearly slipped from the canvas" and was now a "seamed wreck of his genius" (Redgrave and Redgrave 1866, 596, 171; Southall 1996).

Pertinent to this discussion, however, is the context of the artist's studio. Svoboda and van Vooren give the example of "Albert Groll, friend and artist, [who] watched Ryder in his studio attempt to close open fissures with a red-hot rod." explaining the direct implications of this action to conservation approaches in Ryder's paintings: "This is important because it tells us that, in at least this instance, and probably many more, the cracks opened prior to when the painting left Ryder's studio. It follows that he would not have hesitated to overpaint these cracks if the hot iron did not work. So, although typically paint over cracks indicates retouching by an individual other than the artist, in Ryder's case, this conclusion can-not safely be drawn." (Svoboda and van Vooren 1989).

These views regarding whether to treat or leave untreated were found in the C&R archives. The conservation files[51,52,53] were consulted at the scientific archives of The Centre de Recherche et de Restauration des Musées de France (C2RMF), for two paintings with alligatoring: a work by Eugène

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[51] "Procès-verbaux 1913 (PVCR1913)", 28 Fev 1913;

[52] "Procès-verbaux 1914 (PVCR1914)", 29 Jan 1914;.

[53] Zezzos, G. 1939. "Rapport de Restauration (P 254)". Paris

Delacroix (1798-1863) *La Noce Juive au Maroc*, 1839 (Figure 1.5), and by Jean-Auguste-Dominique Ingres (1780-1867), *Le compositeur Cherubini (1760-1842) et la Muse de la poésie lyrique*, 1842 (Figure 1.7). These records provided a timeline for the conservation of these paintings and showed the emphasis that had been given to the "profondes craquelures" in both works in terms of their visual impact.

Figure 1.5: Painting by Eugène Delacroix (1798-1863) *La Noce Juive au Maroc* or *Jewish Wedding in Moroco* from 1839, at the Louvre. ©Marques 2018. The white squares identify areas of detail shown below (Figure 1.7).

Figure 1.6: Details showing alligatoring in the painting *La Noce Juive au Maroc*, by Delacroix. These details (marked in Figure 1.6) in normal (a) and specular reflection (b & c) show the paint islands and disruption of the surface.

Figure 1.7: Painting by Jean-Auguste-Dominique Ingres (1780-1867*), Le compositeur Cherubini (1760-1842) et la Muse de la poésie lyrique or Luigi Cherubini and the Muse of Lyric Poetry* from 1842, at the Louvre. ©Marques 2017. The white squares identify areas of detail shown below (Figure 1.9).

Figure 1.8: Details from the painting *Le compositeur Cherubini (1760-1842) et la Muse de la poésie lyrique* by Ingres (marked in Figure 1.8) showing the alligatoring in the hair and face of the Muse (a) and the significant drying cracks in the face and clothes of the Muse (a & b).

According to the Minutes or "Procès-verbaux" in 1913, the museum committee reported that both the Ingres and Delacroix paintings have had deep cracks for a long time, which the committee had already examined several times and decided to leave as they are. The minutes record that the cracks are the result of the light “bitumi” [bituminous] sketch which preceded the execution of the paintings (cited in the Minutes or "Procès-verbaux" from 1914[52]). Two systems of restoration were discussed in 1913, one which called for infilling and reintegration of the cracks and the other, the Mr Guédy system, which involved melting the edges of the cracks (1 and 2, Figure 1.9). The minutes record the warning that in both systems, the restorer would be obliged to substitute the artist’s work, for example, to reinvent the eyes and nose in the face of the Muse of the Cherubini portrait.

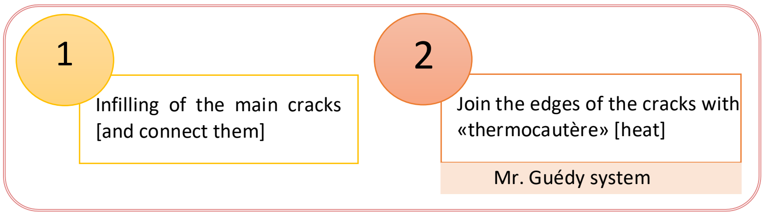

Figure 1.9: Two restoration systems proposed in 1913.[51]

In the 1914 minutes, Mr. Leprieur[54] is recorded to have recalled that the committee had decided several times, and in particular at its meeting in 1913, against the use of the «thermocautery» process, which he stated was undoubtedly ingenious but dangerous.[52] The reasons for rejecting this option were based on the fact that this method:

- Consists of liquefying the damaged parts of the paintings, and involves the displacement of matter which necessarily alters the forms;
- In this “scientific” process a significant part is left up to the interpretation and invention of the restorer.

Furthermore the minutes report that:

- Mr. Guédy cannot be entrusted with important works such as the “Cherubini" of Ingres, the "Noce au Maroc" of Delacroix, or the paintings from Prudhon;
- It is pointless to take on new expenses to restore, in a way that is considered defective, these paintings;
- It is unnecessary to make new attempts [to correct the problem].

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[54] According to Agnès Callu, Paul Leprieur became head of the Louvre's Department of Paintings and Drawings, joining the Museum's committee somewhere between 1900 and 1903 (Callu 1994, 225).

The minutes record paintings already treated with Mr. Guédy system: two by Ary Scheffer (one of which was “Larmoyeur” (see Figure 1.11) and one painting from Count de Forbin and Falguière's Woman with a fan. The latter is mentioned as the subject of an essay by Mr. Guédy. [51],[52]

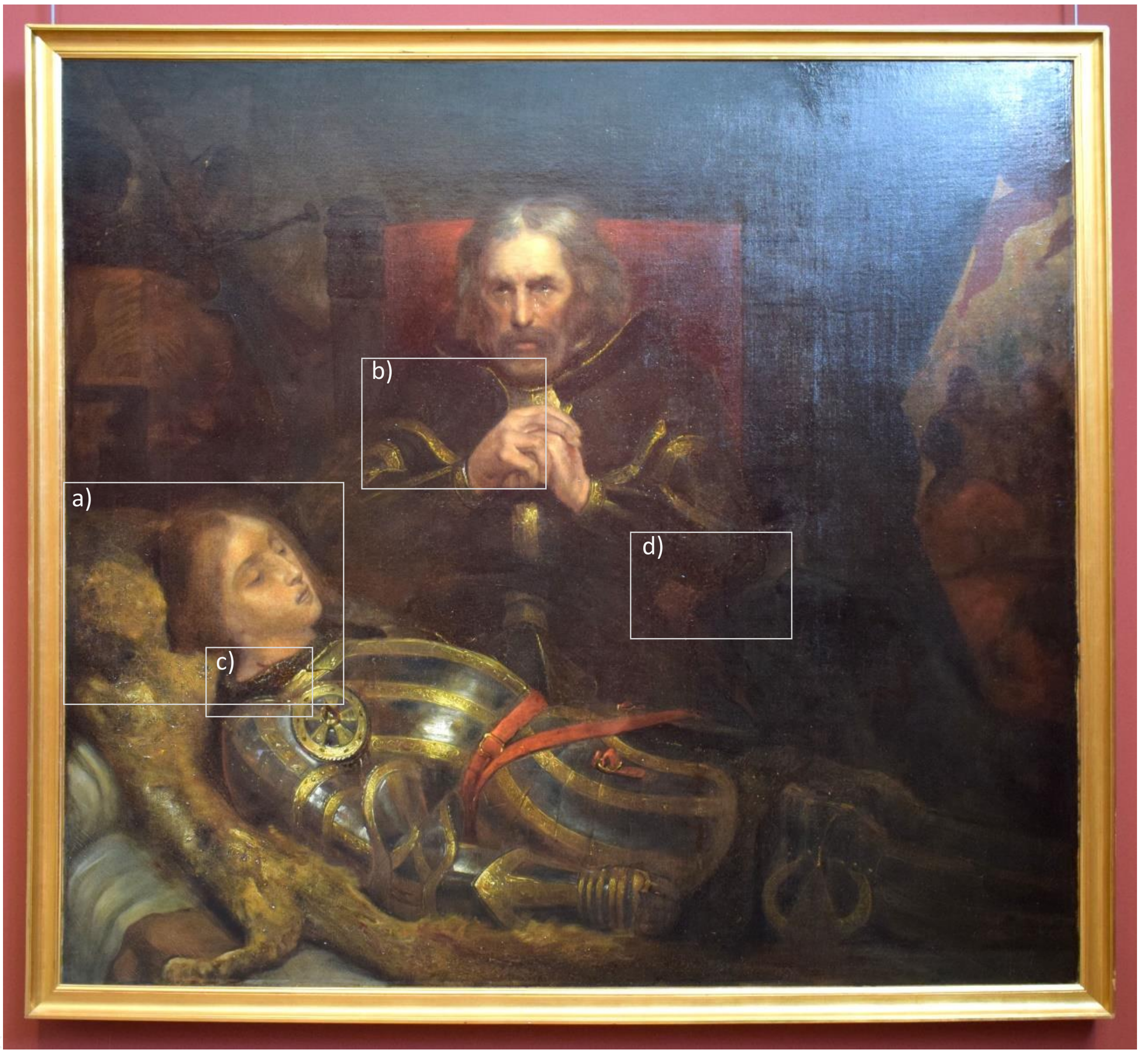

Figure 1.10: Painting by Ary Scheffer (1795-1858) *Eberhard, comte de Wurtemberg, dit Le Larmoyeur, pleurant la mort de son fils*, dated 1836, at Musée de la Vie Romantique, France. ©Marques 2018. The white squares identify areas of detail shown below (Figure 1.12).

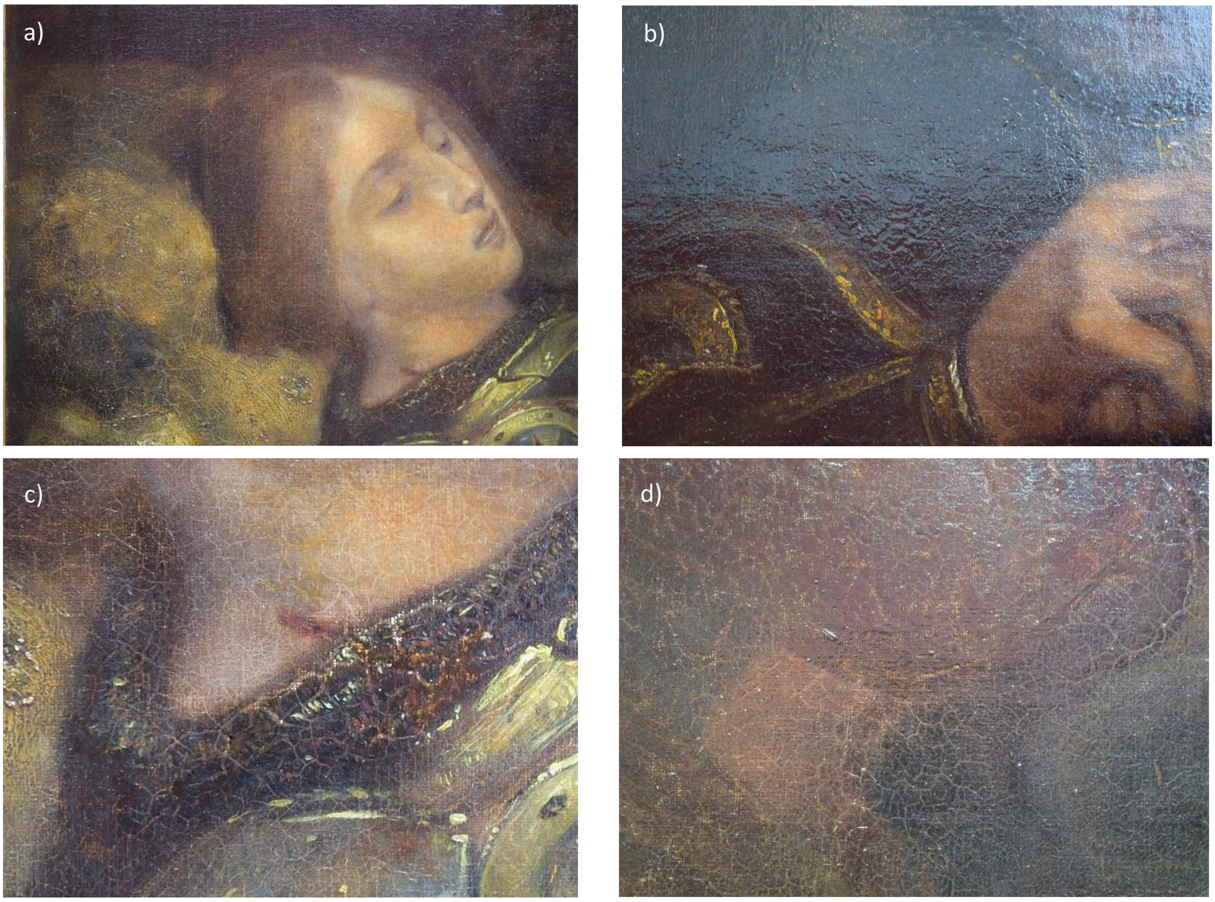

Figure 1.11: Details of the painting by Ary Scheffer (1795-1858) *Eberhard, comte de Wurtemberg* (Marked in white in Figure 1.11). ©Marques 2018. The painting looks heavily ironed and retouched (a & c), with flattened paint and visible texture from the canvas (c & d). The alligatoring is still noticeable in some areas due to the paint islands texture (b) or wide crack apertures (c & d).

As a result of the discussion, the 1914 minutes record that Mr. Guédy's option was rejected. Instead the committee voted to clean the two paintings and place them behind glass, which would even out the background by preventing the light from reaching the cracks in the bitumen in the darker parts. No further information is available to confirm whether these steps were carried out. [51]

Nowadays "Mr. Guédy system" wouldn't even be considered as it goes completely against the ethical code of the professional - involving a heat treatment, that intended to liquefying the damaged parts of the paintings, in order to bridge the gaps. However, these reports show that it was a method applied to some paintings, fortunately not to these two paintings from the Louvre, because already at the time this was seen as an invasive treatment and rejected by the museum committee, which points to the accountability and responsibility of the persons involved in the decision-making.

Further information on the subject appears in a restoration report from 1939, where the restorer at the Louvre, Zezzos, wrote that for the restoration of *La Noce Juive au Maroc,* to reduce the ugly effect of the cracks, one could choose between two options (1 and 2, Figure 1.12), each of which was defensible. He noted that in both cases, the pictorial aspect and the firmness of the drawing, would also be restored. The report[53] records that the second method was preferred (see 2, Figure 1.12), but gives no further information to whether or not the treatment was performed.

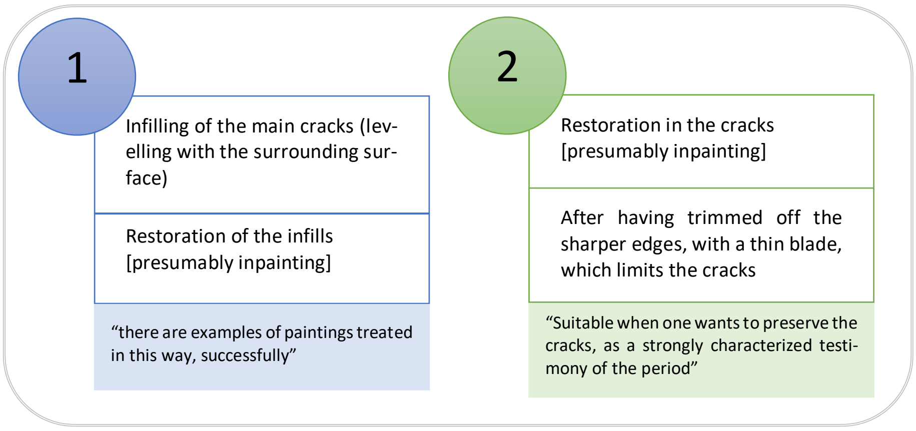

Figure 1.12: The two options mentioned by Zezzos. Sequence of steps and a note concerning each.

This investigation of the records highlights the importance of thoughtful reflection on conservation treatment decisions made by committees and the need for such consultation with numerous people to prevent damaging and highly invasive treatments.

In the case of the two paintings by Delacroix and Ingres, both are on permanent exhibition in the Louvre, and although significant, their drying cracks do not prevent image readability.

Altogether, these examples raise questions that are essential to address when dealing with paintings with alligatoring. While in some cases the image legibility is not completely compromised and the painting can still be on exhibition, in other cases the problem is so severe that the paintings are not exhibited and remain in storage indefinitely. In these latter cases:

- What is the current and future status within museum collections of paintings whose images are no longer readable?
- What values and interpretations should be explored and preserved?
- What viable options are there for their preservation?
- How to understand and represent these works which are otherwise consigned to neglect in perpetual storage?
- How can access be afforded to these works and opportunities made available to bring new value to these works of art? (e.g. through research access or education department's initiatives)

A full discussion of these ethical questions is outside the scope of this dissertation, nevertheless some points will be considered when addressing the case study *O Cardeal D. Henrique recebendo a notícia da morte de D. Sebastião* (see Chapter 2).

2

CASE STUDY

2.1 The Artist, *Marciano Henriques da Silva*

> "Little more was said about the artist and his work. Leaving the mystery in the romantic mists. The blackness of his paintings stained with confusing shadows the vagueness of that romanticism." [55] (translated from D. de Macedo 1951, 3)

As noted in the Introduction, in order to shed light on the problem of alligatoring, a painting by Marciano Henriques da Silva, entitled *O Cardeal D. Henrique recebendo a notícia da morte de D. Sebastião,* and painted in 1861 was chosen for study and examination.

Documentary research on the artist and his oeuvre was carried out in the National Library and the National Archive[56] of Portugal. The sources consulted consist of monographs, academic research (thesis and dissertations), articles in periodical publications, letters, account books and invoices of artist materials purchased by Marciano.

The authoritative works by Diogo de Macedo (1951) and Hugo Xavier (2013) were consulted for the artist's biography and context, along with additional sources which are cited throughout section 2.1. As stated in Macedo's monograph, he relied on information from papers and detailes passed on from friends, making the identification of his primary sources difficult to track. However, clear similarities exist between the information present in the published sources of D'Athaide (1915), D. de Macedo (1951) and Pamplona (1988), respectively.

Further information on the artist's personal life and clarification of some discrepancies in the published sources was found in original records of Marciano's baptism and death, as well as the

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[55] "Do artista e da obra pouco mais se falou. Ficara o mistério das névoas românticas. O negrume dos seus quadros manchara de sombras confusas o vago desse romantismo." (D. de Macedo 1951, 3)

[56] National Archive of Torre do Tombo

baptism of a son of Marciano. A time line was constructed for this thesis from this information and from that already published showing Marciano's life in terms of his education, travel, and his professional and personal achievements (see Figure 2.2).

Throughout this section the quotes in the text have been translated into English with the original quote given in a footnote.

2.1.1 The Artist's Biography

2.1.1.1 Personal Life & Education

Marciano Henriques da Silva (Figure 2.1) was born on the 5th of June of 1831[57] on *São Miguel* Island in the Azores, Portugal. Son of Francisco Henriques da Silva and Roza Henriques da Silva[58], his father was a soldier[59], then a merchant and later a teacher of French and English (D. de Macedo 1951, 4).

Figure 2.1: Marciano Henriques da Silva (left) and a portrait of his wife Selina Maria (right) painted by the artist himself, ca. 1867, 59,5 x 49 cm, inventory number MCM05203. Museu Carlos Machado, Azores.©(Estrutura para a Casa da Autonomia n.d.)[60]

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[57] Information confirmed through Marciano's record of baptism (see Figure B.1, Appendix B). Except for Macedo (1950b, 144) all the other sources including Macedo (1951) state that Marciano was born on the 7th of June of 1831 (D'Athaide 1915, 148; D. de Macedo 1951, 4; Xavier 2013, 65). The sources also state that he was born in the civil parish of *Fajã de Baixo*, however the record of baptism belongs to the civil parish of *São Sebastião*.

[58] The mother's name does not appear in any of the published sources consulted. It was compiled from Marciano's record of baptism noting "Roza Flora" and Marciano's son Affonso record of baptism that states "Roza Henriques" (see Figures B.1 and B.2, Appendix B, pages 249, 251).

[59] Liberal soldier in the Portuguese Civil War (1832-1834).

[60] https://ccmuseus.azores.gov.pt/index.php/Detail/objects/62358

Marciano's first mentor was the English priest Brandt from whom he took drawing lessons. Following this there were paintings lessons in 1847 from Charles Martin, another foreigner living on the island. During this period, Marciano begins exhibiting oil paintings and gains recognition with influential individuals such as the poet António Feliciano de Castilho and the Civil Governor D. Pedro da Costa (D. de Macedo 1951, 4–5). At the age of 18 Marciano traveled to Lisbon where he enroled in drawing classes offered at the Fine Arts Academy of Lisbon. He also established a connection with Sr.ª D. Maria Rita da Silveira later the Viscountess of Fontainhas, whose protection and connections promoted Marciano contributing to his life in Lisbon (D. de Macedo 1951, 6–7). The young artist also met and socialized with a group of painters lead by Tomás da Anunciação[61] (D. de Macedo 1951, 8).

In 1850 Marciano had lessons with the painter Visconde de Meneses (1817-1878) who had just arrived from Rome, and after a year (prompted by Meneses and the Viscountess of Fontainhas) he travelled to Paris on a small grant (D. de Macedo 1951, 9).

During his three years in Paris, Marciano frequented the atelier of Ary Scheffer[62] (1795-1858). During this time, Marciano also attended the *Académie [des Beaux-Arts*] where he took lessons from Horace Vernet (1789-1863) (D. de Macedo 1951, 9; Xavier 2013, 68).

In 1854 Marciano moved to London and frequented the studio of Prescott Knight[63] (1803-1881). While in London he met Miss Selina Maria[64], a watercolourist, whom he married (Figure 2.1). With his wife, Marciano returned to Lisbon in 1856. By then he had completed 5 years of training abroad (D. de Macedo 1951, 10). Soon after, with the protection of Marechal Duque de Saldanha (1790-1876), who was influential among the Monarchs D. Fernando II and his son D. Pedro V, Marciano obtained a grant to continue his studies in Rome. Marciano and his wife arrived in Rome in 1857, staying in "Santo António dos Portugueses"[65]. Marciano restored portraits of Portuguese monarchs, painted copies of old masters from famous galleries in the city and attended the "Academia de S. Lucas" where he befriended the Portuguese painter Miguel Ângelo Lupi (1826-1883). After two years, with an additional

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[61] The group included Tomás da Anunciação, Francisco Metrass, Vítor Bastos, José Rodrigues e João Cristino da Silva. http://www.museuartecontemporanea.gov.pt/ArtistPieces/view/33 (accessed 28th of April 2022). Apart from Vítor Bastos who was a sculptor, the other four artists were important Portuguese Romantic painters. Tomás da Anunciação, Francisco Metrass, Vítor Bastos and João Cristino da Silva were all Professors in the Fine Arts Academy of Lisbon.

[62] Romantic painter, of Dutch origin, living in Paris since 1811. Considered "one of the most representative artists of Romanticism" in 1830 the artist settled in nº 7 of Rue Chaptal (currently the *Musée de la Vie Romantique*) where he had two studios, one for work, the other for entertaining (Le Musée de la Vie Romantique 2015).

[63] D'Athaíde, Macedo and Pamplona all write "Prescothnight", which is likely a typo error when referring to the Royal Academician painter John Prescott Knight.

[64] Both spellings - Celina and Selina - appear in the sources, in this dissertation the version Selina was chosen because it is the spelling on handwritten records (her son's baptism record and Marciano's death record, see Figure B.2 and B.3, Appendix B, pages 251-252). Those records also show that her last name was Samwell.

[65] Nowadays designated "Instituto Portugês de Santo António em Roma". This nationalized institution is, and was in the 19th century, a place to host Portuguese artists and scholars who went to Rome.

monthly grant given by D. Pedro V, Marciano was able to move on to paint independent compositions (D. de Macedo 1951, 11; Xavier 2013, 68).

Diogo de Macedo (1951) details the interaction between Marciano and the Fine Arts Academy of Lisbon, starting in 1860, while Hugo Xavier (2013) confirms and complements the information with the documental sources from the Academy's Archive.

In 1862, while still in Rome, Marciano won the post as the Substitute Professor of Historical Paintings at the Fine Arts Academy of Lisbon. Hugo Xavier notes that the interim nomination was based on his painting, *O Cardeal D. Henrique recebendo a notícia da morte de D. Sebastião,* that belonged to the Fine Arts Academy. The painting had been submitted to the Academy shortly before for Marciano's application to receive the designation, Academic of Merit. The nomination for his Academic of Merit title was endorsed by the artists and Professors Tomás da Anunciação, Francisco de Assis Rodrigues e Joaquim Pedro de Sousa (Xavier 2013, 69). In January 1864, Marciano was nominated "Academic of Merit"[66] and in that same year appointed "Professor"[66] of Historical Paintings in the Fine Arts Academy of Lisbon.

Macedo transcribes a letter from Marciano to the Marechal Duque de Saldanha dated 16 of June of 1863 where Marciano requests monetary help for his move to Lisbon. This request reaches the Palace and a month later, His Majesty King D. Luís I sends Marciano the money (D. de Macedo 1951, 13). On their way back to Portugal both Marciano and Miguel Lúpi, travelling together, went to Paris first (D. de Macedo 1951, 18).

After the death of D. Pedro V (1837-1861) in 1861, his brother D. Luís I (1838-1889) was crowned King[67]. Like his brother before him he continued to protect Marciano, an artist whose international experience had gained him important recognition. On his return to Lisbon, the King invited Marciano to hold prominent positions such as his personal painting's professor[68], Painter of the Royal Chamber[69] and later Director of the Royal Gallery in the National Palace of *Ajuda*[69] (Xavier 2013, 71). In 1865, an atelier was created in the Palace of *Ajuda* where Marciano worked and taught the King and in that same year, by royal appointment, Marciano was awarded the Order of Saint James of the Sword (an award given by exceptional and outstanding merits in literature, science and the arts) (Xavier 2013, 62–63).

The greatest evidence of Marciano's friendship with the King was the fact that the King became the godfather of the artist's son in August 1867 (Xavier 2013, 63) (see Figure B.2, Appendix B, page 251). According to the record of Marciano's death, the artist and his wife had four children (see Figure B.3, Appendix B, page 252).

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[66] "Académico de Mérito" and "professor proprietário".

[67] https://www.casarealportuguesa.org/dynamicdata/Cronologia.asp (accessed April 2022).

[68] "o sr. Marciano é professor de pintura de el-rei" according to "Diário de Notícias" from 12th of September of 1865, as cited in Xavier 2013, 63.

[69] "Pintor da Real Câmara" and "Director da Galeria do Real Paço da Ajuda"

After dividing his time between his Royal posts and his appointment as Professor in the Fine Arts Academy of Lisbon[70] a month after being nominated Director of the Royal Gallery in the National Palace of *Ajuda*, in July of 1867, Marciano resigned from the Professor's position in the Academy (Xavier 2013, 71–72).

According to Xavier this nomination occurred after Marciano's return from a trip to France and Italy where he purchased several paintings for the King's Pinacotheca (Xavier 2013, 62). Macedo had written about this trip and noted Marciano's declining physical and mental health, which had led the artist to travel to his home town in Azores to rest for a few weeks (D. de Macedo 1951, 21–22; Xavier 2013, 74).

The King's appreciation for Marciano and public perception of him is summarised in a newspaper article from *Diário de Notícias* that describes a visit of King D. Luis I to Marciano's atelier in June 1869: "King D. Luis I visited Friday afternoon the studio of the talented painter of the Royal Chamber, Marciano Henriques da Silva, director of the *Ajuda* Gallery. It is not the first time that the illustrious painter received such an honour; this visit from the monarch is another proof of the esteem and consideration that the King has not ceased to show towards our artist.(…)"[71] (DN, 22nd of June of 1869 as cited in Xavier 2013, 73).

Xavier reports on two letters from Marciano, written in 1869 and 1871, showing that he was feeling unwell with health problems that impacted his professional activities (Xavier 2013, 74–75). Marciano was to live only 2 more years after the last letter, he died in Lisbon on the 3rd of April of 1873, at the young age of 42 (see Figure B.3 and transcription in Appendix B, page 252). The Portuguese newspaper, *Diário de Notícias,* published an extensive obituary of this "esteemed painter who with such notable success cultivated the genre of the historical figure and who had a firm and easy line, vigorous colouring and vast and inspired composition"[72]. The obituary continued, "in our days he was the artist most protected by the King D. Luiz, godfather of one of his sons"[73] (DN, 4th of April of 1873 as cited in Xavier 2013, 76). Later on and published in the same newspaper was a eulogy from the poet Bulhão Pato[74], who had developed strong ties of friendship with the artist (Xavier 2013, 76). Macedo states that Marciano had died with dementia and tuberculosis (D. de Macedo 1950a, 18).

Xavier emphasises the role of Marciano as director of the Royal Gallery in building the collection through the acquisition of paintings (Xavier 2013). The Gallery opened to the public in 1869. Its first

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[70] Where he was increasingly absent leaving the teaching of Historical Painting to the substitute Professor José Maria Franco (Xavier 2013,71-72).

[71] "El-rei o sr. D. Luiz visitou sexta feira de tarde o estudo do talentoso pintor da real camara Marciano da Silva, director da galeria da Ajuda. Não é a primeira vez que o illustre pintor recebe tal honra; esta visita do monarcha foi mais uma prova da estima e consideração que el-rei ainda não deixou de dispensar ao nosso artista. (…)"

[72] "estimado pintor que com tão notável êxito cultivou o género da figura histórica e que tinha um traço firme e fácil, colorido vigoroso e composição vasta e inspirada".

[73] "nos nossos dias foi o artista mais protegido por el-rei D. Luiz, padrinho de um dos seus filhos".

[74] The only Portuguese person at the time to appear in the Royal Gallery in a portrait painted by Marciano (Xavier 2013, 76).

catalogue demonstrates the recent acquisitions which Marciano would have been responsible for (this was continued in following years and led to the publication of a new catalogue in 1872).[75]

Despite his extraordinary artistic and social standing, Marciano's reputation and his works, have largely fallen into oblivion. Both Macedo and Xavier argue that this is likely due to the deterioration of his paintings (D. de Macedo 1951, 24; Xavier 2013, 65, 76). As pointed out by Xavier "Only the National Palace of *Ajuda* and the Museum of *Carlos Machado* (Azores) offer evidence today of the ill-fated painter whose celebrated memory quickly faded, shrouded in shadows and mysteries typical of the Romanticism"[76] (Xavier 2013, 77).

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[75] According to Xavier, after this purchases became more sparse which Xavier felt was certainly due to the death of Marciano in 1873 and the "uninterested direction" of Tomás da Anunciação (Xavier 2013, 78).

[76] "Apenas o Palácio Nacional da Ajuda e o Museu Carlos Machado (Ponta Delgada) evocam hoje em dia o malogrado pintor cuja celebrada memória depressa desvaneceu, envolta em sombras e mistérios próprios do Romantismo."

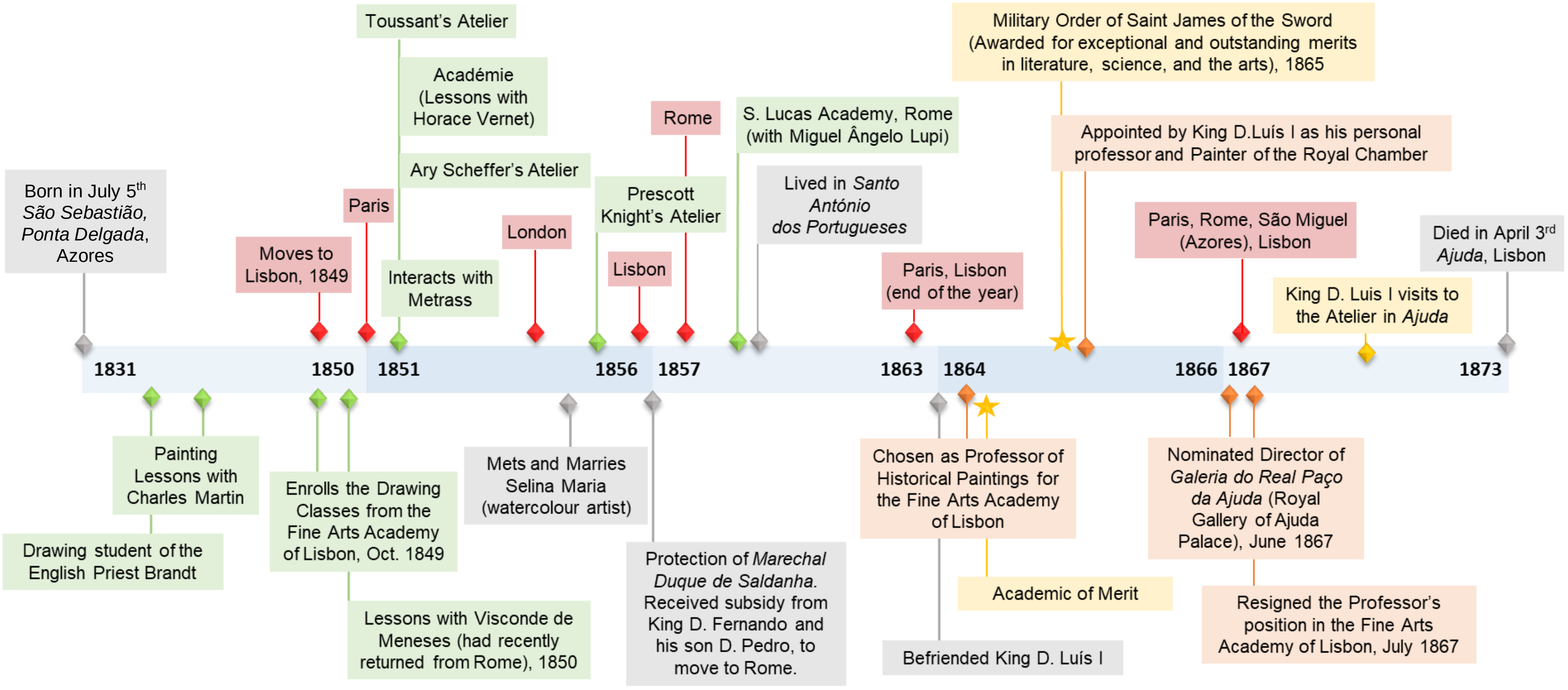

Figure 2.2: Marciano's biographical information summarized, revealing personal milestones (in grey), the places where he lived (in red), studious and artists with whom he worked (in green), as well as important moments of his career (orange and yellow).

2.1.1.2 The influence of Marciano's background

This section provides an opportunity to clarify how Marciano’s connections and mobility influenced the development of his career, and most importantly, whether the technical problems encountered with his painting can be related to the larger context of severe alligatoring found in many 19th century European paintings.

Under consideration are the following topics and respective questions:

- Connections/Patronage
    - What was the social context and how crucial were the personal connections for the development of Marciano's career?
- Mobility
    - What motivated Marciano’s choice of locations for his apprenticeships abroad, in particular, what led to his decision to study in London?
- Technical problems
    - Is it possible to relate the impact of his mobility upon his choice of materials and techniques?
    - Can these international influences be related to the extreme film-forming defects found in the painting *O Cardeal D. Henrique recebendo a notícia da morte de D. Sebastião*?

Patronage

The first topic addresses the social, economical and political context in which Marciano moved. As discussed in the previous section throughout his career Marciano benefited from the esteem and support of nobility which culminated in his relations with three different Kings of Portugal.

At this period in Portugal, Royal patronage played an important role but went hand in hand with private patronage (Silvestre 2012, 36). The status of Patron, associated with philanthropy, was viewed as something of value which denoted a social responsibility, and was accepted as distinctive and noble (Silvestre 2012, 34). In terms of Royal patronage, the example of D. Fernando (Prince Consort, artist, collector and patron) who had a "policy of protecting the Fine Arts and Letters" and would distribute scholarships and letters of recommendation, as well as purchasing works, making donations and opening diplomatic channels (Silvestre 2012, 37). These actions were continued by his sons the Kings D.Pedro V and D. Luís I.

Therefore, such patronage conferred on Marciano not only artistic merit but also a considerable intellectual/social capability to move in an enriched environment and to gain the esteem and support necessary to grow professionally.

Mobility

Marciano's training and early painting experience took place mostly abroad (Figure 2.2) and through individual masters and ateliers rather than at Academies. He went first to Paris, from 1851 to 1854; then to London from 1854 to 1856; and on to Rome remaining there from 1857 to 1863.

Paris and Rome were artistic centres and part of the normal route for Portuguese artists studying abroad. According to Maria Helena Lisboa (2007), Paris and Rome were also the destination for graduates from the Fine Arts Academies of Lisbon and Porto after 1866 when scholarships formally began (Lisboa 2007, 164). The preference for scholarship trips to either Rome or Paris appears to have varied, documents from 1844 and 1861 indicate that Rome was favoured as the place to perfect the craft of Portuguese graduates (staying in *Stº António dos Portugueses*). Later on in 1866, Paris became the better option due to the French teaching system which was more organized and systematized, but this included the possibility of a subsequent visit to Italy for the best students to finish their training (Lisboa 2007, 160–62; Aguiar 2012, 46). Before the official introduction of scholarships there were graduates with funding from the State or from private individuals, and the option of pursing their studies at their own expenses (Aguiar 2012, 46) which followed similar routes to Paris and/or Rome. This was the case of Marciano Henriques da Silva which Lisboa (2007) states was funded by Visconde de Meneses (Lisboa 2007, 166).

Contrary to what was common practice for his Portuguese contemporaries, Marciano also went to London, stating in a letter that it was "both to study the English school and acquire some means of living" (letter dated 1863, as cited in D. de Macedo 1951, 13). This choice might have been influenced by his early education in Azores with English professors (his knowledge of English and their techniques was certainly an advantage). There is also a curious correlation between his travelling and the route taken by Visconde de Meneses, whose artistic training had begun at the Fine Arts Academy of Lisbon, then continued in Rome in 1844, and on to London where he "hangs out with the Pre-Raphaelites." Visconde de Meneses had portrait lessons with Reynolds and Lawrence, then passed through Paris in 1850, after which he moved back to Lisbon (Silveira n.d.), where he met with Marciano and advised him to study in Paris.

Technical problems

The impact of his mobility and his study locations on his choice of materials and techniques which may have led to the extreme paint defects in *O Cardeal D. Henrique recebendo a notícia da morte de D. Sebastião* is particularly hard to evaluate given the many places he worked and the limited number of Marciano's existing paintings available for study.

However, there is a direct association which can be made with the work of Ary Scheffer (1795-1858) since Marciano studied with him in Paris. Extreme paint defects in the form of pronounced alligatoring have been found in six paintings[77] from Scheffer produced between 1824 and 1837. These defects affected predominantly black, brown and red colours and were located in areas of figures, background and shadows, with varying crack apertures.

In addition, section 2.1.2 will discuss Marciano's artist supplies and his connections to a colourmen from England.

As reported in Chapter 1 paint defects, in particular alligatoring, are found in the work of contemporary British and French artists. Artists of the time congregated in Paris, Rome and London where they communicated with each other and exhibited their works. It is interesting if these artistic centres could also have been the source of technical practices and materials which led to technical problems in their paintings.

There are other examples of artists visiting and working in these locations whose work also exhibits significant paint disruption. The British artist Joshua Reynolds (1723-1792) (Southall 1996; Dubois 2000; Izat 2001) and Henry Fuseli (1741-1825) (Rae 2010, 18) both travelled from London to Rome, and their works exhibit technical problems. In the case of Reynolds, specific materials have been associated with his travelings. Dubois argues that he might have been exposed to the uses of wax "in Italy or during his sojourn in Paris at the end of his Grand Tour in 1752” (Dubois 2000). Considering Reynold's exploration of materials and techniques while in Italy, Izat succinctly concludes[78] that "it is therefore not *simply* lack of training that accounts for poor technique in the late 18th and 19th centuries” but that the “cultural impact of an increase in travel, the growth of the free press, a rising national preoccupation with Italy and the 'ancients' ran in tandem with the growth of artistic freedom" (Izat 2001, 5).

Traveling to Rome was also an established route for French artists, particularly for those who were awarded the "Grand Prix de Rome" or even regional variations of this format. One example is the artist Pierre-Paul Prud'hon (1758-1823) who spent four years in Italy (van Zuien 2012) thanks to winning the Prix de Rome régional des états de Bourgogne. Prud'hon's work offers a particularly graphic example of paintings marred by alligatoring, with affected paintings easily identified[79] in French museums and galleries.

Visits to these artistic centres was not only a draw to British and European artists, the American artist Washington Allston (1779-1843), like Marciano, travelled to London, Paris and Rome (L. Mayer

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[77] These paintings were observed in person, since they are all currently on display in collections in and around Paris, France. See Table A.5 in Appendix A.4, page 245.

[78] Referencing Rica Jones "Introduction" in Paint and Purpose: A Study of Technique in British Art, Ed. Hackney, Jones R. and Townsend, Tate Gallery Publishing, 1999, p.12.

[79] Fifteen paintings were observed in person, since they are all currently on display in collections in and around Paris and Lyon, France. See Appendix A.4 (page 244) for survey of affected paintings.

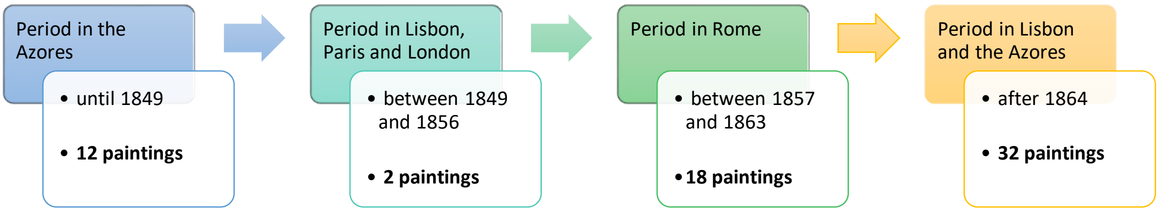
and Myers 2011, 62). His work also suffered technical problems associated with cracking, Hill-Stoner cites Allston's use of "multiple layers of glazes" which likely "contributed to the severe crackle pattern" in his work (Hill Stoner 1990). Interestingly, "Allston disclaimed any credit for the process of glazing, saying that the technique that the French were unaware of was simply 'the English school of color, where I had learned this process.' " (as cited in L. Mayer and Myers 2011, 62). While in Rome he continued to play "an important role in passing on English glazing techniques" where he "demonstrated his technique of glazing over dried paint with mixtures containing megilp, asphaltum, and other colors, again saying that he did not invent the system but brought it from England" (L. Mayer and Myers 2011, 62). However this direct association with British practice is somewhat contradicted by a contemporary source which connects Allston's "early trip to Rome" to his famous use of "Titian's dirt" which was "made from a mixture of asphaltum, Indian red, ultramarine and megilp" (Hill Stoner 1990).

2.1.1.3 Oeuvre & Exhibitions

Despite having held such prominent positions in Portugal later in his career, as noted above, Marciano’s oeuvre is now mostly unknown. From a compilation of Marciano's paintings mentioned in the sources consulted, a total of 64 paintings could be identified (see Table B.1, Appendix B, page 254), however only 14 could be located.

Marciano's total output in paintings (Scheme 1) has been identified primarily through their presence in Exhibition catalogues; Marciano's autobiographical letter from 1863; the Fine Arts Academy of Lisbon minutes/records; and, after 1864, the news in *Diário de Notícias* (due to Marciano's connection with His Majesty King D. Luís I).

Scheme 1 shows Marciano's paintings according to four periods of production related to when and where they were painted as well as their exhibition history and current location.



Scheme 1: Four periods of Marciano's life and career.

The fact that very little information can be found concerning work produced during the time he spent in Paris and London, is explained by Macedo as a consequence of Marciano's student production based on copies of paintings and learning exercises which would have had little value outside the academic environment (D. de Macedo 1951, 10).

Although ostensibly still a student while in Rome, according to Macedo (1951) it is *O Cardeal D. Henrique recebendo a notícia da morte de D. Sebastião*, painted in Rome in 1861, that marks the beginning of Marciano's independent work and establishes his stature as a competent history painter (D. de Macedo 1951, 10).

The only description of Marciano's painting technique is given by the artist regarding his process with the painting *Coroação de D. Inês de Castro*. In a letter to Marechal Duque de Saldanha, dated 1863, Marciano describes his work in progress,

> "The canvas had already twenty-three figures drawn from nude models, in real size, with only two missing for the work to be completed. This process is difficult and very costly; however, nowadays, artists follow [other] method, because of the desire to work fast; when haste should be the last element for the artist. However I follow the system that was followed by the old masters of the great schools, who recommended it as the expression of truth and sincerity of Art; and furthermore I follow it because, in spite of the greater work and greater expenses for me, the artistic results are more advantageous for the paintings and for the study and improvement of the artist.[80] (as cited in D. de Macedo 1951, 15-16).

In the same year, in a letter to Visconde de Meneses, Marciano reinforces the importance of the drawing stating "…at present I listen to no one and keep following my artistic path under your scientific advice: I apply myself to drawing in preference to the rest, as Your Excellency very rightly says, without drawing, which is the basis, nothing can be done with merit"[81] (as cited in 'Artistas Plásticos Em Portugal' 1945, 183).

These quotes seem to imply that Marciano saw himself as someone committed to a more laborious traditional method of working, who trived to produce. This accounts for his perception on the importance of the drawing and the composition of the image, not necessarily the materials and paint application which could relate to the film forming defects in his paintings.

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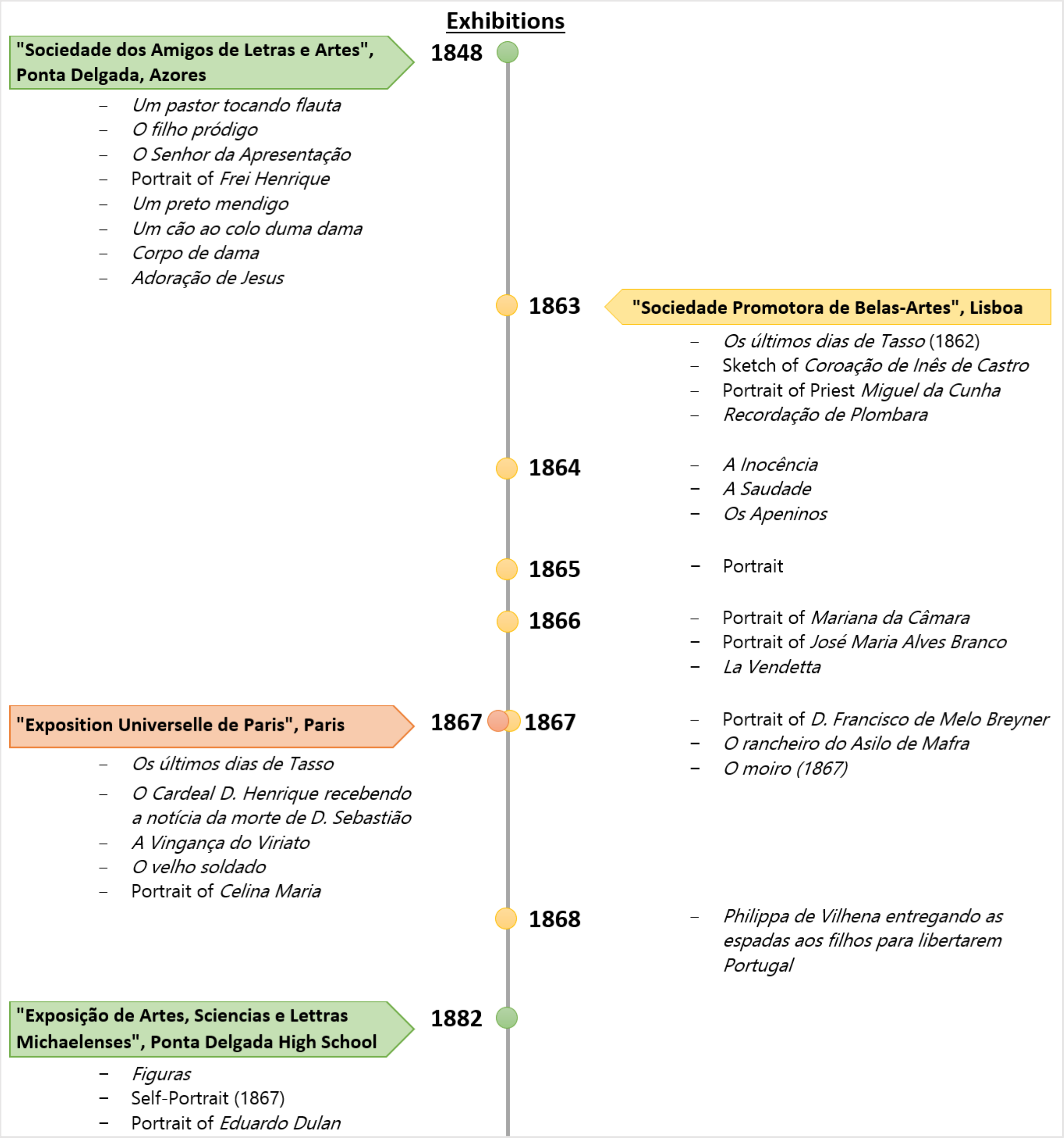
[80] "O cartão tem já vinte e trez figuras desenhadas dos modelos nús, da altura natural, e só faltam duas para o trabalho do nú se achar completo. / Esse processo é difícil e de muito custo; porem artistas seguem hoje este methodo, pelo desejo de trabalharem depressa; quando aliaz a pressa deve ser o ultimo dos elementos para o artista. Porem eu sigo aquele sistema por o que realizavam em geral os mestres antigos das grandes escolas que o recomendavão como a expressão da verdade e da sinceridade da Arte; e alem disso, sigo-o porque, apezar do maior trabalho e de mais fortes despezas para mim, os resultados artisticos são mais vantajosos para os quadros e para o estudo e aperfeiçoamento do artista."

[81] "…presentemente não dou ouvidos a ninguem e vou seguindo a minha estrada artística debaixo dos seus scientificos comchelhos (sic) : appelico-me ao desenho presentemente com preferencia ao resto, como diz V. E. e com muita razão, sem desenho que é a base nada se pode fazer com merecimento".

Exhibitions

Figure 2.3 details which paintings featured in the exhibitions divided by year.


Exhibitions

1848

"Sociedade dos Amigos de Letras e Artes", Ponta Delgada, Azores

- *Um pastor tocando flauta*
- *O filho pródigo*
- *O Senhor da Apresentação*
- Portrait of *Frei Henrique*
- *Um preto mendigo*
- *Um cão ao colo duma dama*
- *Corpo de dama*
- *Adoração de Jesus*

1863

"Sociedade Promotora de Belas-Artes", Lisboa

- *Os últimos dias de Tasso* (1862)
- Sketch of *Coroação de Inês de Castro*
- Portrait of Priest *Miguel da Cunha*
- *Recordação de Plombara*

1864

- *A Inocência*
- *A Saudade*
- *Os Apeninos*

1865

- Portrait

1866

- Portrait of *Mariana da Câmara*
- Portrait of *José Maria Alves Branco*
- *La Vendetta*

1867

"Exposition Universelle de Paris", Paris

- *Os últimos dias de Tasso*
- *O Cardeal D. Henrique recebendo a notícia da morte de D. Sebastião*
- *A Vingança do Viriato*
- *O velho soldado*
- Portrait of *Celina Maria*

1867

- Portrait of *D. Francisco de Melo Breyner*
- *O rancheiro do Asilo de Mafra*
- *O moiro (1867)*

1868

- *Philippa de Vilhena entregando as espadas aos filhos para libertarem Portugal*

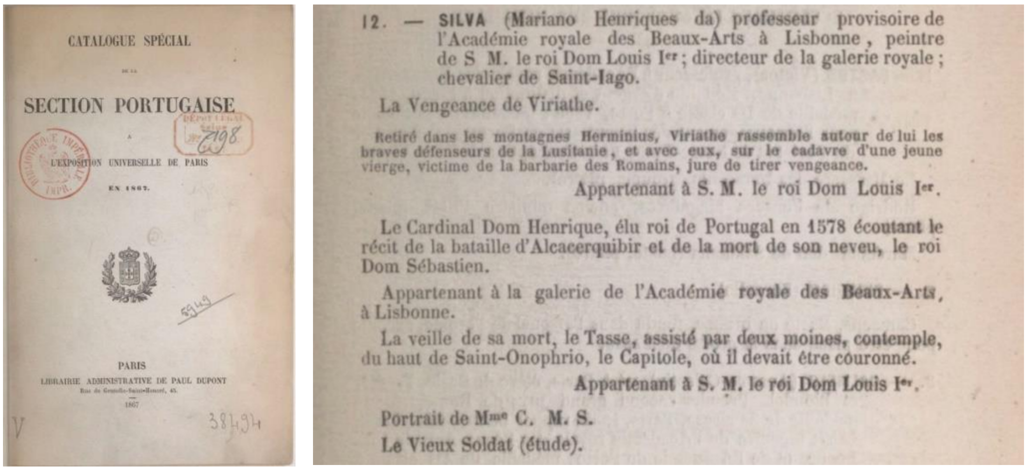
1882

"Exposição de Artes, Sciencias e Lettras Michaelenses", Ponta Delgada High School

- *Figuras*
- Self-Portrait (1867)
- Portrait of *Eduardo Dulan*

Figure 2.3: Exhibitions divided by year, with the list of paintings by Marciano.

Marciano's stature as an artist is evident by his presence in the *Exposition Universelle de Paris* in 1867. In the catalogue Marciano is described as *Provisional Professor of the Academy, Painter for His Majesty King Luís, Director of the Ajuda Gallery and Knight of Saint James.* In the Portuguese section of the Catalogue five paintings are identified, the first three are historical paintings, the fourth is a portrait and the last is a study (Figure 2.4).



CATALOGUE SPÉCIAL

SECTION PORTUGAISE

A

L'EXPOSITION UNIVERSELLE DE PARIS

EN 1867.

PARIS

LIBRAIRIE ADMINISTRATIVE DE PAUL DUPONT

1867

12. — **SILVA** (Mariano Henriques da) professeur provisoire de l'Académie royale des Beaux-Arts à Lisbonne, peintre de S M. le roi Dom Louis I^{er}; directeur de la galerie royale; chevalier de Saint-Iago.

La Vengeance de Viriathe.

Retiré dans les montagnes Herminius, Viriathe rassemble autour de lui les braves défenseurs de la Lusitanie, et avec eux, sur le cadavre d'une jeune vierge, victime de la barbarie des Romains, jure de tirer vengeance.

Appartenant à S. M. le roi Dom Louis I^{er}.

Le Cardinal Dom Henrique, élu roi de Portugal en 1578 écoutant le récit de la bataille d'Alcacerquibir et de la mort de son neveu, le roi Dom Sébastien.

Appartenant à la galerie de l'Académie royale des Beaux-Arts, à Lisbonne.

La veille de sa mort, le Tasse, assisté par deux moines, contemple, du haut de Saint-Onophrio, le Capitole, où il devait être couronné.

Appartenant à S. M. le roi Dom Louis I^{er}.

Portrait de M^{me} C. M. S.

Le Vieux Soldat (étude).

Figure 2.4: Left image: Cover of the Portuguese Section of the Special Catalogue of the Universal exhibition of Paris in 1867; Right image: List of paintings exhibited from Marciano Henriques da Silva. ©gallica.bnf.fr

Paintings by Marciano which have been located

The fourteenth paintings which can be located belong to three collections:

- National Museum of Contemporary Art (MNAC), Lisbon - 1 painting
- National Palace of *Ajuda* (PNA), Lisbon - 3 paintings
- Museu Carlos Machado (MCM), Azores - 10 paintings

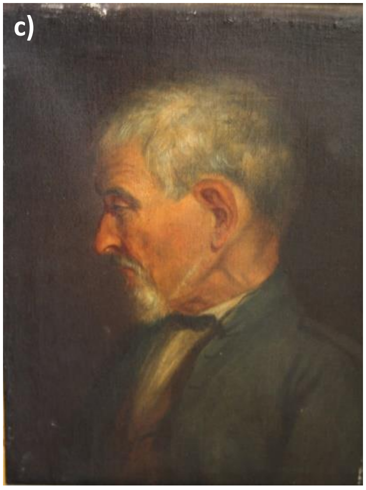
The work at the MNAC is the case study painting *O Cardeal D. Henrique recebendo a notícia da morte de D. Sebastião* which is presented in detail below (see section 2.2, page 91).

From the PNA collection (Table 2.1), in addition to the two paintings which were later transferred to MCM, *Tasso na véspera de morrer* and Portrait of *Bulhão Pato*, there were four more paintings listed in the PNA collection. One of these, the painting *Um filósofo* mentioned in the sources (D'Athaide 1915, 150; D. de Macedo 1951, 23; Pamplona 1988, 60) could not be found.

Two of the paintings currently in the collection, *Mulher de perfil* and *Um mouro*, are signed and dated, while *Busto de velho* is attributed to Marciano Henriques da Silva, with no signature or date visible. Access to the collection was obtained to observe these three paintings in person.

Table 2.1: Information and photographs of the paintings currently in PNA, Lisbon.

Title	Date	Dimensions	Inv. number	Photograph
a) *Mulher de perfil*	1864	55.6 x 46.2 cm	PNA 2814	©MatrizNet[82]
b) *Um mouro*	1867	90 x 72 cm	PNA 4117	©MatrizNet[83]
c) *Busto de velho*	n.d.	27 x 19 cm	PNA 2887	©MatrizNet[84]



Finally, MCM has the larger collection of paintings by Marciano Henriques da Silva with 10 paintings (see Table 2.2), much due to an effort of presenting and preserving the works of art of the *first micaelense*[85] *artist of the 19th century* (D'Athaide 1915, 152).

Table 2.2: Information and photographs of the paintings currently in MCM, Azores.

Title	Date	Dimensions	Inv. number	Photograph
a) *Cabeça de Turco - estudo*	ca. 1847	55 x 41 cm	MCM5346	© (Estrutura para a Casa da Autonomia n.d.)
b) Self-portrait	1849	49.5 x 39 cm	MCM5347	
c) Portrait of *Celina*	ca. 1867	59.5 x 49 cm	MCM05203	
d) Portrait of *Senhora*	n.d.	61.5 x 49 cm	MCM5204	
e) Portrait of *Celina Maria*	ca. 1860-62	36 x 30 cm	MCM5011	
f) Portrait of *Inês Dulan*	1871	75 x 63 cm	MCM5012	
g) Portrait of *Senhor Scholdtz*	n.d.	76 x 64 cm	MCM5010	
h) *Um negro/* Portrait of a slave – *Tio Paulo*	n.d.	43.5 x 36 cm	MCM5188	© Carlyle 2019

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[82] http://www.matriznet.dgpc.pt/MatrizNet/Objectos/ObjectosConsultar.aspx?IdReg=1043426

[83] http://www.matriznet.dgpc.pt/MatrizNet/Objectos/ObjectosConsultar.aspx?IdReg=991220

[84] http://www.matriznet.dgpc.pt/MatrizNet/Objectos/ObjectosConsultar.aspx?IdReg=1046177

[85] Person from the Island of *São Miguel*, Azores.

i) *Os últimos dias de Tasso*	1862	156 x 225 cm	MCM5202
j) Portrait of *Bulhão Pato*	1871	65 x 54 cm	MCM5201

Paintings Condition

From Marciano's paintings which could be located, only *O Cardeal D. Henrique recebendo a notícia da morte de D. Sebastião* (1861) (see section 2.2, page 91) and the portrait of *Bulhão Pato* (1871) had severe paint defects in the form of alligatoring and drying cracks.[86]

Regarding the portrait of *Bulhão Pato,* the photograph printed in Macedo's book (1951), shows clear paint defects in dark areas, mainly hair and clothes (Figure 2.5), with a contrasting white ground layer showing through the cracks. The author, blaming the poor quality of the materials used by Marciano such as asphalt and pitch, writes that the portrait of *Bulhão Pato* began to suffer from the same evil as *O Cardeal…*, but was rescued in time (unlike *O Cardeal…*) (D. de Macedo 1951, 21). A current photograph of the painting (Figure 2.5) shows the inpainting of the cracks, which has improved the reading of the image and likely led to Macedo's assumption that the problem had been solved. However this inpainting is an aesthetic restoration and merely covers up the paint defects which are still clearly visible as a disturbed paint surface when the painting is observed.

Figure 2.5: Portrait of *Bulhão Pato*, dated 1871, 65 x 54 cm, Inv.: MCM5201, Museu Carlos Machado (Azores). Photographs from D. de Macedo 1951 (left) and ©Carlyle 2019 (right).

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[86] A surface examination of the painting Mulher de perfil (PNA 2814) showed micro-cissing in the brown hair. Micro-cissing is a term coined by Rica Jones to describe a form of "microscopic drying crackle" (Jones 1990; Jones et al. 2013).

It may be that the lack of information on the location of the much larger body of work by Marciano could have been because many more of his works suffered from severe paint defects and have not been kept. To date this hypothesis cannot be confirmed.

2.1.2 Artist Supplies

In addition to the information from Portuguese archival sources on Marciano's life and career, there is an entry in a customer account book from the British colourman, Roberson[87] dated Friday 27th of October, 1865 showing that Marciano, by now the painting's professor of King D. Luis I, had purchased painting supplies from this company in England and had them shipped to Lisbon.

Figure B.4 in Appendix B (page 253) shows the original page image and transcription listing the materials purchased. Although there are no details about the 76 tubes of oil colours which were listed, there is information on additional tubes, these are described as " P. Flake White"[88], "Cobalt"[89], "Ex[tract of] Ver[milion]"[90] and "Carmim". Additionally, there were powdered pigments sold in bottles: "Scarlet Vermilion", and three lake pigments "finest Crimson", "Pink Madder" and "Rose Madder". These have the added note of being "sp gr^{d}" [specially ground].

Interestingly, no artist's Medium or varnish were listed, only Pale and Dark Drying Oil. Marciano also purchased "Hog hair Varnish Brushes" in addition to paint brushes described as "flat" and "Ex[tra] fine R^{d}[round] Hog Tools" with different sizes/numbers.

The fact that Marciano purchased commercial artist's materials from an English supplier emphasises the work developed in Part II with the reconstruction of a production record for Bitumen brown paint from the English colourman Winsor & Newton.

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[87] Charles Roberson & Co. 27 Oct. 1865 (HKI.MS. 106-1993, p. 194a). The Roberson Archive is part of the Hamilton Kerr Institute, University of Cambridge. (Ferraz 2017b, 285; Woodcock and Churchman 1997).

[88] Likely Permanent Flake white (also known as Freeman's White), which is a mixture of lead sulphate and zinc white (Carlyle 2001, 515; Eastaugh et al. 2008, 166). It should not be confused with the pigment "Flake white" which is a lead carbonate, "finely crystalline lead white" (Eastaugh et al. 2008, 163). This is an excelent example of why it is crucial to understand materials and their names in the 19th century and earlier.

[89] No indication for which colour, could be Cobalt blue, Cobalt green, Cobalt yellow, etc… Carlyle believes this reference to cobalt most likely refers to cobalt blue, not to the variations of cobalt green or yellow which would likely have been specified in the account book (personal communication, November 2022).

[90] Based on the colours listed in the sales catalogues for Winsor & Newton and Reeves (Carlyle 2001, 535, 539). According to Carlyle, Roberson purchased it directly from Field in the period of 1843-1854 (Carlyle 2001, 512). Salter (as cited in Carlyle 2001, 511) stated that it was a particularly vivid form of vermilion introduced by Field. Although Salter states that by 1869 the name was synonymous with scarlet vermilion (Carlyle 2001, 511), since both colours are listed in Marciano's purchase in 1865, at that time it can be assumed that these colours were still variants of Vermilion. This is further confirmed in W&N c.1896 catalogue where Extract of Vermilion appears as "now synonymous with Scarlet Vermilion", with Scarlet Vermilion being "described, like Vermilion, as sulphide of mercury" (Carlyle 2001, 512).

In Portugal, Dr. Hugo Xavier located invoices[91] in the National Archive of *Torre do Tombo* showing that Caetano José Gomes[92], bought materials for the Royal Gallery in National Palace of *Ajuda*.

The invoices from 1870 and 1871 show purchases for canvas, brushes, tubes of oil paint, "verde imperial"[93], varnish and glue, from two Portuguese artist's supply stores: the "Armazém de Música e Instrumentos" and the "Drogaria de Productos Chimicos – Raposo e Sobrinho". Ferraz's described both stores in her survey of painting material suppliers stating that the former was owned by J. Figueiredo[94] and was located in *Rua Nova do Carmo*, 45 and 47, Lisbon, and it was open from 1825 to at least 1885 (Ferraz 2017b, 337). The second store, later known as "Raposo Sobrinho & C.ª" was also located in Lisbon and was open from 1840 to at least 1908. This latter store was known for selling English paints, varnishes from Roussel-Van Geel in Brussels and was the supplier for the Fine Arts Academy of Lisbon (Ferraz 2017b, 376).

Currently the National Palace of *Ajuda* collection comprises materials for watercolour, pastel and oil painting that belonged to the King D. Luís I and the Queen D. Maria Pia (1847-1911) with supplies from English companies such as Roberson and Rowney, as well as the French suppliers Mulard and Lefranc (Ferraz 2016; 2017a, 228).

This shows how materials were also in circulation. Artist's could purchased them not only from what was available in Portugal at the time but also order from suppliers/manufacturers in different countries. This adds another level of mobility, it is not only the mobility of artists at the time (see section 2.1.1.2), where they encounter each other and share techniques, but also from the materials.

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[91] Personal Communication, email 30th of October of 2017. Xavier notes from the IAN/TT pertaining to the Archive of the Royal House, boxes 4928, 4954, 4957, 4958 and 4959.

[92] Conservator of the Royal Gallery in Palace of *Ajuda* (Xavier 2019).

[93] Designation given to all green paints obtained from copper arsenate (Ferraz 2017b, 176).

[94] Personal communication, February 2018.

2.2 The Painting, *O Cardeal D. Henrique recebendo a notícia da morte de D. Sebastião*

The painting *O Cardeal D. Henrique recebendo a notícia da morte de D. Sebastião*[95] (Figure 2.6), was selected as the case study for this thesis since it suffers from a severe case of alligatoring (which has so compromised the image that the painting has not been exhibited for over 100 years). The owner, The National Museum of Contemporary Art - Museum of Chiado (MNAC) kindly made this painting available for research.

Figure 2.6: *O Cardeal D. Henrique recebendo a notícia da morte de D. Sebastião* (137.5 x 99.6 cm) by Marciano Henriques da Silva painted in 1861, MNAC, Lisbon (Inventory no. 337). ©Marques 2017.

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[95] For detailed information on the painting's title see Appendix B.2.1, page 256.

2.2.1 Description of the image

A brief description is available in the painting's inventory file on MatrizNet[96], stating that it is a History Painting, with Cardinal D. Henrique seated in the foreground, turned to present the sitter's right profile, with his head bowed, and wearing a cardinal's robe. Standing behind him and to the right of the overall image is the bearded high court dignitary, Jorge Serrão, reporting the death of King Dom Sebastião. It is also noted that, historically, the Cardinal-King received the news of D. Sebastião death in the Portuguese city of Alcobaça (MatrizNet n.d.).

This description omits aspects of the figure's surroundings which points up the problem with the legibility of the scene caused by the extremely deteriorated paint. Despite the highly compromised state of the paint it is possible to discern what is likely the red coloured chair-back behind the Cardinal and a table where the sitter rests his left arm. Jorge Serrão stands behind this table with his hands crossed. In his right hand he is holding what appears to be the hilt of a sword (Figure 2.13), it is now indistinguishable whether or not he is holding something on the left hand. Serrão is wearing a jacket with a ruffled collar and on his chest is a red ribbon with a medal bearing a red cross. The cross appears similar to the Portuguese Cross of the Military Order of Christ (Figure 2.7 a)[97]. On the table, sits a jewelled crown (the jewels are indistinct) (Figure 2.7 c), and a gilded frame surrounds a painting. The subject is possibly a portrait of a man wearing a crown, presumably the King D. Sebastião (Figure 2.7 e). Also a rolled parchment with a red ribbon which sits beyond the cardinal's left hand (Figure 2.7 d), and in the Cardinal's right hand, a white feather (presumably from a quill pen) is visible (Figure 2.7 b)[97]. The Cardinal's wrists rest on the arms of his chair, with his hands hanging down (Figure 2.13).

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[96] MatrizNet is the collective on-line catalogue of Portuguese Museums, DGPC. Link for the painting: http://www.matriznet.dgpc.pt/MatrizNet/Objectos/ObjectosConsutar.aspx?IdReg=201524&EntSep=3#gotoPosition

[97] This assumption is corroborated by Diogo de Macedo description of the painting stating that "in the background is a knight of Christ (Jorge Serrão)", the author also mentions the quill pen, the table with a portrait of D. Sebastião, a crown and a parchment with a seal (D. de Macedo 1950a, 18).

Figure 2.7: Details of the painting, a) Red cross on Jorge Serrão necklace; b) quill pen on the Cardinal's right hand; c) Crown; d) Rolled document with a red ribbon; e) golden frame with a portrait of a man wearing a crown.

2.2.2 The painting's history

As noted above (section 2.1.1), the painting was executed in Rome in 1861 and then sent to Lisbon. The exact date and conditions of transport are unknown but the painting did successfully arrive at the Fine Arts Academy of Lisbon, and remained part of the institution's collection until 1884[98].

In 1867 the painting travelled to Paris to be shown in the *Exposition Universelle de Paris*. Given the importance of the exhibition and the artist in that period, and knowing that Marciano selected his own paintings for the exhibition, it should be safe to assume that the painting would still be in good condition. However, F. J. Rezende[99] after visiting the exhibition states in a letter to Conde de Samodães that "The Cardinal D. Henrique seems to be in the dark; either the paints have changed or the location

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[98] This date is based on the inauguration of "Museu Nacional de Belas-Artes e Arqueologia" (currently MNAA).

[99] Francisco José Resende (1825-1893) was a Portuguese painter and Professor of Historical Paintings at the Fine Arts Academy of Porto, Portugal, in 1851 and between 1856-1885 (Ferraz 2017a, 102).

is bad."[100,101] This observation points to a possible alteration of the surface or an overall darkening, but leaves room for ambiguity by also referring to its hanging place.

The fact that this painting could be exhibited in 1867, suggests that for at least six years prior to completion the painting had not undergone the level of drastic change in appearance that is currently seen, this information fits well with the time frame discussed in Chapter 1 (see 1.2.2, page 20). If the records are accurate and the painting had remained at the Fine Arts Academy in Lisbon until being sent to Paris, then this exhibition also marks a change in terms of the painting's environment which was also a variable mentioned by the Redgrave brothers when describing bituminous paintings: "under favourable circumstances, they will remain many years without disruption; but a change in hanging, or in the temperature of the room or gallery, an exposure to the sun's rays, and above all varnishing, will, though heretofore free from harm, crack them in a few weeks." (Redgrave and Redgrave 1866, 593).

The Redgrave brothers also made an observation worth close attention regarding the exposition of paintings at the International Exhibitions in Paris (1855) and London (1862) and their role in drawing attention to the state of preservation of those paintings on loan, stating that:

> "In many respects the loan of works formed a fortunate epoch in their condition; as while deposited in these exhibitions they were most carefully looked after and attended to, and the dust of years removed. Moreover, as to some, the possessors on their return - for once while in their possession - minutely looked them over; and if they laid the evils that had been progressing for so many years to those who had had them temporarily in charge, they were at least awakened to the sense of their decay, and likely to take better measures to preserve them in future." (Redgrave and Redgrave 1866, 599).

In 1884 the "Museu Nacional de Belas-Artes e Arqueologia" (currently MNAA) was inaugurated and was closely associated with the Academy of Fine Arts of Lisbon, sharing the same director (Rodrigues 1999, 7). In 1911, the collection was divided having the works produced prior to 1850 remaining in MNAA and the works produced after 1850 becoming part of the newly founded MNAC (Rodrigues 1999, 18).

This information is relevant to the painting's history since a letter of 1912 from Manuel de Macedo, at MNAA to the director of MNAC, indicating that *O Cardeal D. Henrique…* had remained in the MNAA collection when it should have been transferred to the MNAC however it had been forgotten due to its degraded condition. Furthermore the letter states that the painting had been "removed

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[100] "O cardeal D. Henrique parece estar ás escuras; ou as tintas alteraram ou o local é mau."

[101] Letter by F. J, Rezende. Pariz 18 de Setembro de 1867 from "O Commercio do Porto" - Porto/28.9.1867 - B.P.M.P.", "Documento n.º 162" as reproduced in Cor e melancolia, vol. III (Mourato 2000, 249).

from the gallery some fifteen years ago, because it was in an advanced state of ruin"[102]. This establishes that the painting had undergone significant deterioration in its appearance by 1897.The only past image of *O Cardeal D. Henrique* … found thus far was published in Macedo's book in 1950 and shows the painting in black and white (Figure 2.8). Although a direct comparison is difficult, primarily because of the quality and resolution of the black and white image, there does not appear to have been significant changes in the state of the paint between then and now. There is a clear correlation between the areas affected and the size of the paint islands (for example larger paint islands in the background, and smaller paint islands in the Cardinal's face) between the 1950 photograph and the painting's current condition (Figure 2.8).

Figure 2.8: On the left is a photograph published in Macedo (1950a), the photographer and date of the photograph are unknown. On the right is a photograph of the painting taken in 2017.

The painting was given in a long term loan to the Department of Conservation and Restoration of the NOVA School of Science and Technology for research purposes in April 2014 (inventory number FCT-PNT.128).

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[102] "Concorreu para semelhante omissão, aliás, o facto de o referido quadro estar retirado da galeria, haverá uns quinze anos, por se achar em adiantadissimo estado de ruina" (Manuel de Macedo, letter from 18th of October of 1912).

2.2.2.1 Historical descriptions of the Painting's condition

Apart from that early mention by Rezende, in 1867, that the paints could have altered because the painting appeared dark, the only other reference to it’s appearance is the letter from Manuel de Macedo, in 1912, cited above. It is worth considering this letter in more detail, as it presents information about the degraded condition and probable causes for the problem:

- "not only by having been painted with a certain haste, but also by the artist's abuse of the use of bitumen or asphalt of Judea on layers of paint that were not completely dried"[103]
- "visibly caused by the abuse of bitumen or asphalt, or Jew's pitch by the artist, and perhaps because it was painted with excessive haste, on a bad ground, and without giving time to the various layers of paint for their indispensable drying"[104]

Similar information is reproduced by Diogo de Macedo in three published sources where he mentions the painting's appearance, pointing to the use of asphalt/bitumen as the main reason and emphasising that the sole purpose of the painting is as a study piece for scientific research:

- "(…) it is lost altogether, like a black, indecipherable blur. The same disaster may have happened to others, since the quality of the paints used by the painter was treacherous, and he certainly applied them to many of his [paintings]. This would be [nice] to know, but it is knowledge that can only be given by those who own these paintings that were subjected to the blackness of the bitumen he used."[105] (D. de Macedo 1950b, 144)
- "This painting has become a black, bituminous, almost indecipherable blur, conserved in the Museum as a useful document for students and scientific investigations, as to the quality of the paints and the ways they were used."[106] (D. de Macedo 1950a, 17–18)
- "(…) [it has] never been shown to anyone but [scholars] in the problems of the speciality, given its particular state of deterioration, whose beginning of ruin dates back to at least 1900. Due to the use of asphalt from Judea, Jew's pitch, ivory black or simply black

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[103] "(…) não só por háver sido pintado com certa precipitação, senão que ainda pelo abuso por parte do artista, do emprego do betume ou do asfalto de Judêa sobre camadas de tinta ainda não absolutamente enxutas."

[104] "(…) motivado, visivelmente, pelo abuso do betume ou do asfalto, ou pêz judaico por parte do seu autor, e talvez, pelo facto de haver sido pintado com excessiva precipitação, sobre um mau aparelho, e sem dar tempo ás diversas camadas de tinta para o indispensavel enxugo."

[105] "(…) está perdido de todo, como um borrão negro, indecifrável. A outros poderá ter acontecido o mêsmo desastre, visto a qualidade das tintas empregadas pelo Pintor ser traiçoeira e, por certo, ter aplicado essas em muitas das suas telas de que há notícias. Ora também disto comvinha ter-se comhecimento, que só pode ser dado por quem possua esses quadros sujeiros ao negrume dos betumes que ele adoptava."

[106] "Este quadro tornou-se um borrão negro, betuminoso, quase indecifrável, comservado no Museu como documento útil a estudantes e investigações científicas, quanto à qualidade das tintas e modos de serem utilizadas."

> bitumen, which the artist used and abused, it contaminated the neighbouring paints and crumbled into clusters of coarse stains, like a worn-out and illegible carpet"[107] (D. de Macedo 1951, 21)

Despite not specifying the painting's condition in terms of its stability, and providing a more detailed description of the alligatoring phenomenon present, Macedo's words offer precious evidence of the deterioration evident by the early 1950s.

No records were found of conservation and restoration treatments ever having been performed on the painting, nor, as will be seen in section 2.2.3 below, is there evidence of this on the painting itself.

2.2.3 Examination and Condition Report for *O Cardeal D. Henrique…*

This section focuses on the examination of the painting using photographic documentation, X-radiography, stereomicroscopy, and a close visual observation. The full description of the painting's condition is available in Appendix B.3, page 266. The characterization of the materials and paint stratigraphy will be discussed next in Chapter 3.

As noted above, overall the painting appears to be stable, with no visible alteration in terms of the alligatoring since the publication of the black and white photograph in 1950 (Figure 2.8). Since it was placed on long term loan to the DCR at FCT/NOVA in 2014, no changes have been observed on the paint surface using photographs taken in those early years and visual comparison with its current condition.

As will be seen, the investigation of the painting in terms of its condition and structure revealed an important finding: the current image is painted on a ground which was applied on top of a previous painting.

2.2.3.1 Support and Ground Layers

Auxiliary support

The painting is stretched onto a wooden stretcher that appears to be a hard wood, possibly oak (Figure B.6, Appendix B, page 258). The corner construction of the stretcher is a "Double Fork Mortise

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[107] "(…) onde nunca foi mostrado senão a examinadores estudiosos nos problemas da especialidade, atendendo ao seu estado de deterioração muito particular, cujo começo de ruina data, pelo menos, de 1900. Devido ao emprego do asfalto da Judeia, pez judaico, preto de marfim ou simplesmente betume negro, que o Artista adoptava e do qual abusava, este comtaminou as tintas vizinhas e desagregou-se em aglomerados de empastamentos grosseiros, como de tapete gasto e ilegível"

with one key"[108], the member bars are beveled and the corners are keyed. The stretcher appears to be original, since there is no indication on the top tacking margin of different holes from previous fixtures (the top tacking margin is the only one visible, the others are covered by a wood strips (possibly applied to protect the otherwise exposed tacking margin, or representing an adjustment to the size of the painting to fit a previous frame).

There is one deteriorated paper label (approx. 10 x 4 cm) glued to the horizontal cross bar (Figure 2.9) which reads "[R]eme[tt]ido pela commissão local de [Be]llas-artes de Lisboa"[109] in a printed writing which is followed by a hand-written number "[Nº] 32".

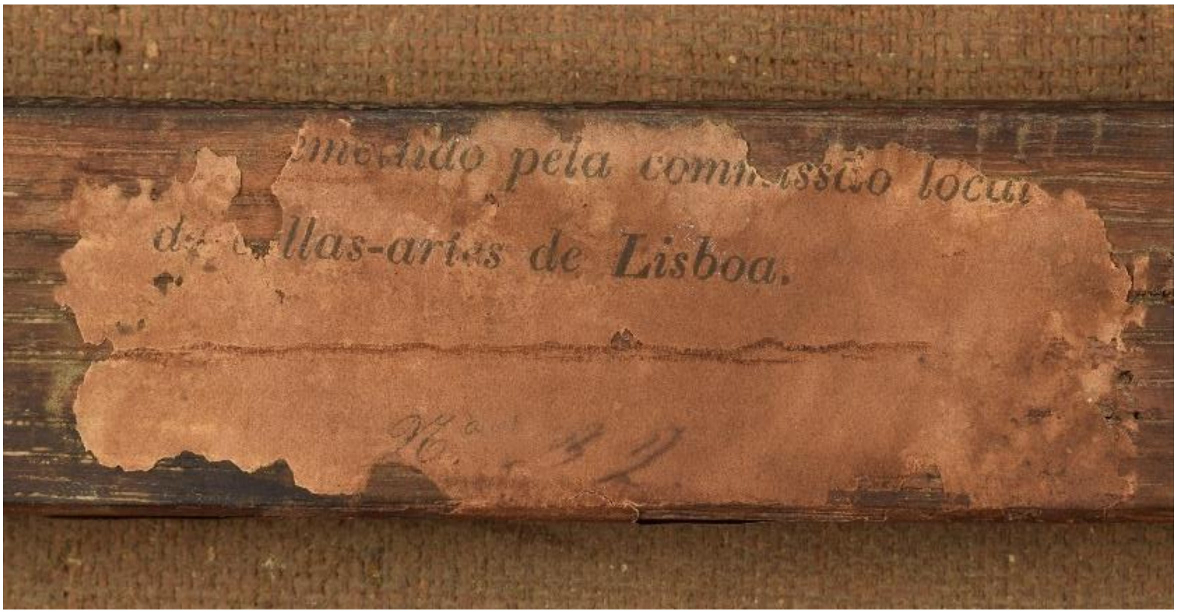

Figure 2.9: Paper label glued to the horizontal cross bar of the stretcher.

Canvas

The canvas is plain, open weaved, with an average of 8 by 8 theads/cm. The threads have an irregular thickness, slugs and imperfections which could point to a hand-woven canvas. The tacking margins are present but only easily visible on the top, since on the other three sides they are covered by the strips

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[108] Based on the reference "Stretcher/Strainer Corner Illustrations, Powerpoint: Edited by L. Carlyle, NOVA, June 2011, based on the course hand-outs 1983/84, Queen's University, Masters of Art Conservation Programme. The Queen's handout was likely prepared by Richard Buck, Intermuseum Laboratory, Oberlin, Ohio around 1970. A later version with fewer images, appears in Kaplan, A., *American Artist's Materials*, Vol. II, (Sound View Press, Winsconsin, 1992) pp. 46-62."

[109] "Remettido" is an old Portuguese spelling that means "delivered by" and relates to the participation of the painting either in a contest or an exhibition (information provided by Dr. Ângela Ferraz, personal communication December 2022).

of wood. Since the selvedge edge is present on the left side, it is possible to establish that the warp direction is vertical and the weft horizontal.

The back of the canvas is heavily stained (Figure B.6, Appendix B, page 258), but there is no visible correlation to the composition or paint islands present on the front of the painting. It is however possible that these stains are related to the application of the previous painting or even the upper ground layer. Aside from more general diffused stains, there are also darker stains that seem to follow crack lines, accretions and what appears to be paint splash or drips in the lower right corned.

In terms of fabric condition the fibres are brittle and the tension is somewhat slack with significant movement of the canvas. The tears and damages are mapped in Figure B.13, page 265.

With the X-radiograph (Figure B.11, Appendix B, page 263) and by visual observation of the back of the canvas it is possible to see distortions in the fabric weave, especially in the left and right margin, due to being held under tension at some points (the fabric appears aligned with the existing nails visible in the x-radiograph). This might be an indication that the painting has never been off the stretcher, since this regular distortion is known as cusping and is often "fixed" into the fabric by the ground/paint layers.

The canvas is attached to the stretcher with 62 bent metal pieces (headless "twisting" nails, with only the nail shaft present), which were bent after being hammered into the stretcher, these fixtures have corroded and the canvas has oxidized and there are losses/tears in the canvas fabric (Figure 2.10) surrounding 3 out of the 14 nails visible on the top margin. With the X-radiograph it is possible to see that both the top and bottom margin have 14 nails each, while the left and right side have 17 nails each (Figure B.11, Appendix B, page 263).

Figure 2.10: Corroded bent nail shaft causing oxidation and loss in the canvas.

There are two stencilled inscriptions on the back of the canvas, one in the central upper part (approximately 21 x 15 cm) with the number "609." topped by a crown (Figure 2.11 a). The second is in the left lower part (17 x 6 cm) with the inscription "MUSEU N.A.C." and "337" (Figure 2.11 b). The first inscription (Figure 2.11 a) is an inventory number, which appears associated to the painting in the

1912 letter from the MNAA director, the second (Figure 2.11 b) clearly belongs to the current owner of the painting - MNAC - and its respective inventory number 337.

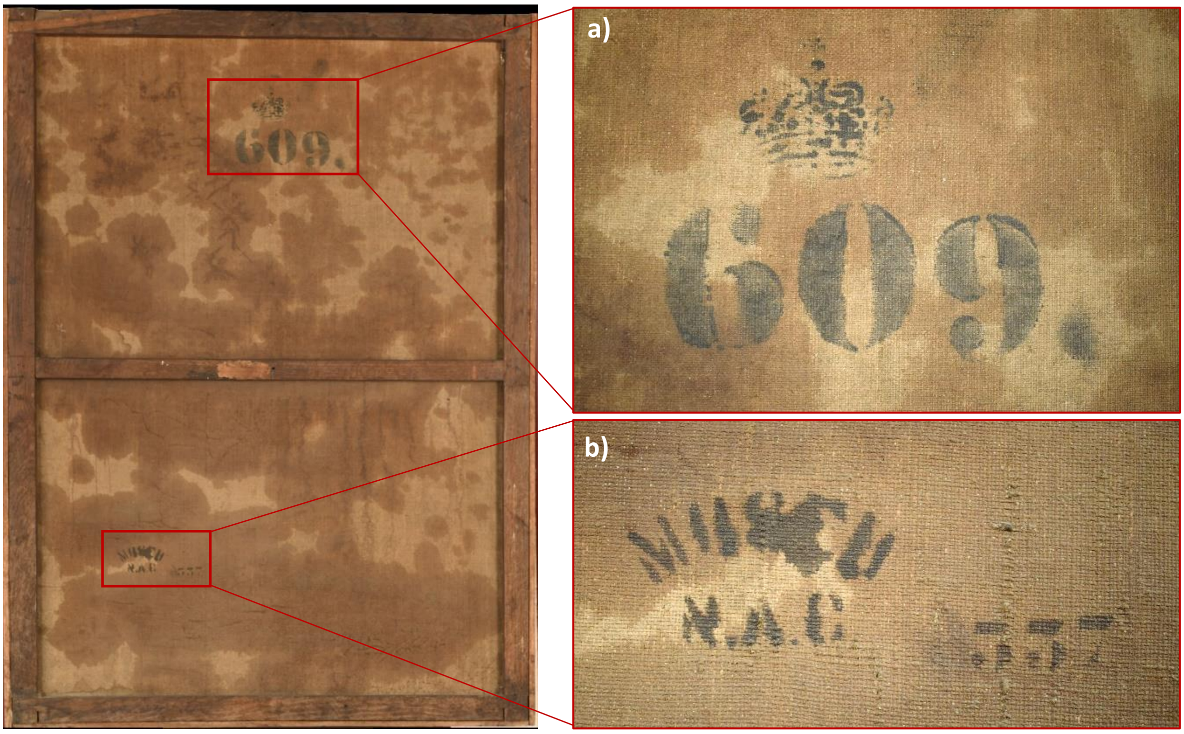

Figure 2.11: Stencils on the back of the canvas. Zoomed areas identified in the painting (in red) for both stencils.

Ground Layers

The presence of a size layer was not visible during the visual examination and will be discussed in Chapter 3. The observation of the ground layers was possible on areas of tears and paint losses due to impact (see Damage Mapping, Figure B.13). Overall the ground and paint layers are cohesive and stable with good adherence to the canvas.

There are two distinct ground layers (see numbers 1 and 2 in Figure 2.12), the first (1 - Lower ground layer) is a grey beige layer with a chalky appearance and sits directly on top of the canvas, the second (2 - Upper ground layer) is a opaque white layer (possibly representing several applications). In some areas these layers appear to be separated by paint layer(s) which vary in colour depending on the damage location (for example in Figure 2.12 this intermediate layer is blue). The presence of these layers is evidence of a previous painting and that the Upper ground layer was applied on top of this painting (further illustrated in cross-sections, see Appendix C.6, pages 286-289).

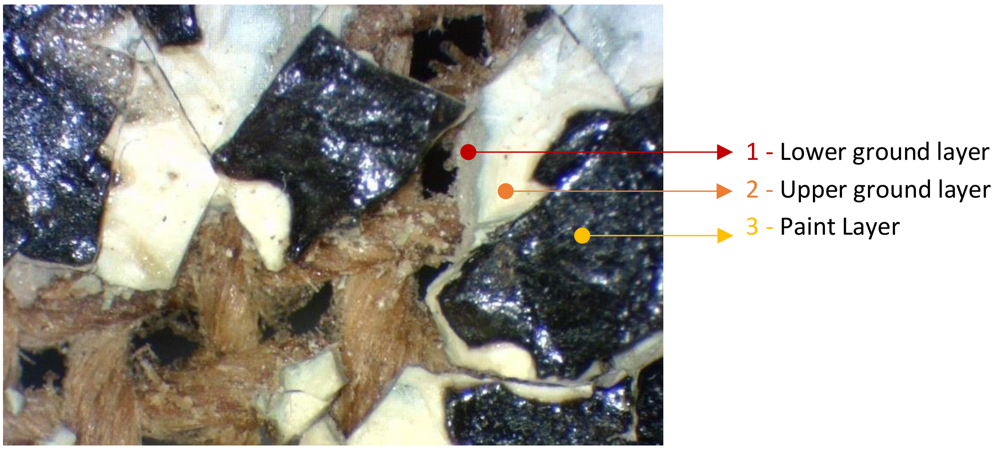

Figure 2.12: Stratigraphy of the ground layers, visible in an area of paint/ground losses. Layers identified with coloured dots and numbers: 1 (red), 2 (orange) and 3 (yellow).

The ground layers cover only the image area (see Figure 2.10), not the tacking margins, which indicates that the first ground was not pre-applied to the canvas on a large bolt of fabric then cut down to size as was common for commercially prepared artist's canvases in the 19th century. The lack of ground on the tacking margins indicates that the ground was applied after the canvas had been stretched onto the stretcher. This does not rule out it having been prepared commercially by a worker/professional for an artist's use, but neither does it rule out the possibility of the ground being prepared by the artist himself.

Underdrawing / Underpainting

No underdrawing or underpainting could be identified with Infra-red (IR) photography or X-radiography, respectively (see appendix B.4 for instrumentation and conditions details, page 267). However with IR photography some compositional elements became clearer such as the arms of the Cardinal's chair (Figure 2.13, left) and the sword that Jorge Serrão holds in his right hand (Figure 2.13, right).

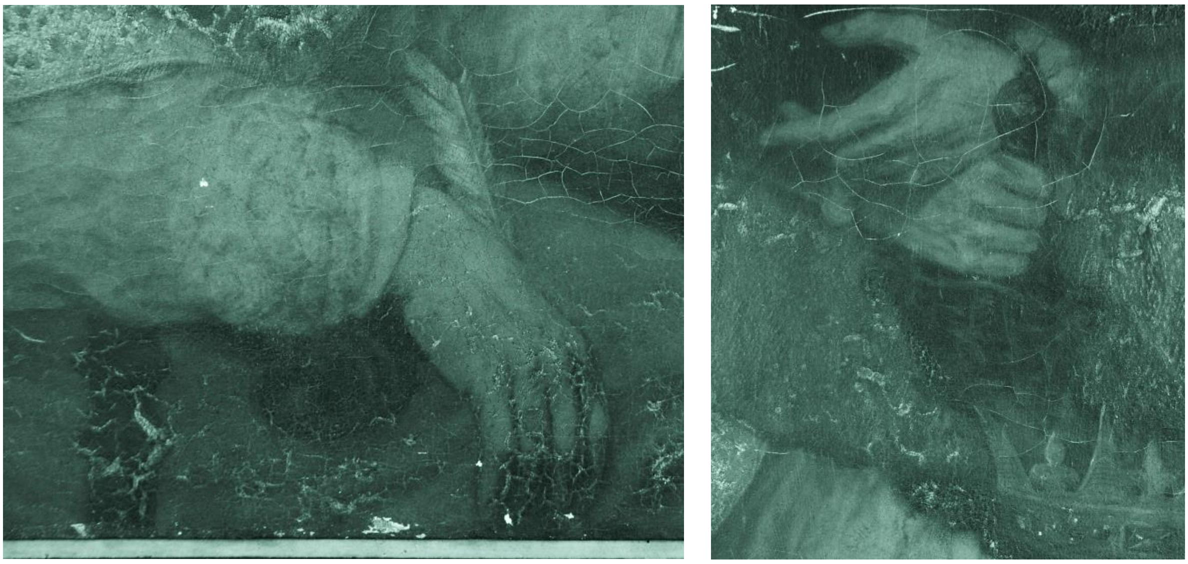

Figure 2.13: IR detail photographs showing the Cardinal's arm chair (left) and the possible sword that Jorge Serrão holds (right).

The X-radiography clearly illustrates the film-forming defects on the painting's surface (Figure B.11, Appendix B, page 263). The lighter areas that look like islands do correlate to the paint islands, which makes sense given that those are denser regions. There are however some lighter areas on the middle upper part of the painting that do not seem to correspond to painted elements in the composition and could be related to the previous painting.

Figure 2.14: *O Cardeal D. Henrique recebendo a notícia da morte de D. Sebastião,* normal light photography (left side image) and X-radiograph (right side image) ©Marques 2017.

2.2.3.2 Paint Layers

Due to the paint film defects it is extremely difficult to describe the painting technique and stratigraphy simply by surface observation. The impact of the severe paint defects on the reading of the painting is especially clear when focussing on details, such as the faces of the figures (Figure 2.15). The faces allow for a good comparison with the other paintings by Marciano (see images in Tables Table 2.1 and Table 2.2) that show how capable the artist was and how dramatic the alligatoring in this painting is.

With raking light (Figure B.7 and B.8, Appendix B, pages 259-260) it is possible to see the topography of the paint with the paint islands being significantly higher than the flat areas. There are bulges and depressions caused by areas where the painted contracted and mechanical cracks appear in areas without alligatoring. Crows foot cracking[110] is visible in the painting, as well as a *pentimenti* (alteration of the composition) in the profile of the Cardinal's face (Figure 2.15).

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[110] For a description of the term see section 1.1.3, page 18.

Figure 2.15: Paint defects in the face of the Cardinal (left) and Jorge Serrão (right).

The painting presents both drying and mechanical cracks (Figure 2.16). The alligatoring is more extreme on brown and red paint areas (Figure B.12, Appendix B, page 264), with larger paint islands that have contracted and left a "trail" of paint striations behind (Figure 2.16). In the background in particular it is possible to see a light brown (translucent layer) which remains below the trail left behind the contracted paint that has formed into islands (Figure 2.16). It appears that this translucent layer remained in place while the brown paint layer contracted and pulled itself apart (Figure 2.18, e). There are also straight marks that resemble brushstrokes (Figure 2.16) and seem to be unrelated to the trails of contracted paint (whose direction is towards the paint islands), these "brushstrokes" could also be related to the ground layer.

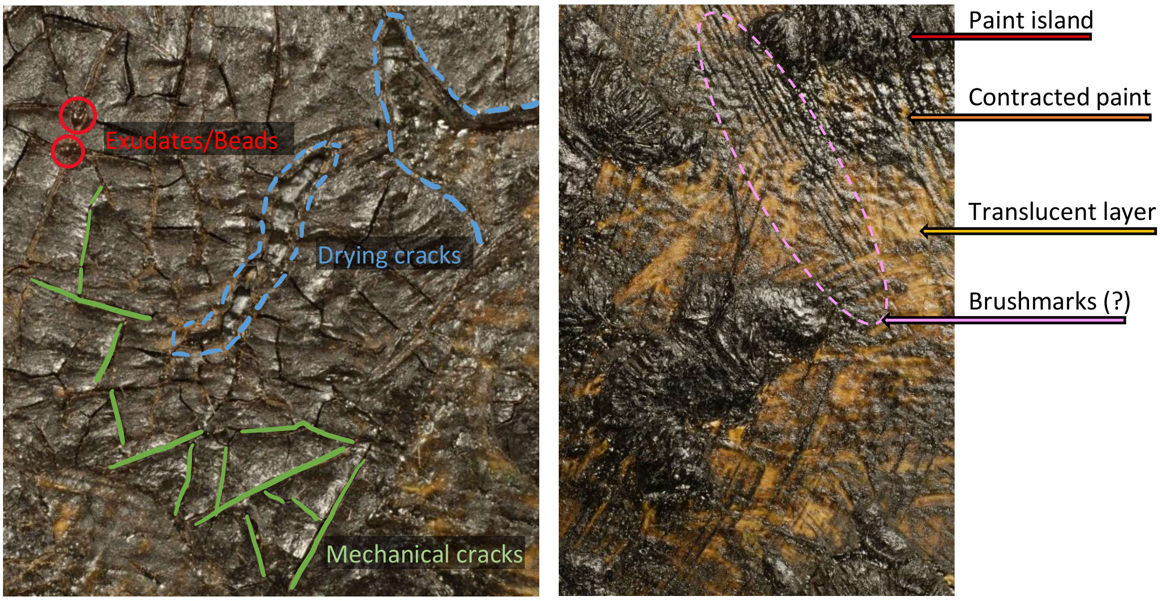

Figure 2.16: Identification of the different surface alterations visible in the painting.

Flesh tones range from areas that are largely unaffected (hands of Jorge Serrão) to extremely distorted paint (such as the Cardinal's face). Areas with white paint are the least affected by paint defects, such as the Cardinal's collar and sleeves, but some passages do exhibit drying cracks in lighter areas with darker shadows such as the Cardinal's hair (Figure 2.15).

Macro-photography demonstrates how highly varied the surface is with paint islands, wrinkled paint, and matt and glossy paint areas. Where the paint is very glossy and surrounds paint islands it is somewhat soft to the touch (exudates[111]) (Figure 2.17 and Figure 2.18). Interestingly there are small beads of material protruding mainly from the red and brown islands but also from cracks (Figure 2.19). Close observation with the stereomicroscope shows that these beads have a similar appearance to the exudates although they are brittle and not soft to the touch.

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[111] See "exudate" definition and discussion below.

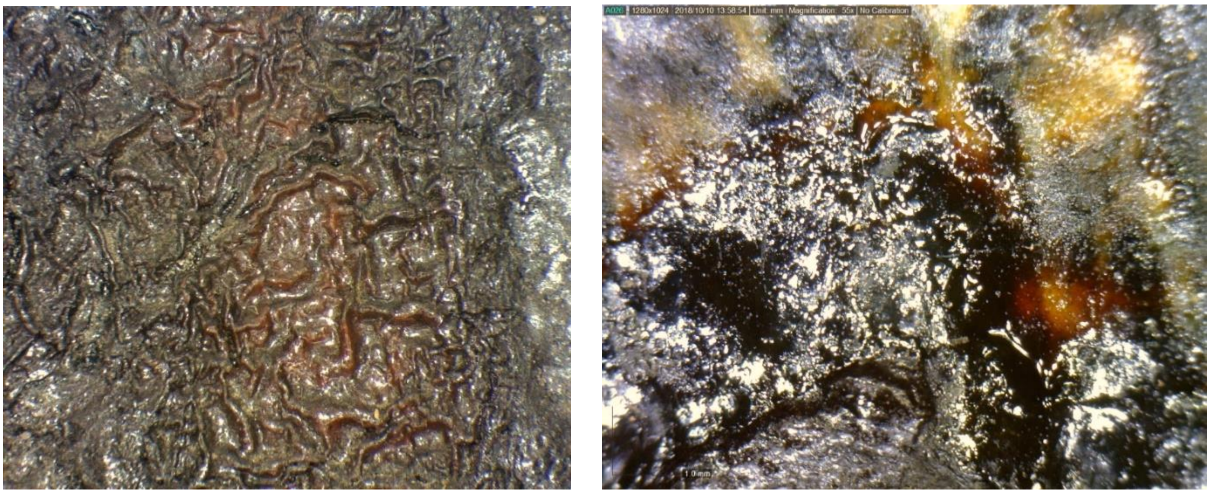

Figure 2.17: Dino-lite images (magnification of 50x) from wrinkled paint, and a yellowish glossy, soft exudate surrounding a paint island.

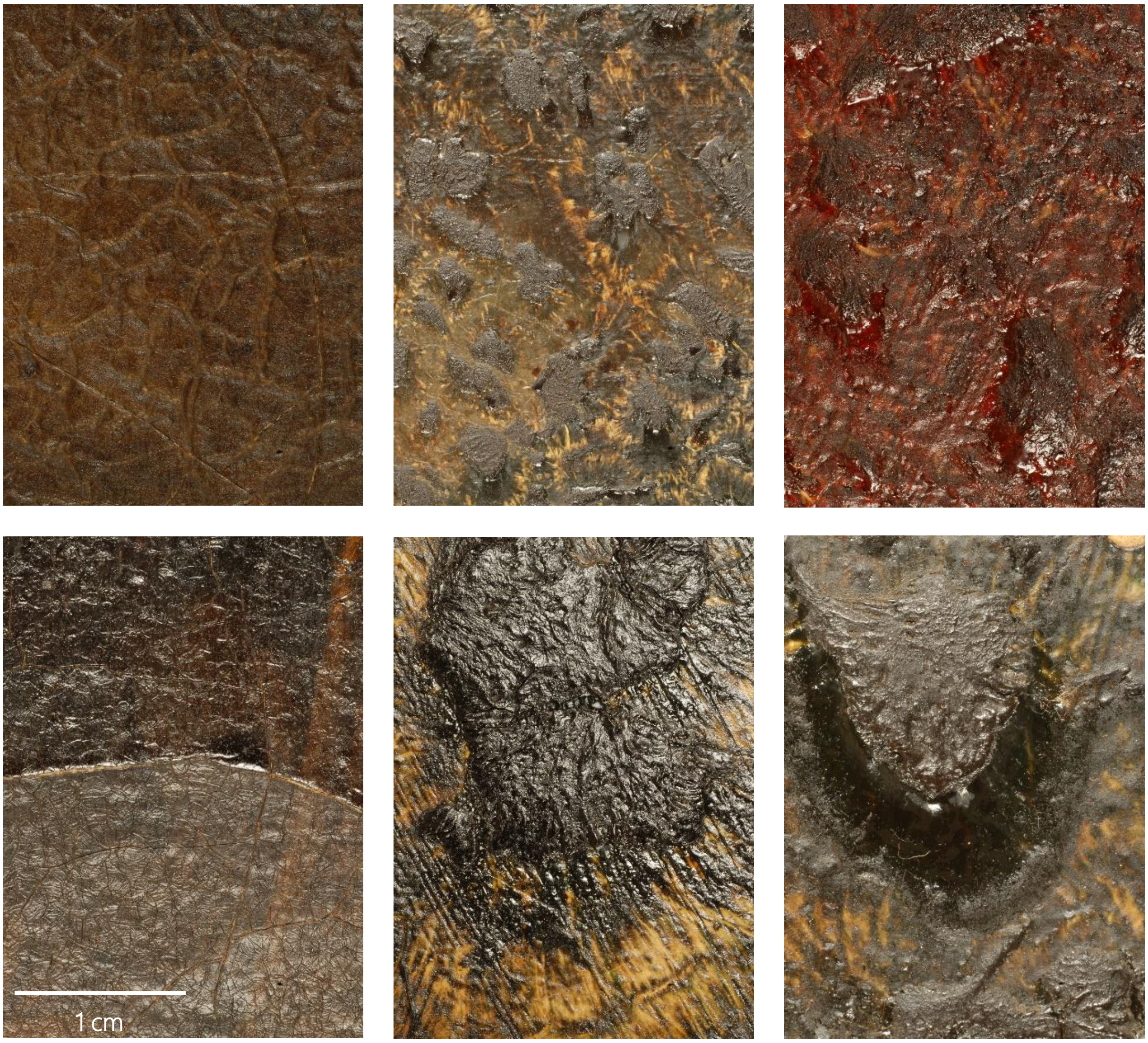

Figure 2.18: Macro-photography of paint defects observed in the painting: islands, exudates and uneven glossy/matt paint.

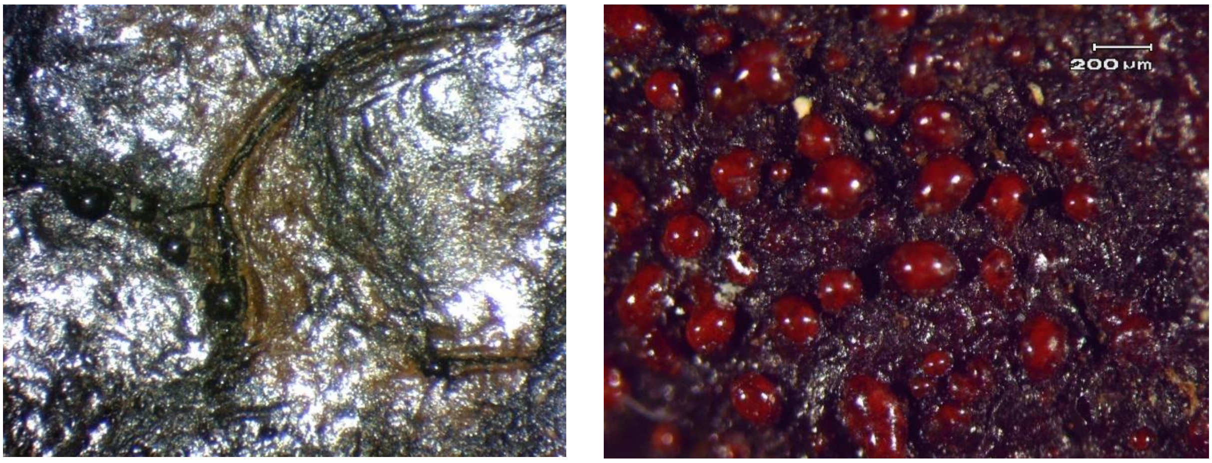

Figure 2.19: Stereomicroscope images of the small beads protruding from brown (left) and red paint (right).

The term exudate has been widely used in the paintings conservation literature, to describe material that oozes out of the paint to arrive at the paint surface (e.g. Carlyle 2017). Exudates can have different properties in terms of fluidity and fluorescence (Bronken and Boon 2014b; Boon and Hoogland 2014; Bronken and Boon 2014a; Bronken et al. 2016; Boon and Lister 2014). These have been shown to have a relatively higher amount of polar compounds and in the case of paints from Schmincke the appearance of the exudates took about 6-7 years to occur (Boon and Hoogland 2014). This time frame is particularly interesting when considering the discussion in Chapter 1 (see 1.2.2, page 20) and the history of the painting (section 2.2.2, page 93).

Boon and Hoogland suggest that "the increase in polarity in relation to failure to anchor these polar fractions inside the paint is the main physical cause of the formation of exudates that create sticky films or even drips depending on the size of the polar fluid-producing reservoir" (Boon and Hoogland 2014). Further comparison between the painting's exudates and the analytical results from the literature features in the next Chapter (page 150).

If a classification system such as the one used to categorise the colours in a dripping painting by Jean-Paul Riopelle by Bronken and Boon (2014b), were to be used for this painting the two groups identified would be Category B "paints have signs of softness or condition problems connected to the softness of the medium" for the exudates and Category C "solid to brittle condition" to the beads and rest of the paint (Bronken and Boon 2014b).

Figure 2.20: Possible bristles from the paint brush that seem to "repel" the paint.

Another interesting observation was the response of the paint to what appear to be hairs from the artist's brush (Figure 2.20). An explanation is that the brush-hair was originally embedded in (adhered to) the translucent layer below the brown paint. When the paint began to separate into islands, the hair remained in place, and was left partially covered by the underlayer of brown paint (which is also visible eIsewhere in the striations around the Islands). Other hypothesis is that the bristles were left in the brown paint layer and "repelled" it once the paint started pulling away to form the paint islands, leaving them surrounded by the translucent layer.

Varnish and Surface Condition

The presence of a varnish layer is not evident with normal light. Overall the painting has a matt, mostly unsaturated appearance with some exceptions such as the areas with exudates. Observation of the painting under UV light reveals a possible varnish layer, with an uneven distribution (Figure B.9, Appendix B, page 261). Areas where the paint surface is less disturbed have a more uniform fluorescence such as the figure of Jorge Serrão. There are other alligatoring areas where the fluorescence is uneven and can be seen only on the top of the islands, only on the flat areas or on both. During examination in ultra violet light it was not possible to distinguish whether fluorescence was associated with a resin varnish remaining on the surface or the presence of oil based binder at the surface which may have originated from the paint film itself.

An orange fluorescence was observed on the Cardinal's red cape which has been associated with the presence of madder lake (Kirby, Spring, and Higgitt 2005; Kirby, Spring, and Higgitt 2007). This will be further discussed in Chapter 3, section 3.2.4.

Overall the extreme behaviour of the paint, particularly the alligatoring with paint islands, cracks and wrinkles that affect the topography of the painting, has profoundly obscured the original image, leaving the painting essentially unexhibitable.

3

CHARACTERIZATION OF MATERIALS AND TECHNIQUES OF *O CARDEAL D. HENRIQUE…*

This chapter presents the chemical and physical characterization of the painting *O Cardeal D. Henrique recebendo a notícia da morte de D. Sebastião* through a multi-analytical approach. The discussion of the analytical results will follow the painting's stratigraphy: canvas, grounds, translucent layer and underdrawing, paint application and pigments used. Key findings are highlighted for each layer supported by data obtained from the most relevant techniques.

By focusing in-depth on *O Cardeal D. Henrique*, this research aims to investigate how Marciano's choice of materials and his painting technique may have influenced the development of the extreme paint defects found in this painting

3.1 Methodology

The use of a multi-analytical approach allowed for the characterisation of the paint/ground samples and reference materials and to gain insight regarding the detection limits for the techniques employed. In the latter case, this led to the exploration of detection limitations through the use of reconstructions (see Chapter 6). The data and results obtained were compared with findings from the same analytical techniques present in the literature for paintings suffering from film-forming defects.

Given the complexity of the paint stratigraphy in *O Cardeal D. Henrique…* the use of a multi-analytical approach with complementary analytical techniques was crucial to obtain important information on both inorganic and organic fractions.

Sampling and Sample Preparation

As has been shown in Chapter 2, page 106, macro-photography illustrated a paint surface which was highly variable, with some areas wrinkled and matt, others where the paint appears to have pulled itself into islands, and still others which are highly glossy and in fact are soft to the touch (exudates). These variations complicated the sampling strategy, as the goal was to have representative samples, therefore multiple areas had to be considered. For example, in order to identify the displaced layer in areas with paint islands, both profiles of the paint (the flat parts and the islands) had to be sampled.

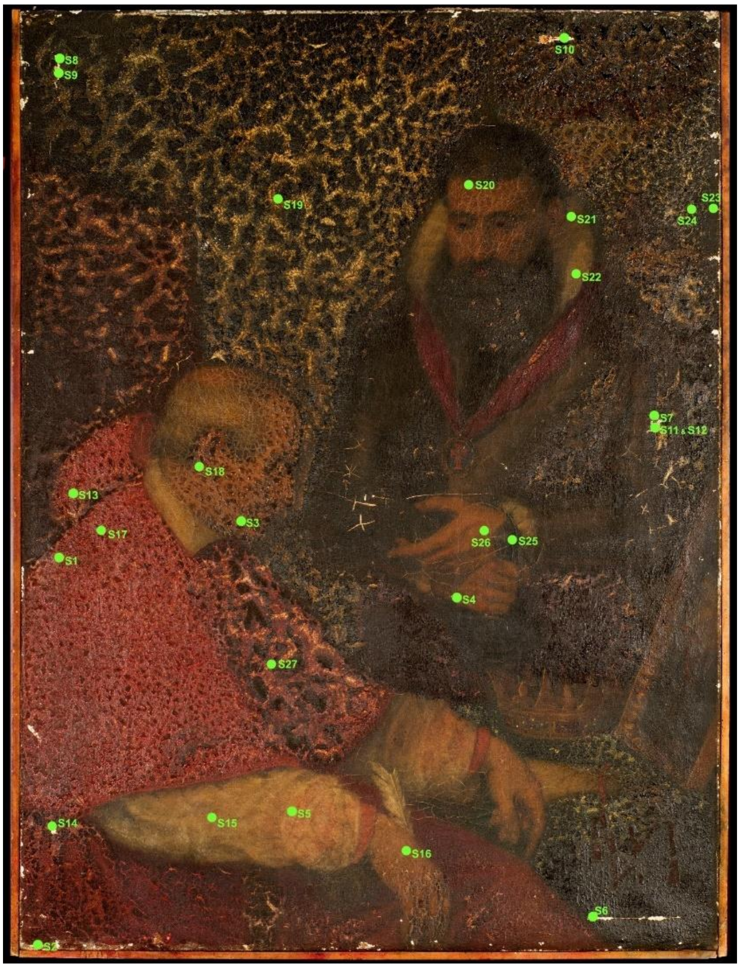

Figure 3.1: Mapping of cross-sections S1 to S27, marked in green.

A total of 27 cross-sections were prepared from paint and ground samples in two sampling campaigns (Figure 3.1, and Appendix C: Figure C.1 and Table C.1 in pages 276-277). The second campaign (samples S14 to S27) only took place after the analysis of the first set and to answer specific questions. Interestingly, the latter set revealed much more complex paint stratigraphies (e.g. Figure 3.2 and Figure 3.3), which emphasises the heterogeneity of the paint composite and interpretation of the data obtained.

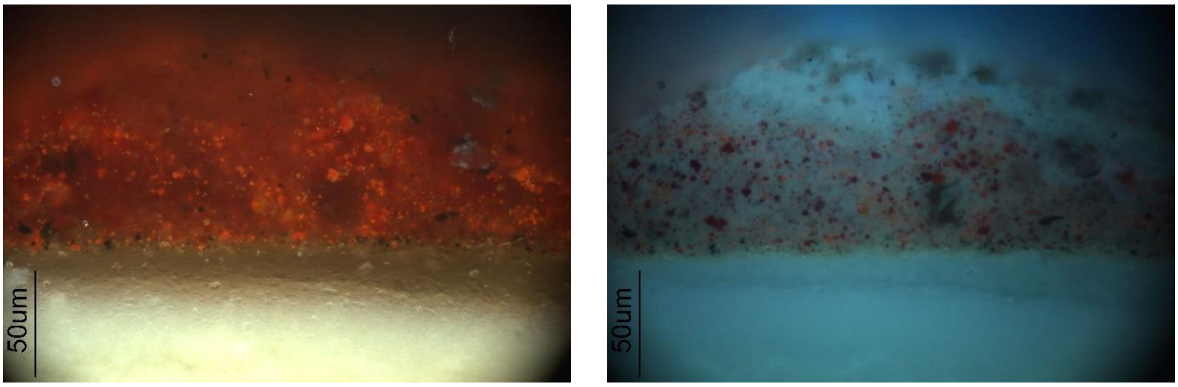

Figure 3.2: Detail of S1, in reflected light microscopy under cross-polarised light (left) and UV radiation (right). Red paint cross-section, from the first sampling campaing.

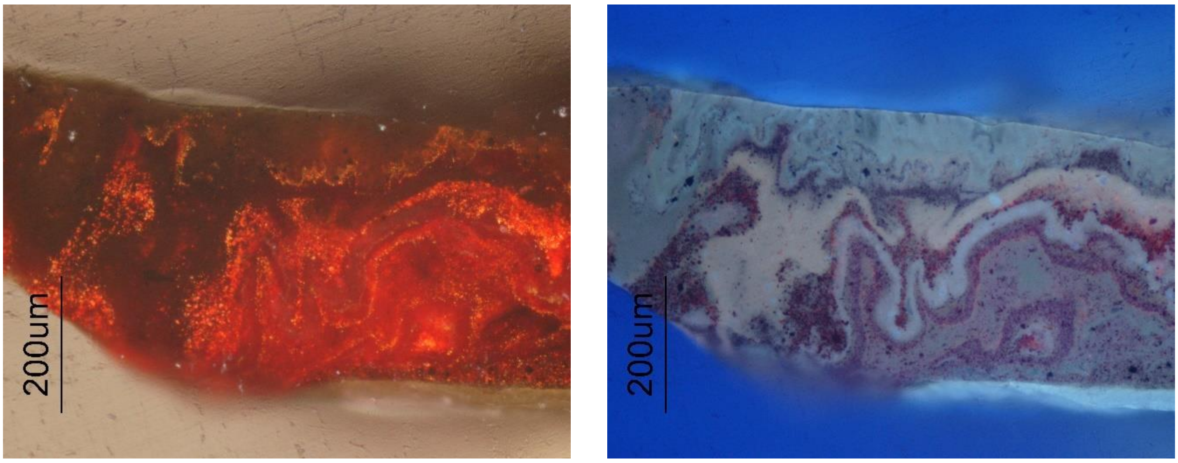

Figure 3.3: Detail of S27, red paint cross-section, in reflected light microscopy under cross-polarised light (left) and UV radi-ati-on (right). Red paint cross-section, from the second sampling campaing.

The number and size of samples were only possible because the painting had been designated by the owners as a study piece.

More samples were removed from brown and red paint layers because they were affected the most by alligatoring, followed by the flesh tones which are partially affected. A limited number of samples were also taken from colours which were less affected for comparison, these are categorised as "other" (Table 3.1).

Table 3.1: Identification of samples by colour area

Colour area	Sample
Brown/Black	S6, S7, S8, S9, S10, S11, S12, S19, S23, S24
Red	S1, S2, S13, S14, S17, S27
Flesh	S3, S4, S16, S18, S20, S26
Whitish	S5, S15, S22
Other	S21, S25

Paint samples were removed from the painting with a surgical scalpel under the stereomicroscope, their positions were recorded. Most samples were embedded in casting resin and then polished to create cross-sections of the layer structure, while others were kept as loose micro-samples for specific analytical techniques. The full description of the sample preparation and the staining protocol is in Appendix C.2, pages 273-275.

Analytical Strategy

The analytical instrumentation and experimental conditions are fully described in C - Appendix to Chapter 3, section C.1, pages 269-273.

Optical Microscopy, µ-EDXRF, µ-Raman and SEM-EDX provided information on the painting's stratigraphy and the composition of inorganic compounds. Pigments in the paint layers were mainly characterised by µ-Raman and SEM-EDX, but as will be described in section 3.2.3.1, the paint layers are complex and predominantly glaze-like, with a low concentration of distinctive pigment particles in the upper layers. This made the identification of pigments through µ-Raman difficult due to fluorescence from the organic materials. SEM-EDX provided clues for the pigments present and their distribution, particularly in terms of lake pigments.

Because the detection of the organic components and possible identification of specific materials held to be responsible for the drying problems was challenging, micro paint samples were analysed with µ-FTIR, FT-Raman and Py-TMAH-GC/MS. Additionally, imaging techniques, such as ATR-FTIR microscopy and TOF-SIMS, performed on cross-sections, were crucial for the identification of organic materials and their distribution on the paint stratigraphy.

Table 3.2: Analytical techniques used (•) in each sample. a acquisition and data interpretation done autonomously, b acquisition done by an expert and c acquisition and interpretation done in collaboration with an expert.

	Samples																											
Instrumentation	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15	S16	S17	S18	S19	S20	S21	S22	S23	S24	S25	S26	S27	Micro-samples
OM^a	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	
µ-Raman^a	•		•	•	•		•	•	•	•	•		•															
SEM-EDX^b	•	•		•	•	•	•			•	•		•		•				•		•		•	•	•	•	•	
µ-EDXRF^a			•												•			•		•	•							
FTIR Microscopy^b	•						•			•									•									
TOF-SIMS^c							•												•								•	
µ-FTIR^b																												•
FT-Raman^b																												•
Py-TMAH-GC/MS^b																												•

As shown in Table 3.2, all cross-sections were investigated with OM, 17 were analysed with SEM-EDX and 10 from the first sampling campaign were analysed by µ-Raman to identify the pigments present in the paint layers. A selection of cross-sections was then analysed with µ-EDXRF, FTIR Microscopy and TOF-SIMS for specific research questions which will be discussed below.

In the following section, the main results obtained with these techniques for each layer, of the painting's stratigraphy, will be detailed and discussed. Further Information about the analyses, experimental conditions and results can be found in Appendix C (e.g. the complete results obtained with ATR-FTIR Microscopy of sample S7, which include the upper ground layer (ground layer 2), translucent layer and brown paint layers, can be found in section C.6, pages 286-289).

3.2 Painting Stratigraphy - Materials and Techniques

3.2.1 Support and Ground Layers

3.2.1.1 Canvas

The canvas is made out of a bast fibre (likely linen), identified due to the transverse cross marks and nodes seen in cross-polarized light, where they also display rainbow interference colours (Figure 3.4), and by observation of the thick cell wall and the narrow lumen in cross-section (D. Mayer 2021, 338–41).

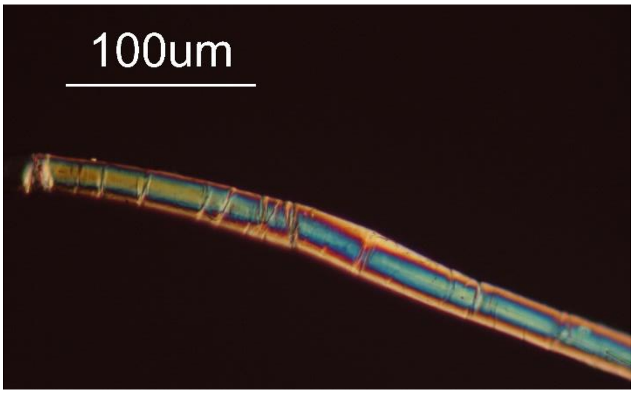

Figure 3.4: Longitudinal view of a fibre from the canvas under cross polarised light, total magnification 200x.

3.2.1.2 Preparation layers

The preparation layers described below, were consistent throughout the paint samples.

Size layer

Under OM, a possible size layer is visible. Staining with SYPRO™ Ruby in five samples (S11, S14, S20, S21 and S24) confirmed that there is a proteinaceous layer below the lower ground layer (Figure 3.5). The protocol used for the staining technique (Schäfer 2013) is detailed in C.2, Appendix C, page 275.

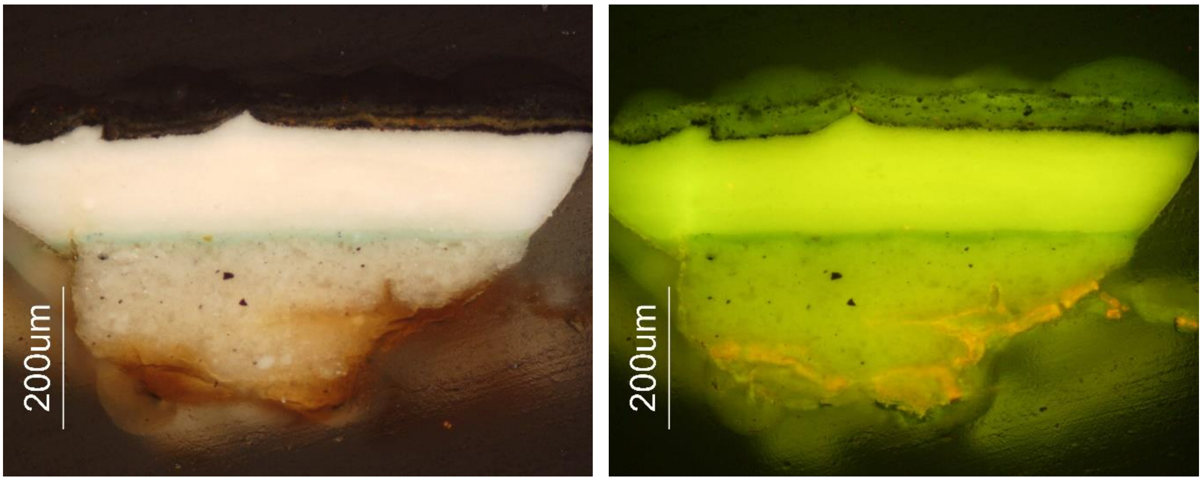

Figure 3.5: Cross-section S21 in reflected light microscopy under cross-polarised light (left) and UV radiation filter set 9 (BP 450-490, FT510, LP515) (right) confirming the presence of protein (orange fluorescence) in the suspected size layer using SYPRO™ ruby staining.

Ground layers

The size layer is followed by a lower ground layer (designated ground layer 1). Above this is a series of paint layers (likely from a previous composition/painting). On top of this is an upper ground layer (ground layer 2) (Figure 3.6).

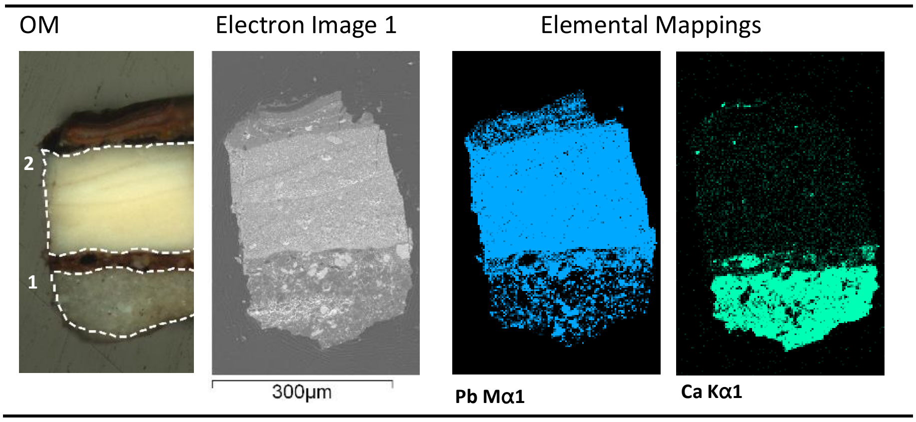

Figure 3.6: Cross-section S5 in normal light (OM) and SEM-BSE image. Lower ground layer (1) and Upper ground layer (2) outlined in white. EDX elemental mapping of lead (Pb) and calcium (Ca) respectively.

Lower ground layer (ground layer 1)

The lower ground layer has a greyish appearance and is composed of a mixture of calcium carbonate ($CaCO_3$) and lead white, where the $CaCO_3$ is present in higher quantity.
SEM-EDX analysis showed that this layer consisted of calcium with some lead containing particles (see elemental mappings in Figure 3.6), while μ-Raman and μ-FTIR indicated calcite and lead white characteristic bands (see Table 3.3).

Table 3.3: Characteristic Raman and Infrared bands identified in the ground layers of the paint samples.

μ-Raman		**μ-FTIR**		**Pigment Identified**
Wavenumber (cm^{-1})*	Assignment**	Wavenumber (cm^{-1})*	Assignment**	
157 (w), 282 (s) 1086 (vs)	lattice mode $\nu_s(CO_3^{2-})$	712 (m), 872 (s) 1397 (vs) 2512 (w)	$\delta_{as}(CO_3^{2-})$ $\nu_{as}(CO_3^{2-})$	Calcium Carbonate $CaCO_3$
1049 (vs)	$\nu_s(CO_3^{2-})$	1048 (m) 1396 (vs) 3536 (w)	$\nu_s(CO_3^{2-})$ $\nu_{as}(CO_3^{2-})$ $\nu(OH)$	Lead White $2PbCO_3.Pb(OH)_2$

* w = weak, m = medium, s = strong, vs = very strong
** (Otero 2018, 254, 265; Correia 2010, 102–4, 136–38; Burgio and Clark 2001)

Paint layer (between the ground layers)

Paint layers were identified in between the lower (ground layer 1) and the upper ground layer (ground layer 2). This points to the presence of a previous painting since the pigmented layers vary in colour and number of layers depending on the sampling area (see Figure 3.7). No discernible image was observed in the X-radiograph (see Figure B.11, Appendix B, page 263).

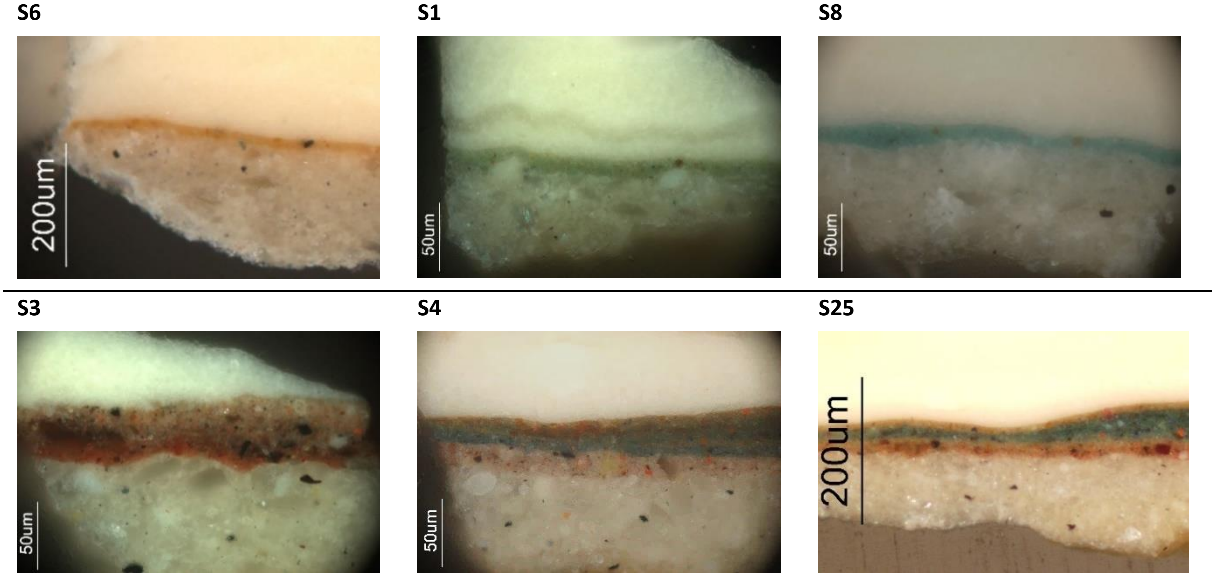

Figure 3.7: Paint layer(s) of different colours (likely from a previous painting) between ground layers, observed in six cross-sections photographed in reflected light microscopy under cross-polarised light.

Elemental mapping of two samples, S4 (Figure 3.8) and S25 (Table C., Appendix C, page 285) selected for containing more paint layers, revealed aluminium, iron, silicon, lead, and particles with mercury, sulphur, potassium, calcium and sodium. These elements are consistent with the pigments identified by μ-Raman: iron oxides (goethite, hematite), Prussian blue, vermilion and carbon black. Lake pigments are also likely present (see discussion in section 3.2.4.2).

Analysis with SEM-EDX and μ-Raman confirmed these results in the other samples, for example point analysis on specific particles (blue and yellow) in S7 showed the presence of iron oxides and Prussian blue, as well as calcium in the black particles. Interestingly in S5, the large black particle in this paint layer has calcium and phosphorus which points to Bone black (animal source). The pigments attributions will be discussed in section 3.2.4 (page 133) given that they were also identified in the paint layers above the second ground which corresponds to the painting *O Cardeal D. Henrique*…

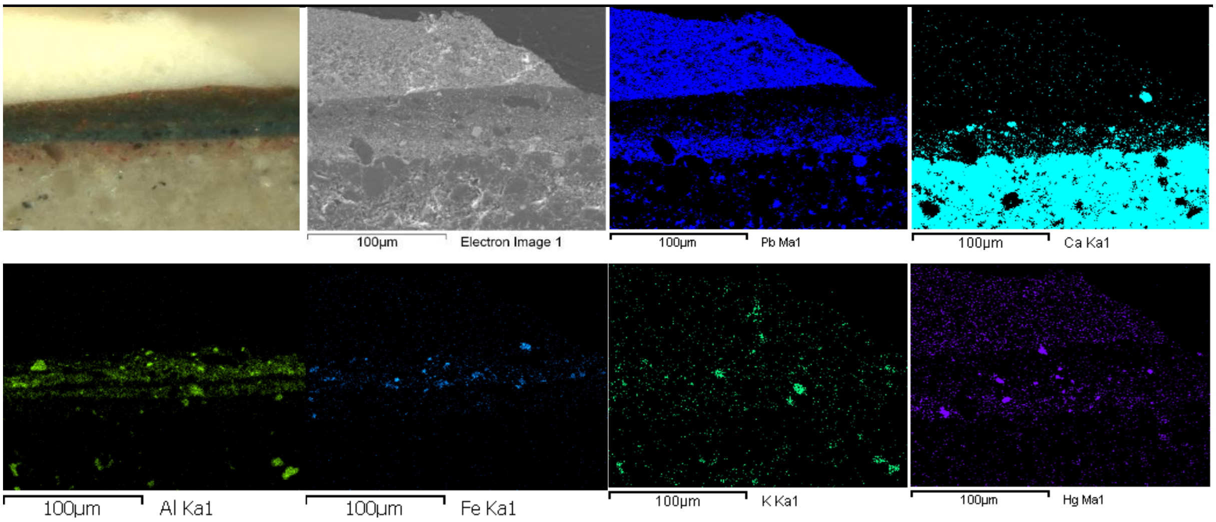

Figure 3.8: Detail of S4 in reflected light microscopy under cross-polarised light, SE image and EDX elemental mapping of the paint layers between the ground layers (distinguished by the map of Ca and Pb).

The presence of this previous painting indicates that Marciano reused the canvas. In the case of the painting *O Cardeal D. Henrique*… Marciano had mentioned the costs and time consuming technique employed, involved in producing and shipping the painting (D. de Macedo 1951) which could suggest financial constraints as this often encouraged reuse of canvases[112].

Whether or not this previous painting was made by Marciano is not known. Although the pallete seems to fit the pigments identified in the paint layers above, the paint stratigraphy is simpler and opaque without the glaze layers that are so charactheristic in the painting *O Cardeal D. Henrique*…. However this might be due to it being an unfinished painting that was still in the earlier stages.

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[112] It is not unusual for painter's to reuse paintings by applying a second ground layer on top of a partial or fully painted image. See for example Vincent van Gogh (1853-1890) in Young (2021, 142).

Upper ground layer (ground layer 2)

The white upper ground layer is composed solely of a lead white paint, for all cross-sections investigated.

SEM-EDX analysis indicated that this second ground layer consists of lead as the main element present, with the EDX Pb mapping (see Figure 3.6) showing the homogeneous distribution of lead in that layer. A small amount of chlorine was also detected, which could be associated either with the production of the pigment (e.g. Niknejad and Karimy 2019) or with lead chlorine as an adulteration of lead white (e.g. Sotiropoulou et al. 2010; Cotte et al. 2017). Further analysis on several cross-sections with μ-Raman and ATR-FTIR microscopy and on micro-samples with μ-FTIR confirmed the characteristic bands of hydrocerussite and cerussite (see Table 3.3).

The chemical map of this upper ground layer was obtained with ATR-FTIR microscopy, by integrating the broad carbonate band, centred at ca. 1398 cm^{-1} (Figure 3.9). The average spectrum from this region shows a mixture of lead white and lead carboxylates in an oil binder. While the peaks at 1398 and 1045 cm^{-1} are due to the stretching of the carbonate ion (asymmetric and symmetric, respectively), the small band at 3536 cm^{-1} is from the hydroxyl stretch of lead white – hydrocerussite – ($2PbCO_3.Pb(OH)_2$) (Possenti et al. 2021). The small peak at 838 cm^{-1} has been assigned to the – cerussite – neutral lead carbonate ($PbCO_3$) (van der Weerd, van Loon, and Boon 2005). The sharp peak at 1508 cm^{-1} is characteristic of lead carboxylates.

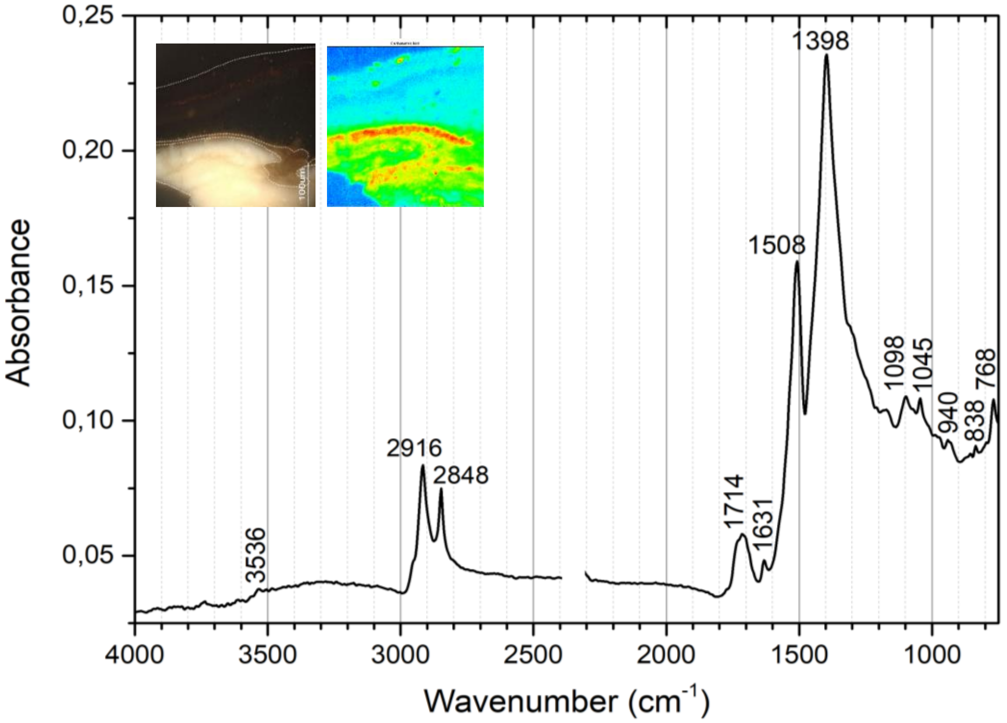

Figure 3.9: FTIR average spectrum of the upper ground layer of S7, acquired from the maximum values (in red) of the chemical map (ROI from 1468 to 1332 cm^{-1}); chemical map shown in the image inset on the right with visible light image on the left.

Analysis with TOF-SIMS provided finer details of the chemical composition of this white ground layer in samples S7 and S27 (Figure 3.10).

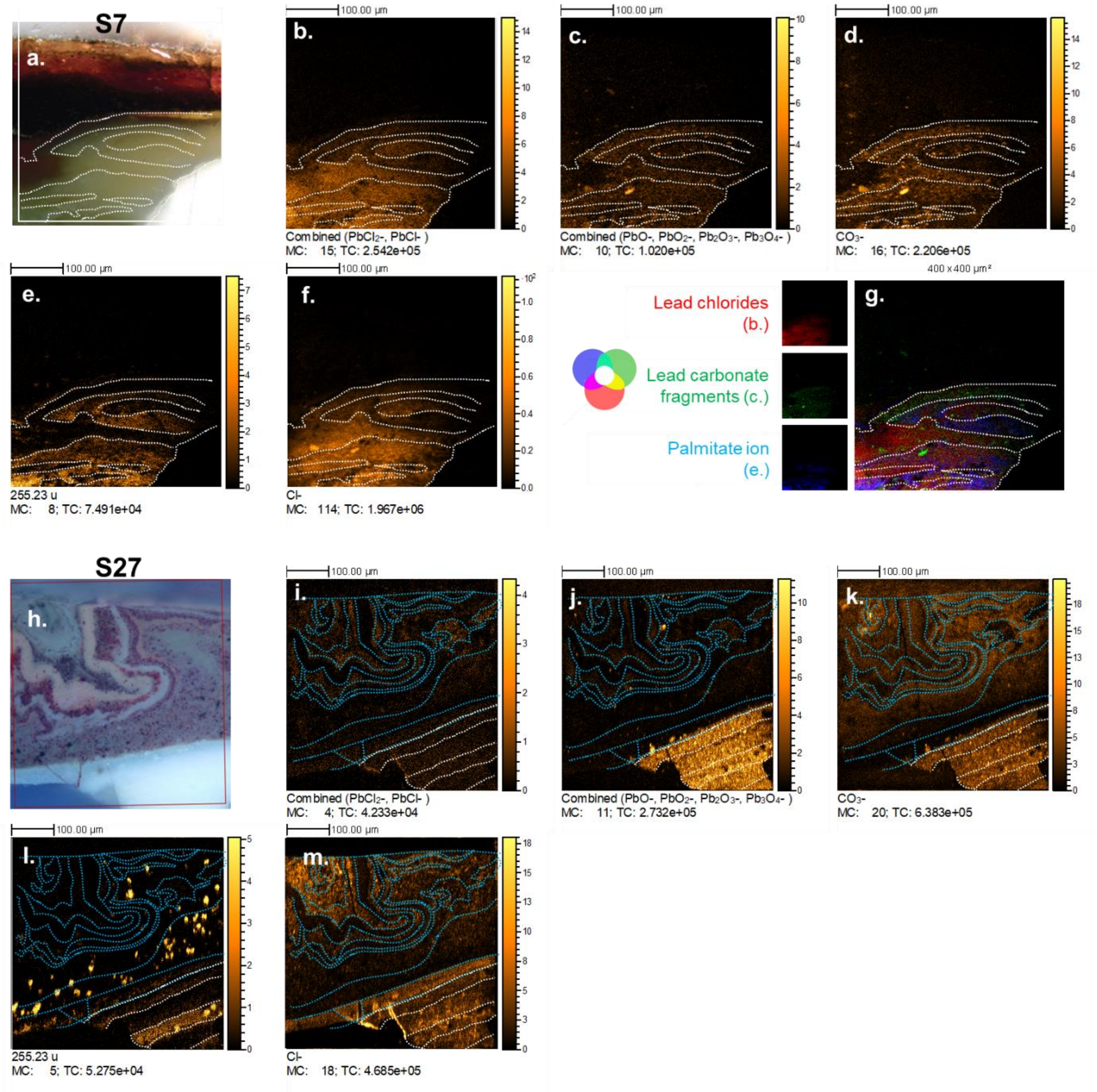

Figure 3.10: Detail of S7 in reflected light microscopy under cross-polarised light (a) and TOF-SIMS images on sample S7 for (b) lead chlorides (PbCl$^-$ and PbCl$_2^-$), (c) lead white fragments (PbO$^-$ and Pb$_n$O$_{n+1}^-$), (d) carbonate ion (CO$_3^-$), (e) palmitate ion (C$_{16}$H$_{31}$O$_2^-$) and (f) chlorine ion Cl$^-$, with the overlay of (b. c. and e.) in (g); and detail of S27 under UV radiation (h) and the same detail in TOF-SIMS images (i) to (m). Ground layer regions are delimited between the white dotted lines.

In these samples this layer varies between 150 and 200 µm and can be chemically mapped and divided into several horizontal regions with variable proportions of carboxylates, lead chlorides and lead carbonate fragments (Figure 3.10). Figure 3.10: Detail of S7 in reflected light microscopy under cross-polarised light (a) and TOF-SIMS images on sample S7 for (b) lead chlorides (PbCl- and PbCl2-),

(c) lead white fragments (PbO- and PbnOn+1-), (d) carbonate ion (CO3-), (e) palmitate ion (C16H31O2-) and (f) chlorine ion Cl-, with the overlay of (b. c. and e.) in (g); and detail of S27 under UV radiation (h) and the same detail in TOF-SIMS images (i) to (m). Ground layer regions are delimited between the white dotted lines.The analysis identified lead carbonates characteristic ions along with fatty acids from the oil, lead palmitate and a little of lead stearate (respectively *m/z* 463.2 $PbC_{16}H_{31}O_2^+$ and *m/z* 491.2 $PbC_{18}H_{35}O_2^+$). Chlorine is also detected with different intensities depending on the area (as seen by SEM-EDX). A 30 µm thick region in the middle of the ground shows a relatively more important lead carbonate detection whereas others are richer in chlorine content. Spectra of grains from each region were isolated and compared with each other suggesting that there are different pigment grades or lots, that vary in chlorine content. The presence of chlorine is hard to interpret here without further information (both degradation processes or production methods could explain it).

3.2.2 Translucent layer

In 20 of the cross-sections, immediately above the upper ground (ground layer 2) exists a layer which appears in OM as "translucent" with a brownish oily appearance in normal light and which is almost transparent in UV light (see Figure 3.12 layer b). This layer is designated the "translucent layer", due to its appearance. It has to be noted that only the 6 cross-sections[113] which do not show the translucent layer were from areas unaffected by the paint defects found elsewhere.

Because of its location and limited thickness this layer proved extremely hard to sample, therefore its characterization was made by analysing the layer in cross-sections and not by micro-sampling. A spectrum obtained with FT-Raman of a "pocket"[114] of this layer (Figure 3.12 "pocket" on the right side of the image) was compared with bibliographic references (Otero et al. 2014) and indicated that the layer contained lead azelate (

Figure 3.11 and Table 3.4).

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[113] S4, S5, S21, S22, S25 and S26 (see Appendix C.4 - Tables C.4, C.5 and C.6 - pages 283, 284).

[114] To define what appears to be an area of accumulated material.

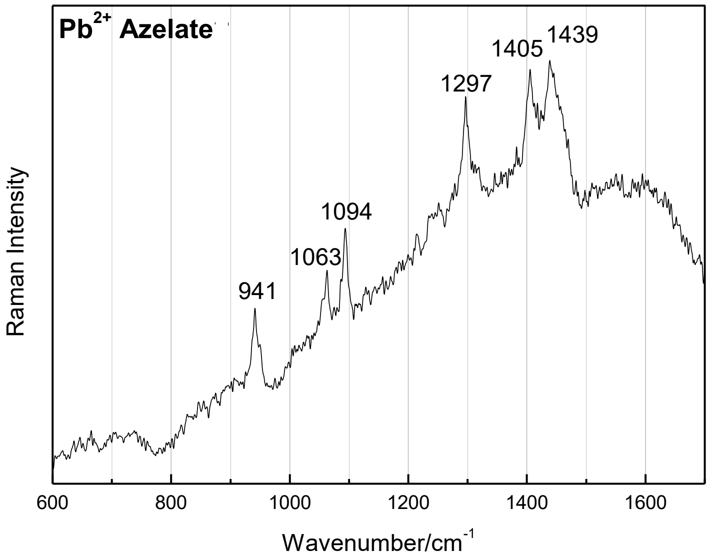

Figure 3.11: FT-Raman spectrum of the translucent layer in S7.

Table 3.4: Characteristic Raman bands and respective attributions for Lead Azelate.

Characteristic Raman bands	
Wavenumber (cm^{-1})	Assignment*
1439	
1405	δ(CH_2)
1297	
1094	ν(C-C)
1063	
941	ρ(CH_2)

* (Otero et al. 2014)

Further confirmation of this result was obtained with imaging techniques - ATR-FTIR Microscopy and TOF-SIMS - that characterized the material and its uniform distribution as a layer in the cross-sections.

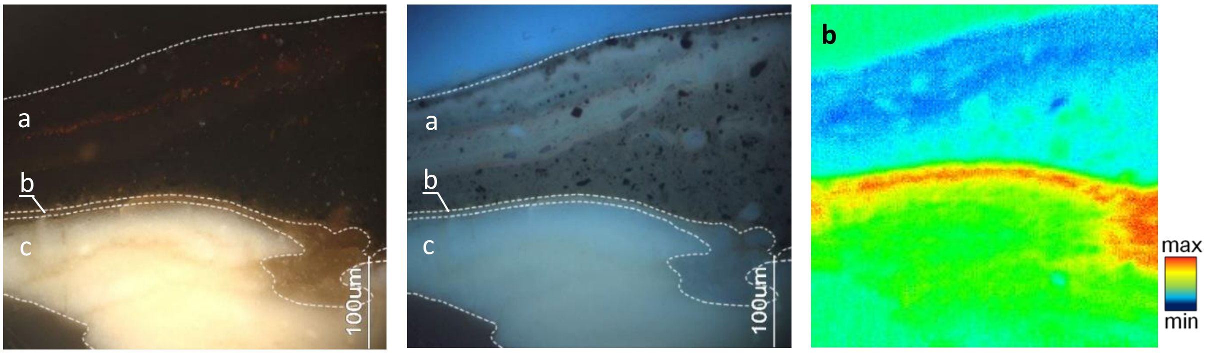

Figure 3.12: Detail of S7 in reflected light microscopy under cross-polarised light (left) and UV radiation (middle), with a white outline of: paint layers (a), translucent layer (b) and upper ground layer (c). Chemical map **b** (right) of the "translucent" layer (intensity from 1557 to 1478 cm-1).

Through ATR-FTIR Microscopy, the chemical map of the translucent layer in sample S7[115] (Figure 3.12, right image - chemical map **b**) was obtained by integrating the peak at 1504 cm^{-1} (ROI from 1557 to 1478 cm^{-1}) (Figure 3.13). The average spectrum in this region shows characteristic peaks for lead azelate at 1504, 1444 and 1402 cm^{-1} (assignments in Table 3.5), as confirmed by the comparison with a reference spectrum of lead azelate (light grey in the inset, Figure 3.14) from Otero et al. (2014).

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[115] The complete results of sample S7 (brown paint sample), which includes the paint layers, translucent layer and upper ground layer (ground layer 2) can be found in section C.6, Appendix C, page 286.

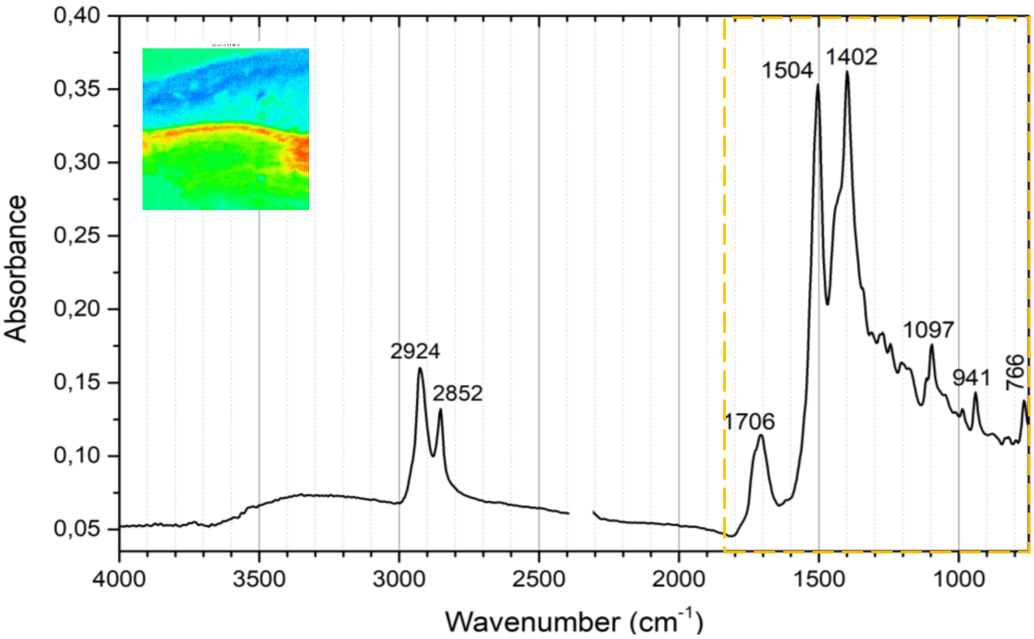

Figure 3.13: FTIR average spectrum acquired in the translucent layer (map obtained by integrating the signal, intensity from 1557 to 1478 cm^{-1}).

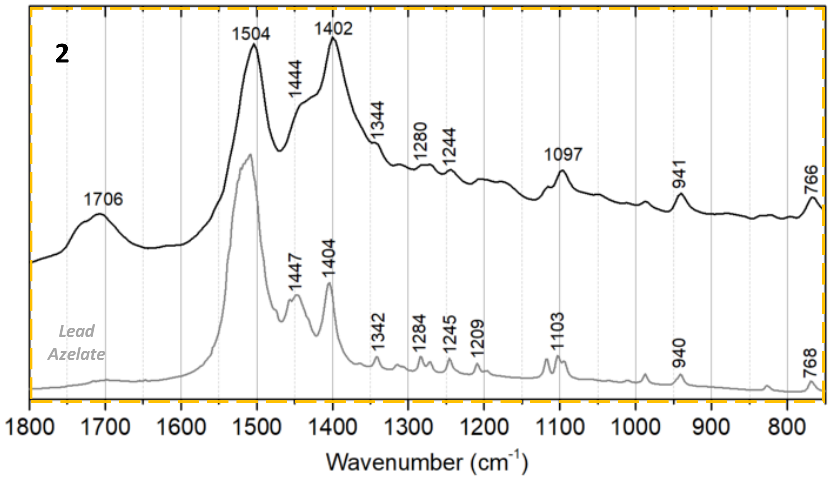

Figure 3.14: *Inset* that shows a detail from 1800 to 750 cm^{-1} of the spectrum in Figure 3.13 (in black) compared with a reference spectrum of lead azelate (in light grey).

Table 3.5: Infrared bands and attributions for Lead Azelate.

Characteristic Infrared bands	
Wavenumber (cm^{-1})	Assignment*
1504	
1444 1402	δ(CH_2)
1344	
1280	δ(CH_2)
1244	
1097	ν(C-C)
941 766	ρ(CH_2)

* (Otero et al. 2014)

Complementary TOF-SIMS analysis confirmed these results and provided further information. In the three cross-sections (S7, S19 and S27, two of brown paint and one of red paint, respectively) where the translucent layer was analysed (Figure 3.15) lead azelate ion ($PbC_9H_{14}O_4^-$ *m/z* 394) and its fragment ions ($PbOC_9H_{13}O_4^-$ *m/z* 409 and $PbCOC_9H_{13}O_4^-$ *m/z* 421) were detected. The proportion of saturated fatty acids and lead carboxylate ions is higher than in the surrounding layers. Moreover, the local value for the P/S ratio is lower (stearate ion being over-represented compared to palmitate) and the relative proportion of unsaturated ($C_nH_{2n}O_2$) *versus* saturated carboxylate fragments ($C_nH_mO_2$, with 2n-2 or 2n-4) is higher. These results indicate a different ageing state of the translucent layer compared the rest of the sample and highlights its likely importance in the overall drying problem occurring in the painting.

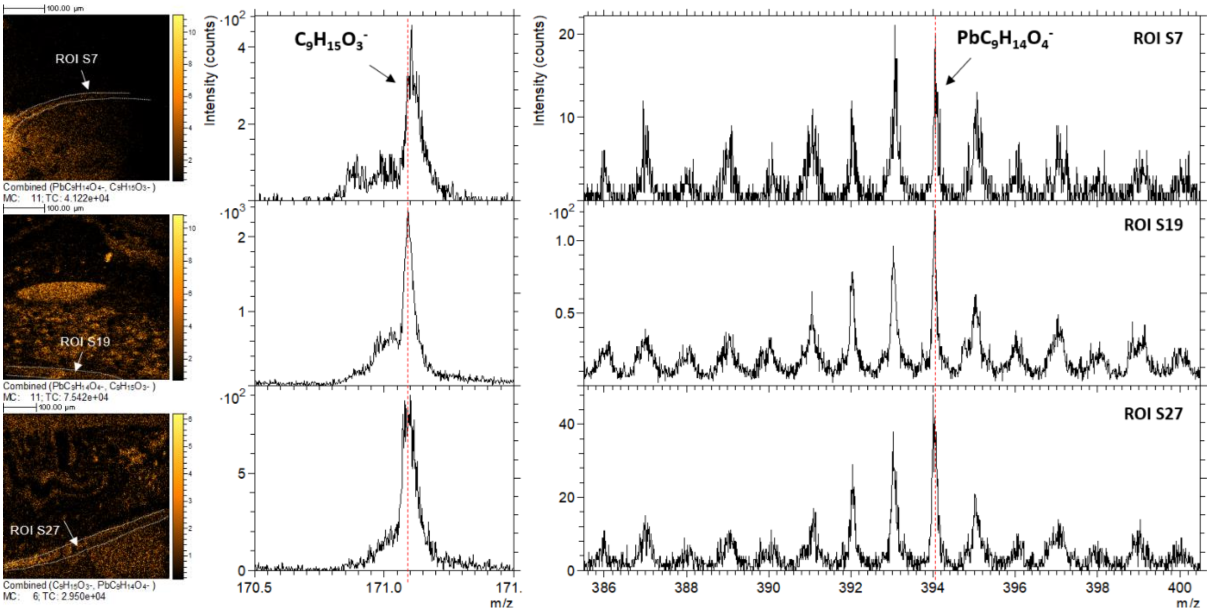

Figure 3.15: Sum of $PbC_9H_{14}O_4^-$ ion (lead azelate) with images of $C_9H_{15}O_3^-$ ions and associated spectra for cross-sections S7, S19 and S27.

The presence of this layer in the painting remains a mystery, but one hypothesis is that it may be an oiling out or sealing layer applied to the ground prior to painting.

Mentions to intermediate or isolation layers have been reported and analysed in 15th and 16th century panel paintings (see Ferreira, Morrison, and Boon 2007). According to O'Donoghue et al., Du Grez in his book *Traité sur la Peinture* (1699) recalls how a colleague "would apply oil to the already grounded canvas and the sketch on top" (Du Grez 3, p.246, as cited in O’Donoghue, Romero, and Dik 1998). Interestingly Melo et al, have recently demonstrated how a charcoal underdrawing would remain fixed in place if drawn on top of an oil-based intermediate layer (Melo et al. 2022).

Concerning 19th century sources, Carlyle (1990) describes how these intermediate layers could have a sealing function to prevent paint absorption, to fix preparatory drawings or even as advised by the author Standage "a coating of zinc white or umber in oil, or even linseed oil alone, is advised over lead white grounds to 'minimise the evils incidental to painting on a lead ground'" (Standage, H. C. 1892, pp.73-74 as cited in Carlyle 1990). Oiling out layers are described in nineteenth century British oil painting instruction books as an intermediate layer between paint applications and as an initial layer over the ground.

The nature of this layer raises some additional questions: why is it mainly composed of lead azelate, in preference to other lead carboxylates? And why did it not crystallize (by forming protrusions, for example), remaining instead as an apparently stable amorphous layer.

In terms of being lead azelate and not an oxalate, stearate or palmitate, is likely intimately related to the composition of the oil, which will be discussed in section 3.2.5 (page 139).

The latter question has been addressed in the literature, Plater et al. (2003) argue that "the higher polarity of azelaic acid and its lead salt, resulting from the shorter hydrocarbon chain and the two carboxylic acid groups, will make these components much less mobile than the monocarboxylic fatty acids" and that "the incorporation of the dicarboxylates into the ordered lamellar structure (…) is likely to be unfavourable" (Plater et al. 2003). By being less mobile and more stable in a 3D metal coordinated network than monocarboxylates (Boon and Ferreira 2006), it is more likely that the lead azelate would remain present in a single layer.

3.2.2.1 Underdrawing

Out of the 27 cross-sections, excluding S13 which is not a complete stratigraphy (cross-section of a "bead"), 20 show the presence of the translucent layer, however in 6 cross-sections[116] the translucent layer is not clearly discernible, there is a layer with black particles (Figure 3.16). Since the particles are spread on top of the ground layer it might be related to an under-drawing. The areas sampled correspond to compositional areas of hands, pleated sleeves and the ruffled collar which increases the probability of being part of the artist's underdrawing.

This possible under-drawing might be concealing the translucent layer. The particles could have become embedded in the translucent layer.

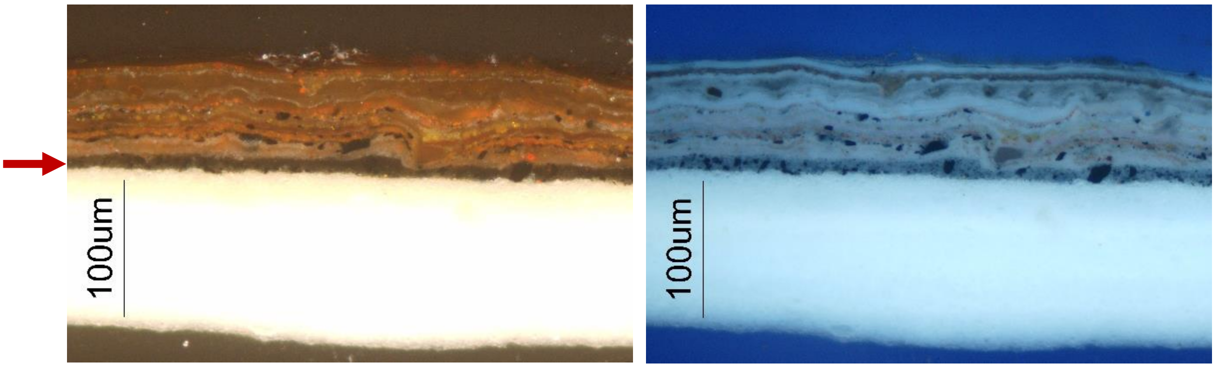

Figure 3.16: Detail of S26 in reflected light microscopy under cross-polarised light (left) and UV radiation (right). Possible layer of under-drawing with black particles identified by the red arrow.

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[116] Samples S4, S5, S21, S22, S25 and S26, removed from areas of flesh, white and greenish tones (see Appendix C.4 - Tables C.4, C.5 and C.6 - pages 283, 284).

Point analysis with SEM-EDX confirmed that the black particles contained only carbon and oxygen. The lack of phosphorus indicates that it is not an animal carbon black, instead it may be graphite (pencil underdrawing) or different burnt vegetable matter such as vine black, cork black or lamp black. µ-Raman analyses show sharp bands of carbon black in these particles (see Appendix C.7, page 290-291) which points to a more crystallized arrangement (Coccato et al. 2015) sustaining the graphite hypothesis.

3.2.3 Paint Layers

Descriptions of the sequence of paint layers visible in the cross-sections will be grouped by colour. Brown and red layers will be discussed first since these are the most affected by alligatoring. Following this will be flesh tones which are partially affected and finally other colours from the least affected areas.

Individual pigments identified in the painting are discussed in section 3.2.4 (page 133). The binder is oil and its characterization will be discussed in section 3.2.5 (page 140).

3.2.3.1 Description of paint layers according to colour

Brown paint

Brown Black

Samples: S6, S7, S8, S9, S10, S11, S12, S19, S23, S24

The brown colour in the painting was achieved by consecutive applications of paint layers. These layers can be distinguished using reflected microscopy under cross-polarised light and UV radiation. The layers are visible in ten cross-sections from samples which were removed from areas of brown paint (see Appendix C.3 and Table C.3 in page 282). The layers can be divided into two primary groups: one with a layer of paint with a significant amount of particles, and the other which appears to be a glaze layer, with less particles and greater fluorescence. These layers can be subdivided and were found to be variable according to their sampling location.

The best sample to illustrate the brown paint layers is S19 since it has captured areas of flat paint as well as layers where the paint had pulled into the characteristic paint islands associated with alligatoring (Figure 3.17), and the layers present are also identifiable in the other brown paint samples.

The 1st paint layer in S19, which is directly above the translucent layer, is a dark brown paint with different coloured particles. On the left of the sample which incorporates the flat paint, this 1st layer appears alone, not covered by subsequent layers which are evident on the right side of the sample.

This 1st layer, seen in the UV (Figure 3.17, bottom) contains a particle that fluoresces bright blue. It is located on the right side of the sample in the area associated with the paint island (see section 3.3.1).

The 2nd, 3rd, and 4th layers visible on the right side of the sample belong to the paint "island" area and seem to be the moving layers. These layers have a glaze like appearance with less visible particles, they are more sinuous and fluorescent in UV. These layers were defined based on the 2nd layer being discernible in normal light with a more orange/yellow colour; the 3rd layer having a rich brown colour with a glaze-like appearance. In UV it is possible to distinguish differently fluorescing layers within the 3rd layer. The 4th layer is most clearly visible under UV radiation and consists of a uniformly dark layer with wavy contours, that delimitate areas of a fluorescent material.

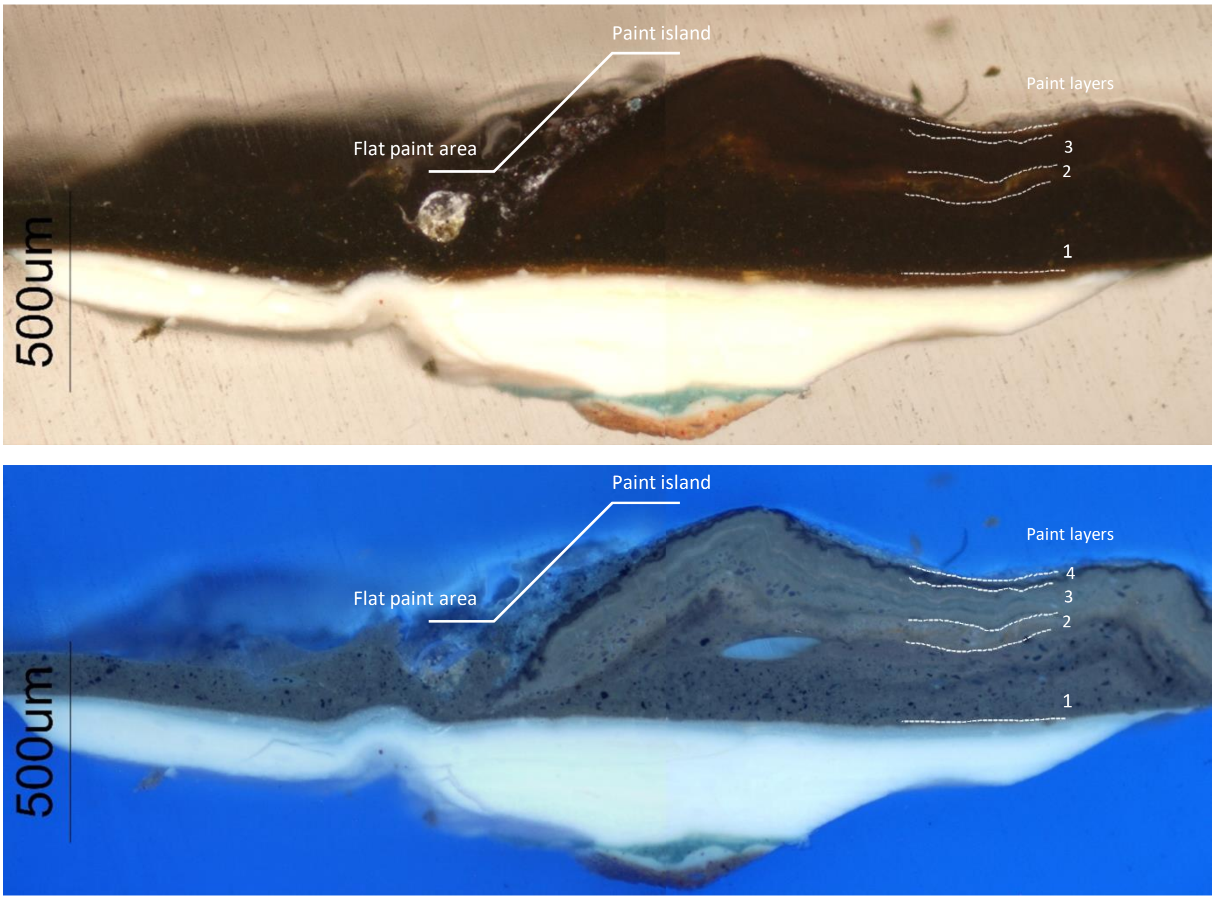

Figure 3.17: Cross-section S19 in reflected light microscopy under cross-polarised light (top) and UV radiation (bottom). The paint layers (1 to 4) and the division of the sample into "flat" paint (on the left) versus the paint "island" (on the right) are marked in white.

Out of the ten brown samples made into cross-sections, only samples S6 and S24 present a different stratigraphy due to the existence of a greenish paint layer (see Table C.3, page 282). In S6 this is the only paint layer visible and in S24 the greenish paint layer is the first layer before a series of glaze layers (Figure 3.18).

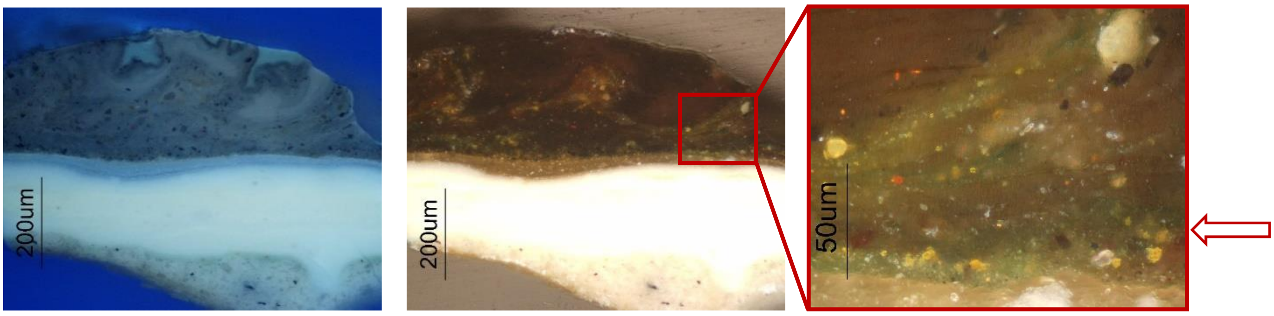

Figure 3.18: Detail of paint cross-section S24: under UV radiation (left) and cross-polarised light (middle). The image on the right consists of a zoomed area (inset in red) to show the greenish paint layer (red arrow).

Red paint

Red

Samples: S1, S2, S13, S14, S17, S27

Unlike to the brown paint, the red paint proved to be more difficult to interpret in terms of its construction since the layer structure appears so distorted. The colour appears to be achieved by the consecutive application of paint layers, but the irregular layer structure and highly distorted (wavy) paint layers observed most clearly in UV (Figure 3.19, bottom) in sample S27, appear to be due to the physical movement of the paint composite during formation of the paint islands. Shimazu (2015) had described "wavy and uneven borders between two paint layers" as indicative of paint shrinkage in the painting with alligatoring *La Descente des Vaches* by Théodore Rousseau (Shimazu 2015, 134), which may be similar to what is evident in S27.

In the six cross-sections removed from areas of red paint, while such distorted layers are visible under cross-polarised light, like sample S27, they are best distinguished under UV (see Appendix C, Table C.2, page 281). In all of the sample cross-sections of red paint there appears to be two types of layers, those with visible pigment particles and those with a glaze-like appearance with less visible pigment particles.

Red paint samples S17 and S27 display the most complex stratigraphy, with a high number of wavy paint layers with differing fluorescence and evidence of pigments (i.e. S27 in Figure 3.19). As can be seen in the right side of sample S27 under higher magnification (Figure 3.20) it is possible to discern what appears to be 10 paint layers. Some of these layers are identifiable in other samples from red paint with a simpler composition.

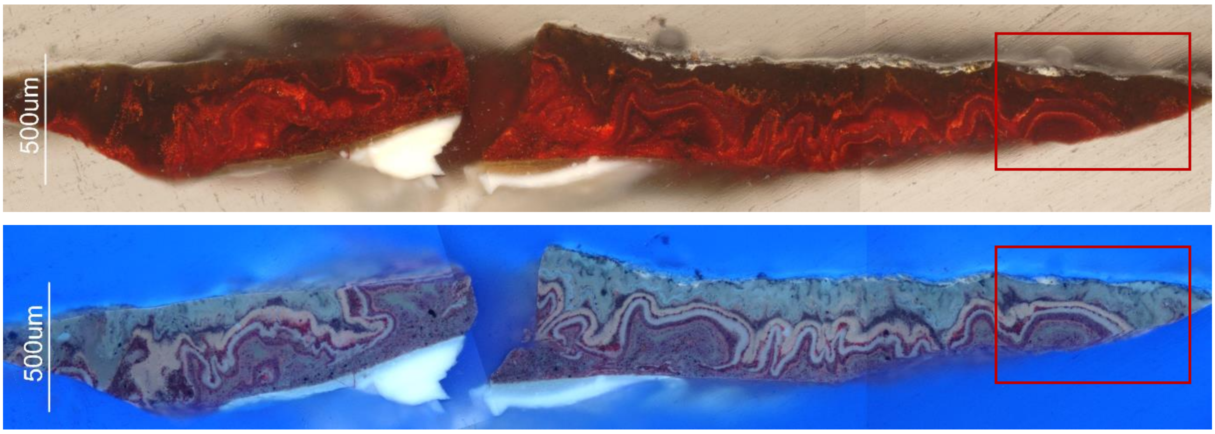

Figure 3.19: Cross-section S27 in reflected light microscopy under cross-polarised light (top) and UV radiation (bottom). Detail area for Figure 3.20 in red.

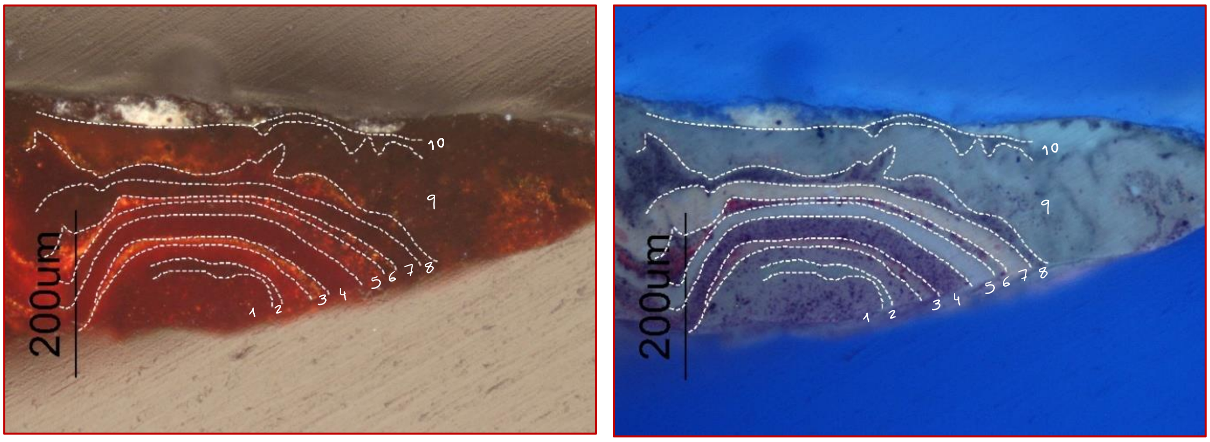

Figure 3.20: Detail from cross-section S27 in reflected light microscopy under cross-polarised light (left) and UV radiation (right). Paint layers marked in white.

Under normal light small red, yellow and black particles can be seen in red paint samples, in some cases followed by areas of glaze-like paint without any noticeable particles (e.g. paint layers 2, 5 7, 9 and 10 in Figure 3.20). Visually, a similar paint layer to the one from S19 (see 4th layer in Figure 3.17) is observed here as a top layer. In normal light it has the appearance of a brown glaze and under UV radiation has a bluish fluorescence with no particles (layer 10 in Figure 3.20).

Sample S13 from a red bead (similar in aspect to the exudates) was made into a cross-section and embedded in the resin such that the centre of the bead can be clearly seen. S13 shows that the bead, is not hollow but is composed of pigment and binder with areas similar to the glaze layers (dark in normal light and more fluorescent under UV radiation) as observed in the stratigraphy of the other red cross-sections (Figure 3.21).

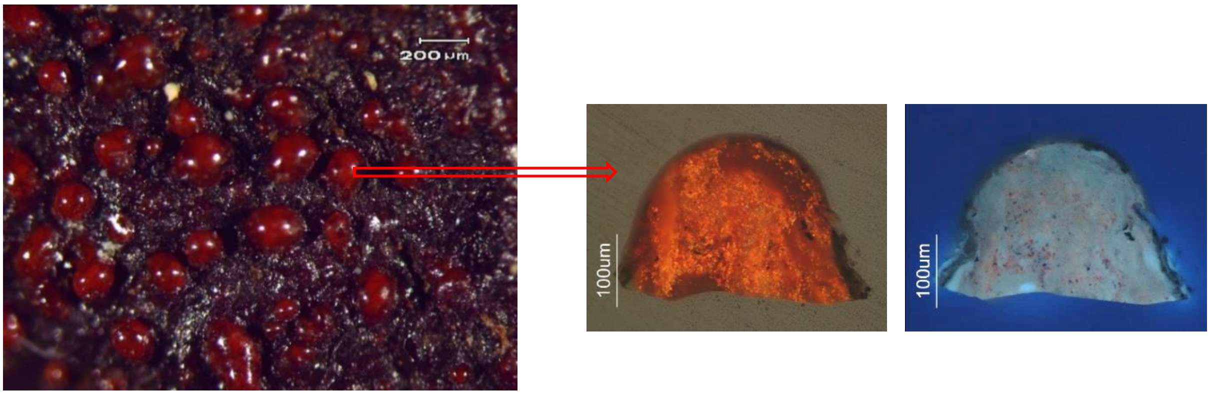

Figure 3.21: Stereomicroscope image (left) of the paint surface showing the red beads on the surface of a red paint island.The red arrow points to sample S13 a cross-section of one bead, which is seen in reflected light microscopy under cross-polarised light (middle) and UV radiation (right).

Flesh Toned paint

Flesh

Samples: S3, S4, S16, S18, S20, S26

The flesh toned paint layers were produced by consecutive applications of paint layers with different pigment mixtures which can be clearly distinguished in sample cross-sections in the OM by their fluorescence in UV. It was also possible to distinguish the layers with cross-polarised light but with more difficulty. A correlation between paint samples from alligatoring areas (S3, S16, S18 and S20) and the presence of the translucent layer was also observed. Samples S4 and S26 from flesh toned areas that were less affected by paint distortions do not exhibit the translucent layer below the paint layers (see Appendix C, Table C.4, page 283).

The six samples from flesh toned paint could be divided into two groups: group 1 includes samples taken from the face (S20) and hands (S4 and S26) of Jorge Serrão and group 2 samples taken from the face (S3 and S18) and hand (S16) of the Cardinal (see Table C.4, page 283). Samples from group 1 present a similar but complex stratigraphy, while group 2 samples are quite distinct: S3 has only two thin visible layers; S16 has a similar stratigraphy to group 1 samples but with lighter colours; and S18 which was taken from a paint island does not have easily distinguishable layers and appears complex.

Despite this group distinction, sample S26 from the hand of Jorge Serrão (Figure 3.22) appears to have an overall stratigraphy which is evident in most of the other samples. Starting from the possible underdrawing layer with black particles (layer 1), thirteen layers are apparent (Figure 3.23) with some being extremely thin (e.g. layers 9 and 11). The layers closest to the white ground appear more pigment rich than the upper layers which, apart from (layer 12), are very glaze-like and fluorescent.

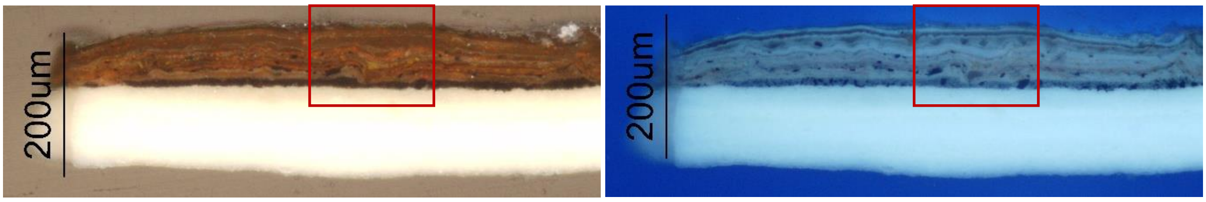

Figure 3.22: Detail from cross-section S26 taken from the hand of Jorge Serrão in reflected light microscopy under cross-polarised light (left) and UV radiation (right). Detail area for Figure 3.23 in red.

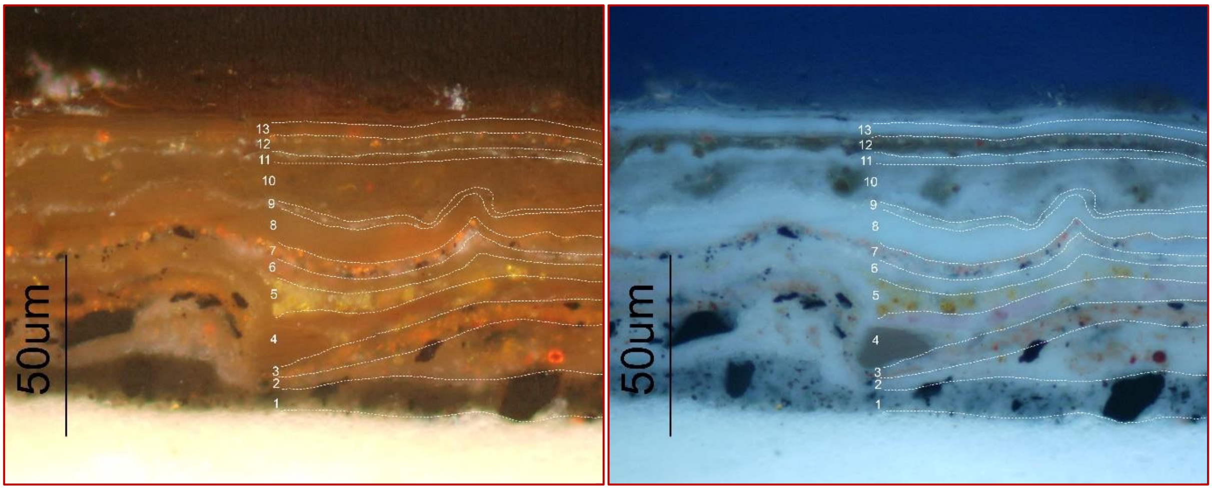

Figure 3.23: Detail from cross-section S26 in reflected light microscopy under cross-polarised light (left) and UV radiation (right). Paint layers marked in white.

White paint

White

Samples: S5, S15, S22

Three samples of white paint were taken: S5 and S15 from the Cardinal's right sleeve and S22 from Serrão's collar (see Appendix C, Table C.5 in page 284). In the embedded cross-sections they appear to have a simpler stratigraphy than the flesh toned paints. The white paints exhibit three main colour layers - yellow, orange and white - as well as a series of glaze-like layers (which fluoresce under UV). The translucent layer is not clearly discernible in these samples, likely due to the presence of the black particles (possible underdrawing).

Other paint colours

Other colours

Samples: S21, S25

The two samples from "other" colours are from a greyish white (S21 - shadow area from Serrão's collar) and a greenish paint (S25 - from Serrão's hilt of a sword) (see Appendix C, Table C.6 in page 284). In both samples the colour was produced by the application of consecutive layers, this construction is more easily identifiable, and complex, in sample S25 both under normal light and UV.

These samples were both removed from areas of paint without alligatoring. Neither shows visible evidence of the translucent layer, however the possible under-drawing layer marked by black particles is visible.

3.2.3.2 Paint Defects

Indications of the paint deformations can also be seen on a microscopic level: as described above, the cross-sections appear to show paint movement with the wavy and uneven layers, particularly in the paint layers from paint islands versus the "flat" paint (which provides insight regarding the paint layers which have contracted). Other feature apparent in SE images are the perpendicular cracks in the top paint layers[117] (Figure 3.24 and Figure 3.25), Shimazu (2015) saw similar cracks in her paint samples from deformed painting in *La Descente des Vaches* by Théodore Rousseau and argued that these cracks are "possibly due to shrinkage of the paint" which could "indicate that the upper paint and varnish layers are relatively harder than the lower paint layers" (Shimazu 2015, 134).

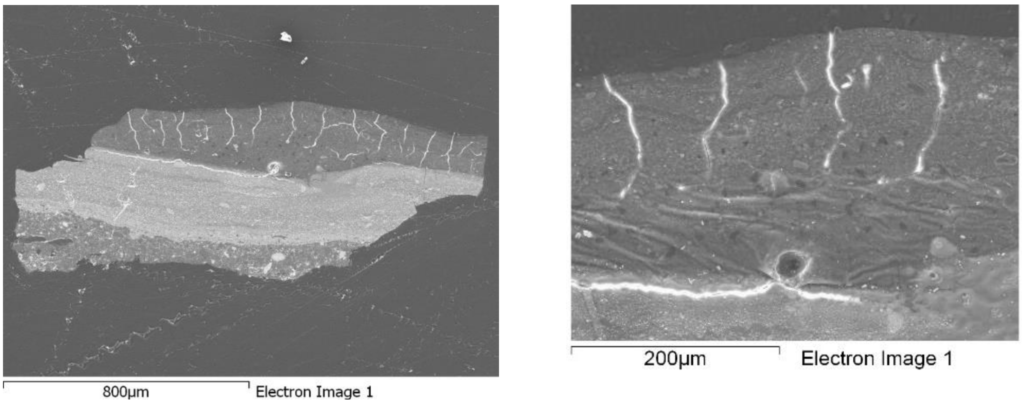

Figure 3.24: Sample S7 (left) and detail of S7 (right) in SE image. The perpendicular cracks on the top paint layers are visible in white (due to charging).

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[117] These were not perceptible in OM before or after the SEM analyses. For this reason, it is unclear whether or not these cracks are a feature of the paint or could have resulted from the SEM analytical conditions.

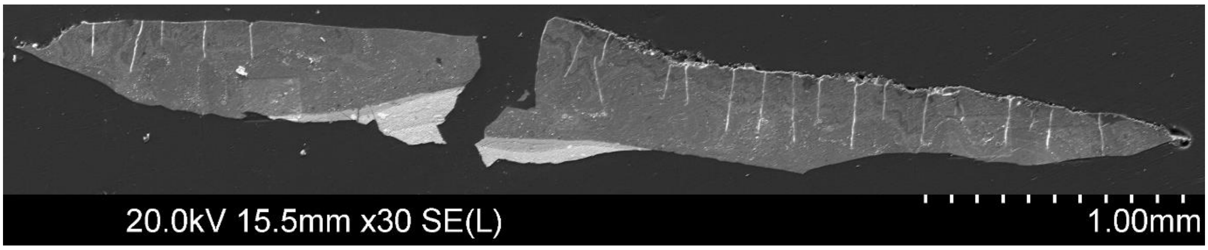

Figure 3.25: Sample S27 in SE image. The perpendicular cracks on the top paint layers are visible in white (due to charging).

3.2.4 Pigment identification

Vermilion, iron oxides, Prussian blue, cobalt blue, lead white, carbon black and Naples yellow were identified in *O Cardeal D. Henrique...* (Table 3.6). The presence of red lake pigments is also clearly evident under UV radiation and will be further explored in section 3.2.4.2 (page 136). The palette is very consistent throughout the painting, with variations due to pigment mixtures and proportions. For example the mixture for the red paint layers is predominantly red lakes, vermilion and iron oxides, while the brown paint layers are mainly rich in carbon black, iron oxides, Prussian and cobalt blue and likely yellow and/or brown lakes.

Table 3.6: Pigments identified in the painting *O Cardeal D. Henrique...*

Pigments Identified			
	Vermilion HgS		Prussian blue $Fe_4[Fe(CN)_6]_3$
	Goethite $\alpha\text{-FeOOH}$		Cobalt blue $CoO.Al_2O_3$
	Hematite $\alpha\text{-}Fe_2O_3$		Naples yellow (Lead antimonate) $Pb_2Sb_2O_7$
	Red lakes		Brown/Yellow lakes
	Carbon Black C		Lead white $2PbCO_3.Pb(OH)_2$

The analytical results from SEM-EDX and μ-Raman and their interpretation are presented in Appendix C.7 (page 290). Results from EDX point analysis and mapping of cross-sections from the different coloured paint layers are given in Appendix C.8 (page 292). Specific pigments and features are discussed below.

3.2.4.1 Cobalt Blue and Naples Yellow

Both cobalt blue and Naples yellow pigments were tentatively assigned based on SEM-EDX results.

The identification of Cobalt blue (a cobalt aluminium oxide), was based on the fact that the blue particles and blue paint layer revealed the presence in co-localisation of cobalt and aluminium (Figure 3.26). Other blue containing cobalt pigments such as Smalt (cobalt-containing potash glass) and Cerulean blue (cobalt tin oxide) were excluded due to the lack of silicon and potassium (see elemental mapping in Appendix C.8, page 299) and tin respectively.

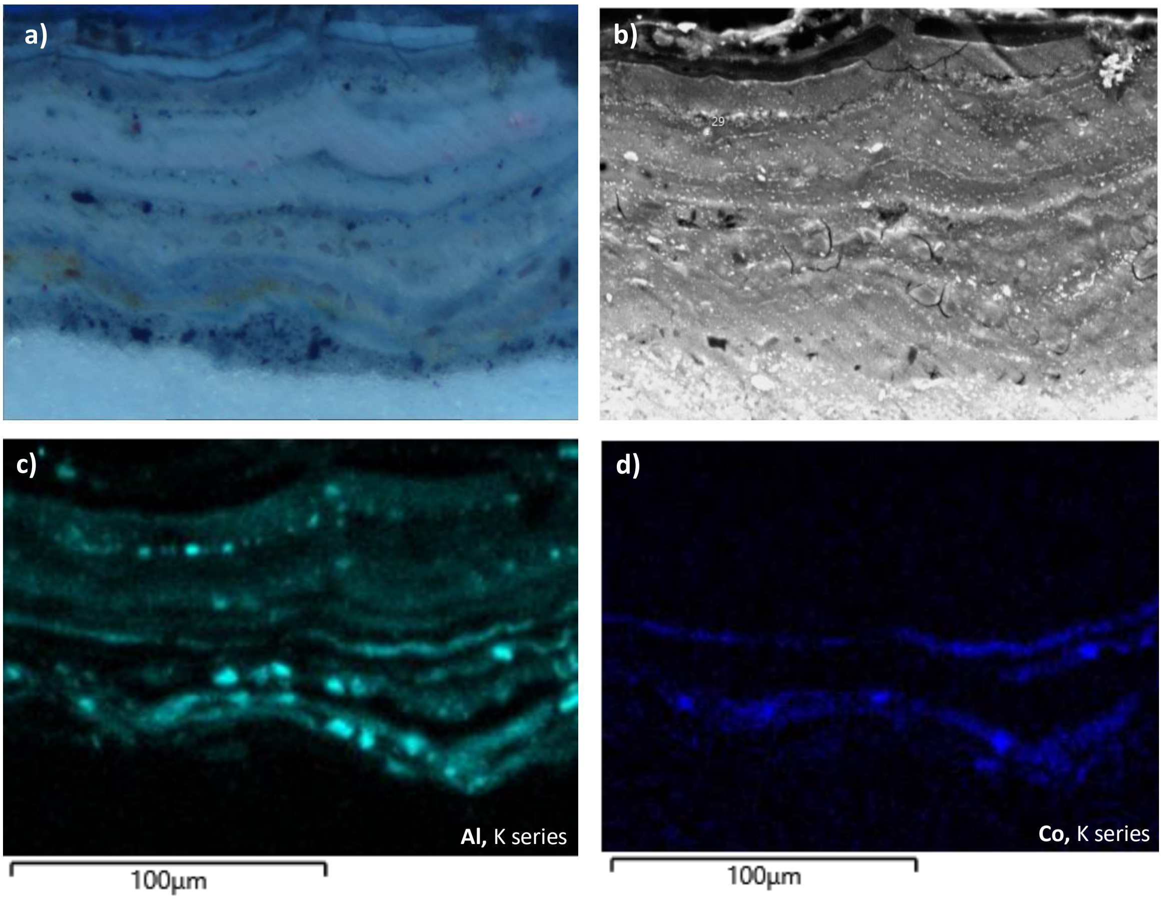

Figure 3.26: Detail of S23 (brown paint from the background): under UV radiation (a) and BSE image (b); EDX elemental mappings of aluminium (c) and cobalt (d).

Similarly the identification of Naples yellow, which is a lead antimonate, was based on the presence in co-localisation of lead and antimony in bright yellow particles (Figure 3.27).

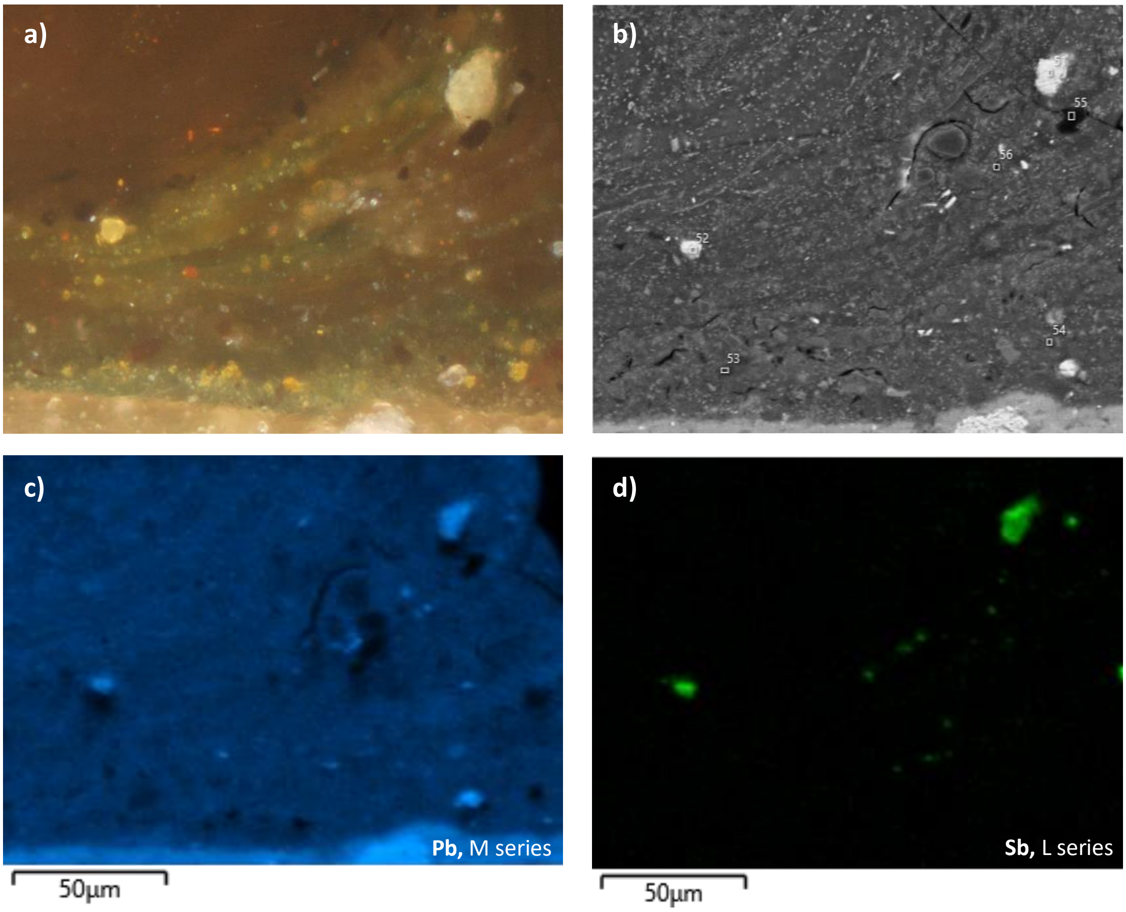

Figure 3.27: Detail of S23: under UV radiation (a) and BSE image (b); EDX elemental mappings of lead (c) and antimony (d).

3.2.4.2 Lake Pigments

The presence of lake pigments in cross-sections of red paint layers was inferred by the characteristic fluorescence in OM under UV of red lake pigments (Figure 3.28 b). This was confirmed by the EDX mapping showing the presence of aluminium (Figure 3.28 d) associated with the fluorescing pink, purple and blue particles as well as the paint layers fluorescing in yellow, white and purple. SEM-EDX analysis on each particle revealed mainly aluminium (Al), sulphur (S) and different trace elements. The latter could relate to the manufacturing process of the lake pigments or the dye's origin (Kirby, Spring, and Higgitt 2005). These elements are summarised in Appendix C.8.2 (page 293).

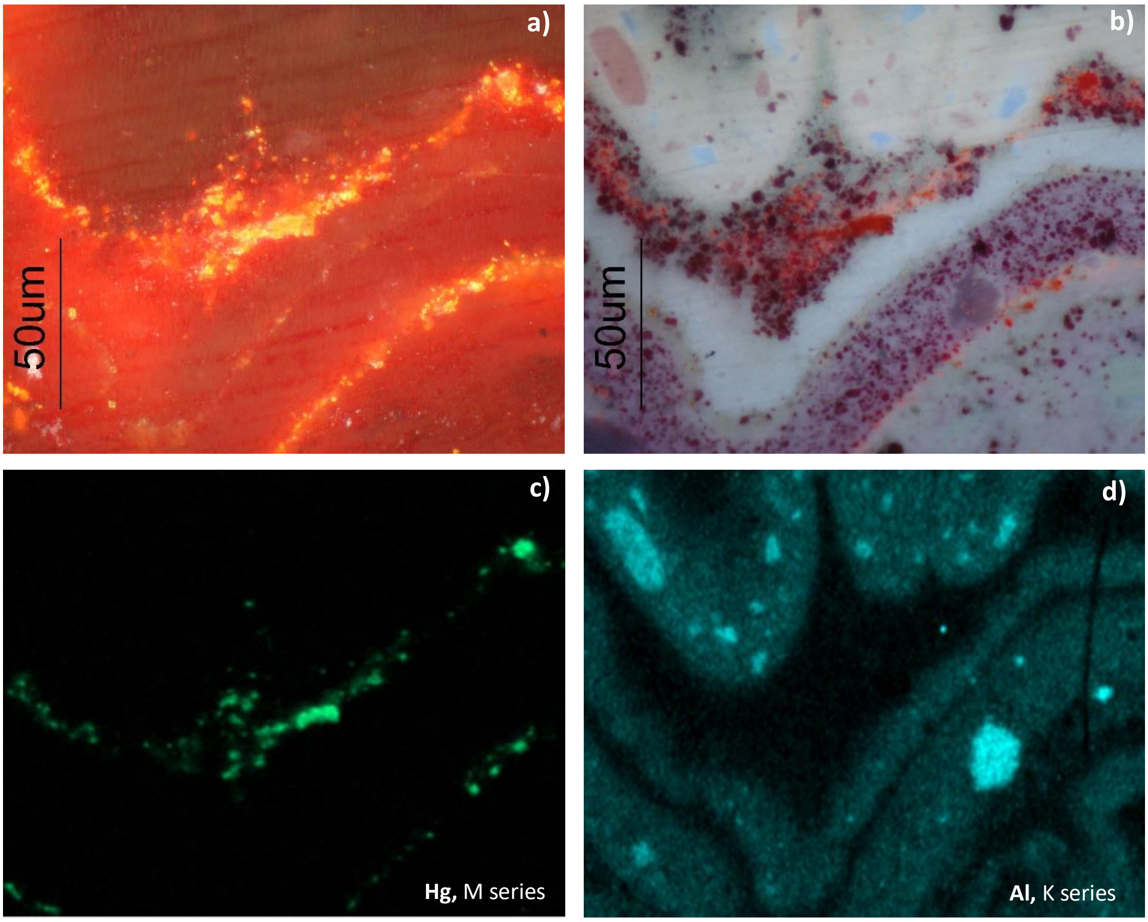

Figure 3.28: Detail of S27: under cross-polarized light (a) and UV radiation (b); EDX elemental mappings of mercury (pigment vermilion) (c) and aluminium (lake pigments) (d).

With TOF-SIMS different types of aluminium compounds, such as alumina (aluminium oxide) and alum (potassium aluminium sulphate) which can be linked to the lake manufacture were mapped (see Figure 3.29). With adjusted conditions of locally-tuned imaging, less destructive for organic materials, it was also possible to detect madder lake characteristic ions in the mass spectra reconstructed on a few particles. Due to their low secondary ion signal intensity, it was however not possible to obtain contrasted image of their localization (see Appendix C, section C.1, pages 269-273, for specific experimental conditions).

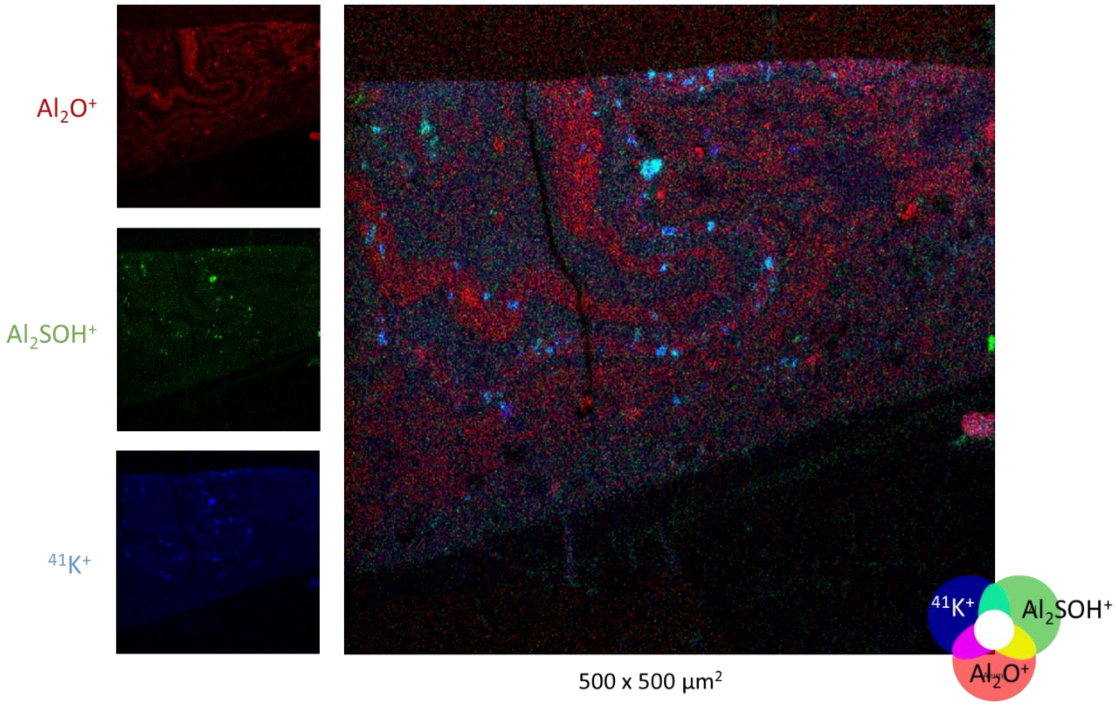

Figure 3.29: TOF-SIMS RGB overlay (on the right) of 3 ion maps (on the left) of the red paint sample S27 in positive polarity mode.[118]

An unexpected finding during elemental analysis was the significant presence of other lake pigments in layers of brown paint (Figure 3.30). Particles with aluminium, sulfur and potassium (K) were identified with SEM-EDX, which could point to the presence of brown lake and perhaps yellow lake[119]. Particles which fluoresce purple under UV, were found to contain aluminium, sulfur and traces of potassium and phosphorous (P) (Figure 3.30), which is consistent with brown (and/or yellow) lake pigments since Al and S may be associated with the pigment substrate and K and P with the source of the dyestuff (Kirby, Spring, and Higgitt 2005).

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[118] The choice of the less-abundant isotope ^{41}K for the ion map instead of the "usual" (^{39}K) was because ^{39}K is usually too intense to be relevant (it saturates the detector, so the contrast loses meaning), while ^{41}K is low enough to map and both isotopes will have the same localisation (Personal communication Caroline Bouvier, June 2022).

[119] For information on 19th century use of brown and yellow lakes see Carlyle (2001, 489-90, 520-21); for description of specific brown and yellow lake pigments (or the broader flavonoids or anthraquinones group) see Eastaugh et al. (2008).

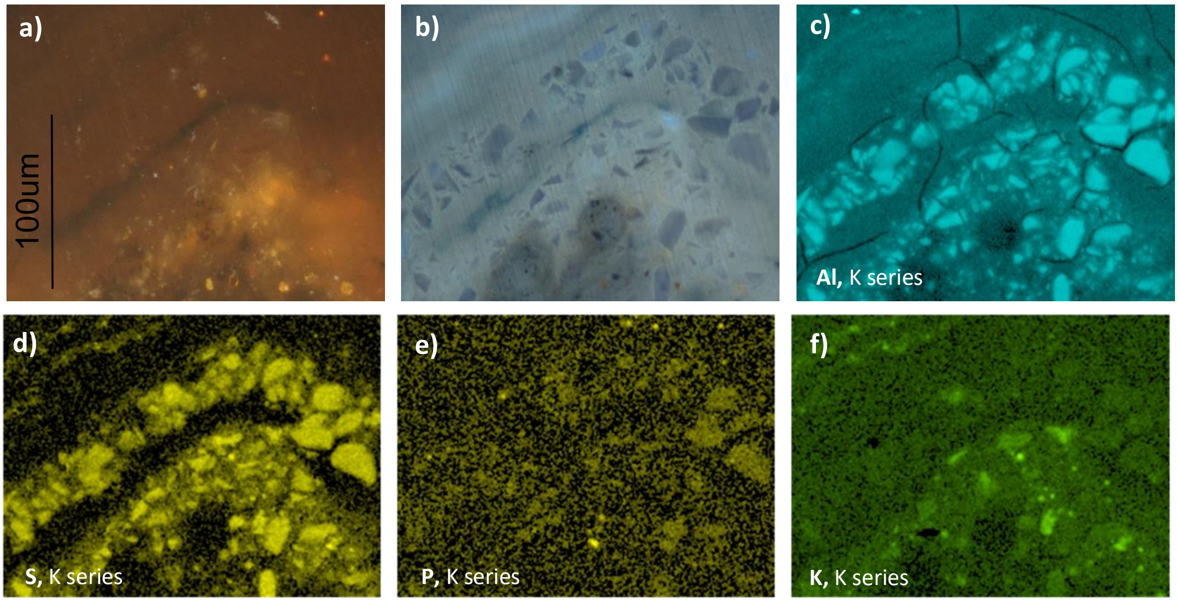

Figure 3.30: Detail of S19 (brown paint, complete cross-section in Figure 3.17) under cross-polarized light (a) and UV radiation (b); EDX mapping of aluminium (c), sulphur (d), phosphorous (e) and potassium (f).

ATR-FTIR Microscopy on the brown paint sample S7 revealed the presence of particles that seem to match the aluminium substrate of lake pigments. See Figure 3.31 for the chemical maps (**a$_{p1}$**) and respective spectra (**1.1**). The indicative peaks are reported for the ν(SO_4^{2-}) and δ(Al-OH) at 1104 cm^{-1} and the ν(Al-O-Al) at 978 cm^{-1} (Zhuang et al. 2020). Kirby et al. have noticed the shift to lower wavelenghts of the sulphate band if phosphate is significantly present (Kirby, Spring, and Higgitt 2005).

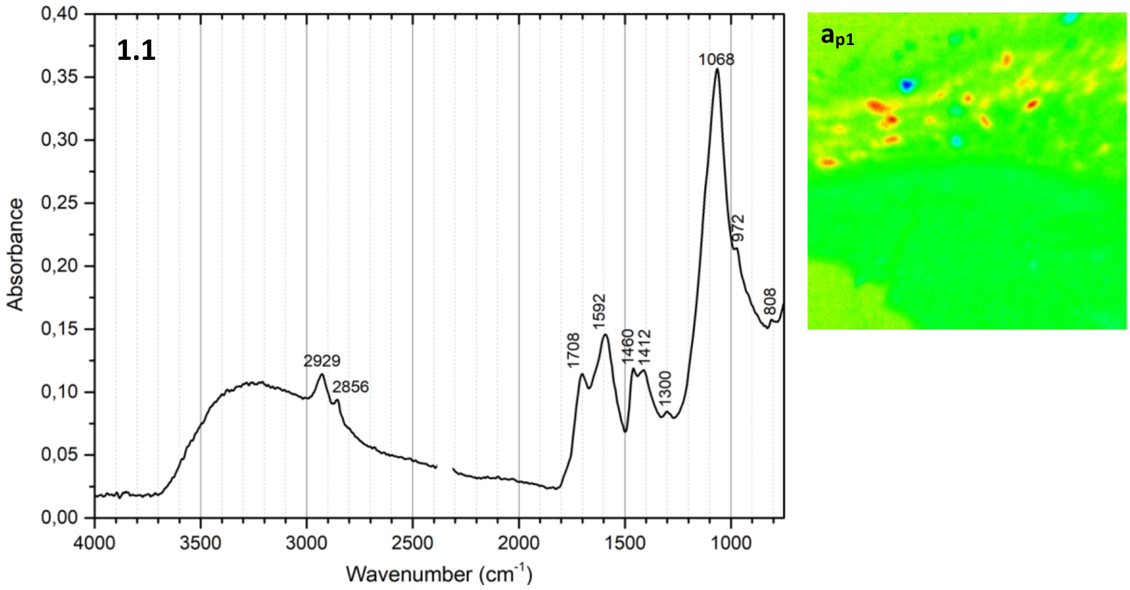

Figure 3.31: Spectrum **1.1**, acquired from the maximum values of the chemical map **a$_{p1}$** (intensity from 861 to 1263 cm^{-1}).

3.2.5 Binder and other organic components

Analysis of the binder, in the ground and paint layers, showed the presence of a drying oil. Considering the condition of the painting and the importance of the binder and possible organic materials present, the results will be discussed in this section for each analytical technique applied.

3.2.5.1 FTIR

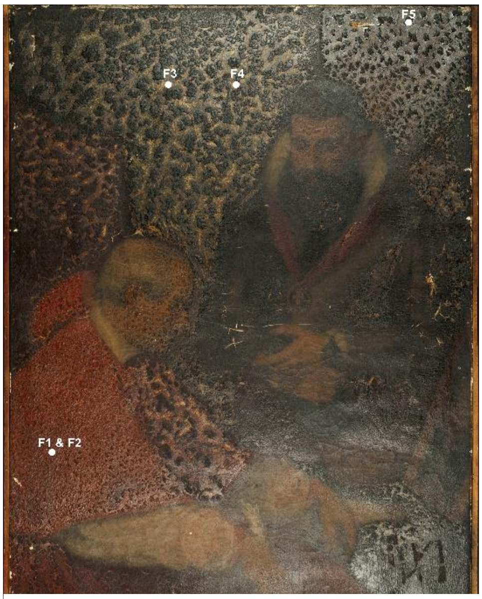

Figure 3.32: Mapping of micro samples for µ-FTIR analyses.

Table 3.7: Identification of the micro sample codes, colour and sampling location.

Code	Description	Sampling location (Left/Right side and Top/Bottom distance)
F1	Red, glossy exudate	L.S. 9.4 cm; B. 39.5 cm
F2	Red paint (paint island)	L.S. 9.4 cm; B. 39.5 cm
F3	Translucent layer	L.S. 33 cm; T. 18 cm
F4	Brown paint (paint island)	L.S. 47.5 cm; T. 18.2 cm
F5	Brown, soft exudate	R.S. 13.2 cm; T. 3.5 cm

µ-FTIR carried out on micro-samples from red and brown paints (Figure 3.32 and Table 3.7) confirms the presence of oil as a binder (Figure 3.33) with characteristic peaks at 2928 and 2855 cm^{-1} assigned to the C-H stretching vibrations and a carbonyl band that appeared shifted from the expected 1740 cm^{-1} to lower wavelengths with values between 1715 and 1700 cm^{-1}. This shift to lower wavelengths with values in the 1715 and 1700 cm^{-1} region, characteristic of acidic fractions, could be inferred to be a sign of a high degree of hydrolysis of the oil (J. van den Berg 2002; van der Weerd, van Loon, and Boon 2005; de Viguerie et al. 2016). This shift is also commonly associated in the literature with a mixture of oil and resin (Joseph et al. 2010) or an indication of the presence of a natural resin (such as mastic or dammar) (Derrick, Stulik, and Landry 1999, 107). It could be that the artist may have used a mixture of oil and resin (such as the Medium Megilp) in the paint binder. However, as shown below, analyses with Py-TMAH-GC/MS do not support this assumption as no evidence of resin was found with these techniques, which appears to confirm the sole presence of a degraded drying oil.

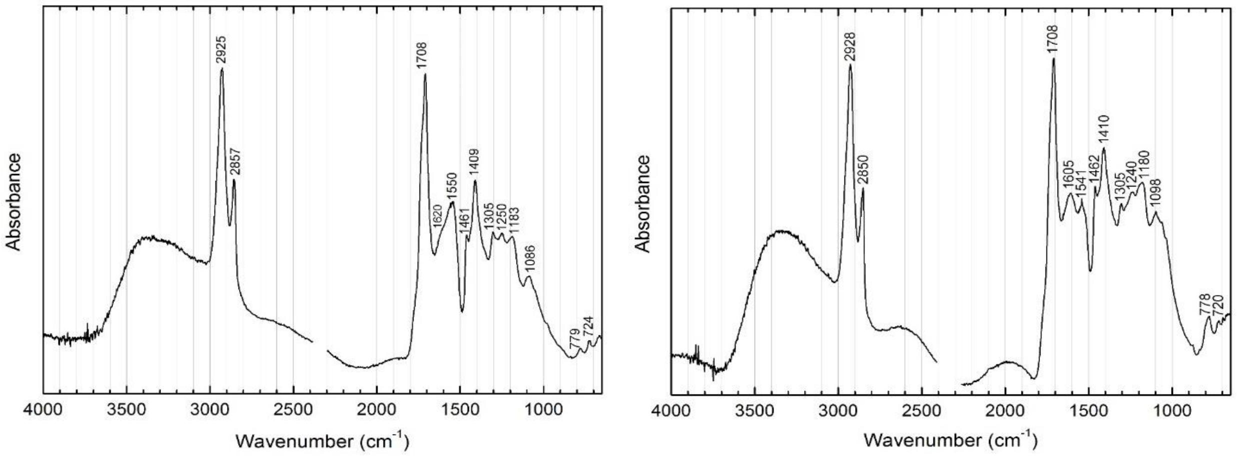

Figure 3.33 - µ-FTIR spectra from the bulk paint layer of red paint (left, and F1 in Figure 3.32) and brown paint (right, and F4 in Figure 3.32).

Both paint layers and exudates (softer material to the touch) (Figure 3.34) were analysed with µ-FTIR and Py-TMAH-GC/MS. Once again the results point to a drying oil with a high degree of oxidation. The main difference between the paint and the exudates (F1 and F2 in Figure 3.32) is in the range of 1655 – 1480 cm^{-1} (Figure 3.34, yellow stripe), which is the region for metal carboxylate soaps (Corkery 1998; Osmond et al. 2012). The preponderance of values in this region in the samples from exudates are most likely due to the presence of lead soaps. The presence of lead in the paint layers as a possible siccative compound was identified with SEM (see C.8.1, page 292, Appendix C). However considering the detection of Zn in the matrix as well as Al, Ca, K and Hg from the pigment particles, other metal carboxylates may be present. For example Keune et al. have suggested "aluminium carboxylate-containing compounds" based on a broad band at 1610cm^{-1} in FTIR analyses of cochineal lake paint reconstructions (Keune et al. 2008). In this case, due to the shifting, overlapping, and broadening of the peaks in FTIR further discrimination is not possible.

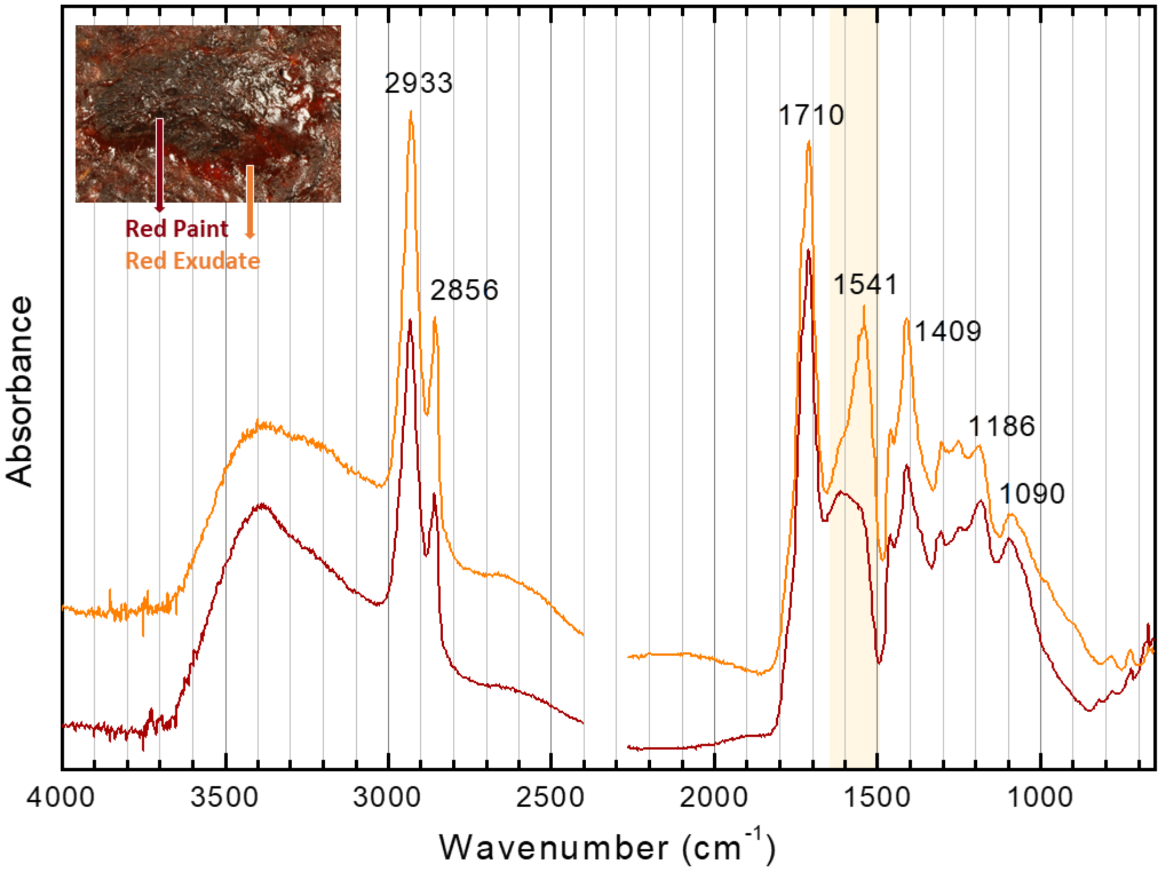

Figure 3.34: µ-FTIR spectra from the bulk of the red paint layer (in red) and the red exudate (in orange). Region of metal carboxylates marked in light yellow.

3.2.5.2 TOF-SIMS

TOF-SIMS imaging confirmed the presence of oil, saponified to some extent, through the co-localized detection of fragment ions coming from both oil and lead carboxylates in both polarities (Figure 3.36 c and d). This technique also allowed further investigation of the metal carboxylates distribution in the stratigraphy, through the images of lead carboxylates (palmitate and stearate) and carboxylates ions, that would originate from the metal soaps. The combined results on the brown paint samples S7, S19 and on S27 (red paint), interestingly demonstrate that lead carboxylates (P and S) are concentrated, for the three samples, in round-shaped regions of about 10-20 µm diameter found in the dark layer above the translucent one (and below the distorted ones in S19 and S27), as shown in Figure 3.35 b), Figure 3.36 and Figure 3.37. Aluminum palmitate could also be detected in a single round shaped region in S7. The presence of aluminum carboxylates would explain the shift observed in the carboxylate characteristic bands in ATR-FTIR microscopy which appear at 1587 and 1460 cm^{-1} notably in the top layer of S7 (Figure 3.35 a).

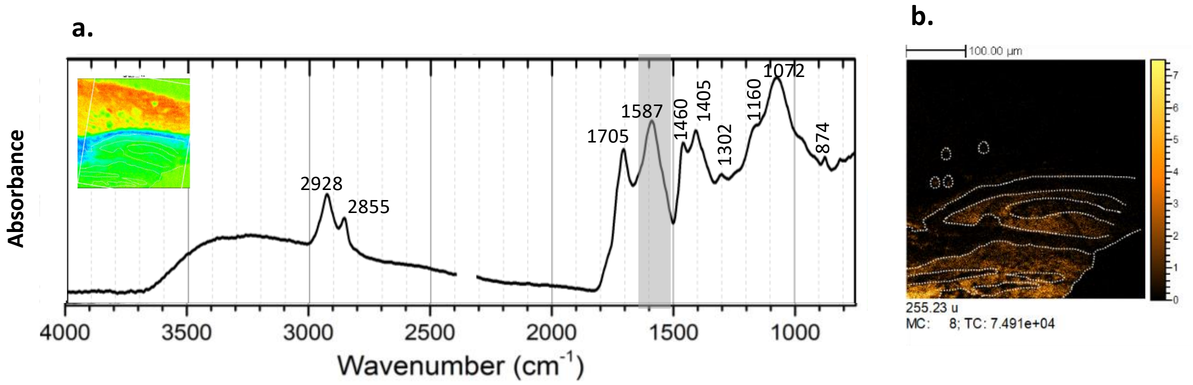

Figure 3.35: FTIR average spectrum acquired in the top paint layer of the brown sample S7 (map obtained by integrating the signal, intensity from 1663 to 1501 cm-1) (a); TOF-SIMS image for palmitate ion in the same area (as a.) of sample S7 (b).

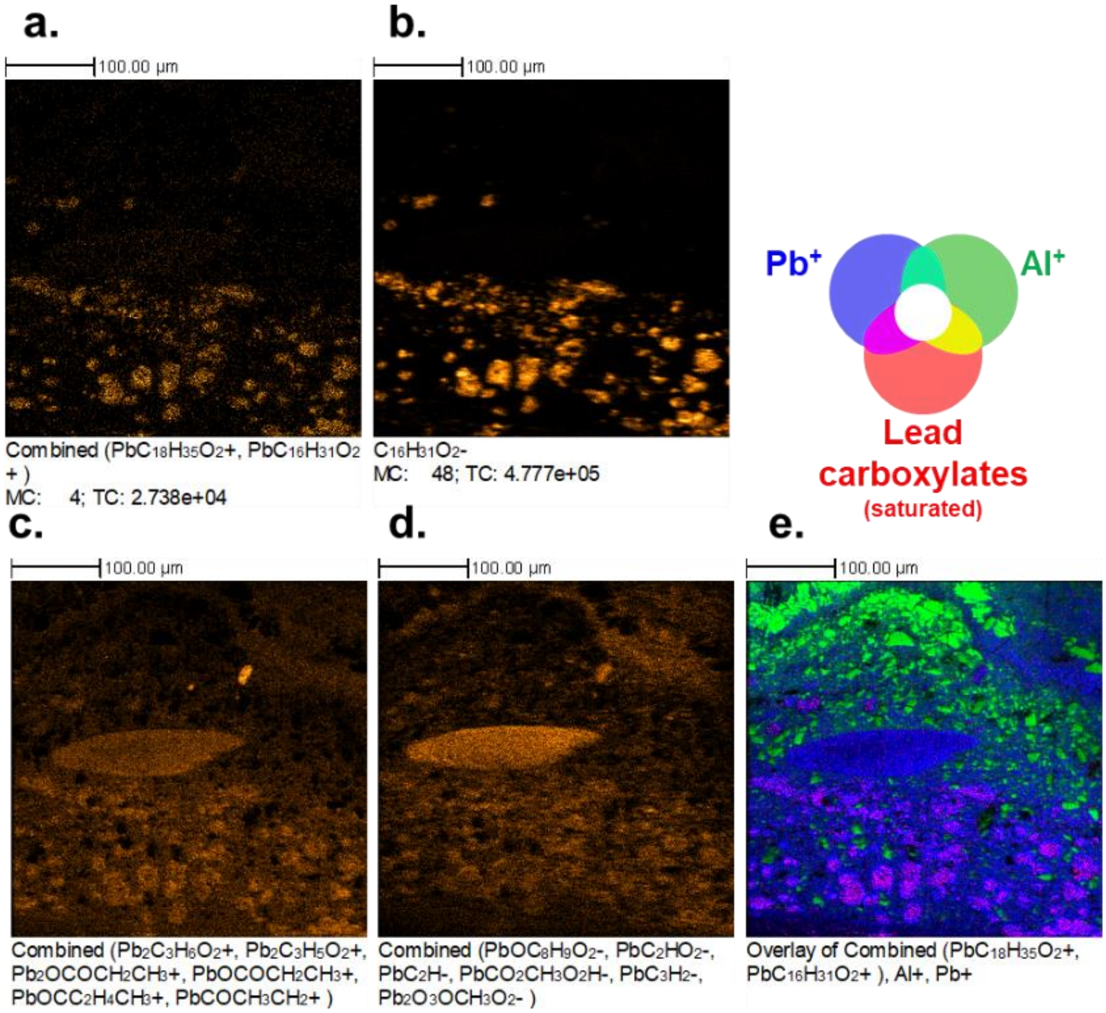

Figure 3.36: TOF-SIMS images for sample S19 of lead carboxylates (stearate $PbC_{18}H_{35}O_2^+$ and palmitate $PbC_{16}H_{31}O_2^+$) (a), palmitate ion ($C_{16}H_{31}O_2^-$) (b), fragment ions coming from saponified oil in positive (c) and negative polarities (d), and three colour overlay of lead carboxylates (in red), aluminium ion (in green) and lead ion (in blue) (e).

No characteristic ions for resin or other additional organic compounds were identified in the paint layers of the three cross-sections (S7, S19 and S27) analysed with TOF-SIMS. The only exception was the large particle in S19, which is the object of a specific analysis in section 3.3.1. However, as Frame reminded the reader in her paper with the old adage, the absence of evidence is not evidence of absence (Frame 2022). This will be discussed in Chapter 6 regarding the identification of asphalt in oil paint samples.

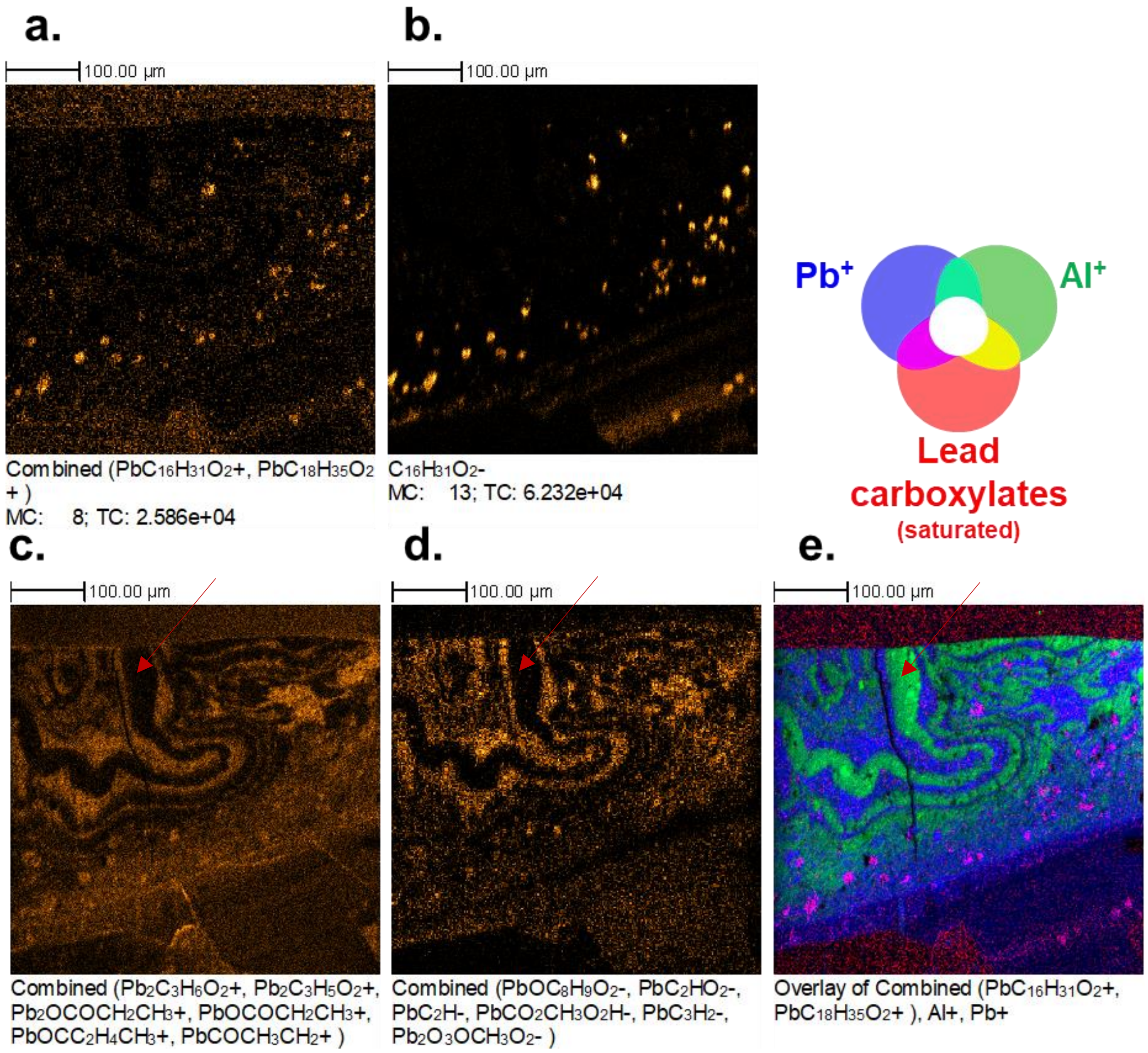

Figure 3.37: TOF-SIMS images for sample S27 of lead carboxylates (stearate $PbC_{18}H_{35}O_2^+$ and palmitate $PbC_{16}H_{31}O_2^+$) (a), palmitate ion ($C_{16}H_{31}O_2^-$) (b), fragment ions coming from of saponified oil in positive (c) and negative polarities (d), and three colour overlay of lead carboxylates (in red), aluminium ion (in green) and lead ion (in blue) (e).

In upper layers in some paint sample cross-sections (e.g. S27, Figure 3.37 (marked with the red arrows)), no signal related to oil binder nor resin could be detected. This apparent absence of organic binder may be due to a detection bias, which is likely produced by the presence of aluminium, as shown in the overlay image of Pb and Al ions (Figure 3.37 e). The local chemical environment can impact the detection of given ions and lead is known to foster the fatty acid signal as there is a co-localisation with lead and hydrocarbon chains and small mass fragments from the fatty acids. It can be assumed that aluminium hinders the fatty acid signal. Another hypothesis would be the formation of a strongly polymerised oil with aluminium having a role in the network, such as an ionomer-like structure that would not form the characteristic ions usually expected to confirm the presence of the binder. No additional ions could be identified that would confirm the assumption of the signal being masked by the presence of an ionomer-like structure with aluminium but the mass range did not go above 800 ua, which may be too low to detect fragments of the polymer/ionomer network.

3.2.5.3 Py-TMAH-GC/MS

Samples from the brown and red coloured paint layers (from the bulk of the paint layers and the glossy and soft exudates) were analysed with Py-TMAH-GC/MS (see Table 3.8). Since the results obtained where consistent despite the colour areas, only the brown paint samples will be discussed below.

Table 3.8: Identification of the samples codes, colour or paint layer and sampling location.

Sample Code	Description	Sampling location (Left/Right side and Top/Bottom distance)
Py1	Brown paint	L.S. 47.5 cm; T. 18.2 cm
Py2	Brown, glossy bead and exudate	L.S. 47.4 cm; T. 18.1 cm
Py3	Brown, soft exudate	R.S. 14.2 cm; T. 3.5 cm
Py4	Red, glossy and soft exudate	L.S. 10.4 cm; B. 40.5 cm
Py5	Red paint (from a paint island)	L.S. 10.5 cm; B. 40.6 cm
Py6	Translucent layer (from a tear in the brown background)	L.S. 23 cm; T. 4.3 cm
Py7	White ground layer (ground layer 2)	L.S. 34 cm; T. 18 cm

The main compounds present in the mass chromatograms of samples Py1 and Py2 (brown paint and exudates, respectively) are diacids and fatty acids[120], identified in Figure 3.38 and Figure 3.39. In fact for both samples, Py1 and Py2, saturated short and long-chain fatty acids (F) from C3F up to C26F could be observed along with short-chain diacids (DF) down to C4DF and glycerol compounds (gly) (Figure 3.38, Figure 3.39 and Table C. in Appendix C.9, pages 305-306).

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[120] The use of tetramethylammonium hydroxide (TMAH) for derivatisation was the easiest means for comprehensively characterizing their presence. As described by Bonaduce and Andreotti the use of a derivatising agent such as TMAH allows the analysis of glycerolipid materials because it transmethylates the carboxylate groups and thus increases "the detectability of fatty acids and dicarboxylic acids, which may be present in a mature paint film as free acids, metal soaps, as well as esterified with glycerol" (Bonaduce and Andreotti 2009, 308).

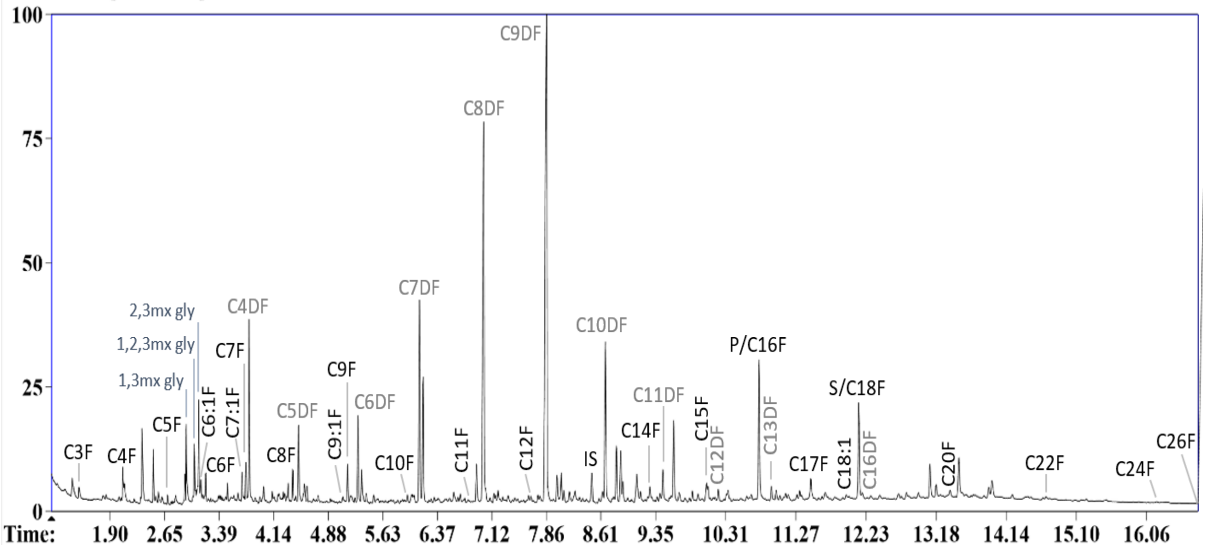

Figure 3.38: Total ion chromatogram of Py1 (brown paint), sample derivatized with TMAH. "F" stands for fatty acids while "DF" for diacids, and "mx gly" identifies the glycerol derivatives.

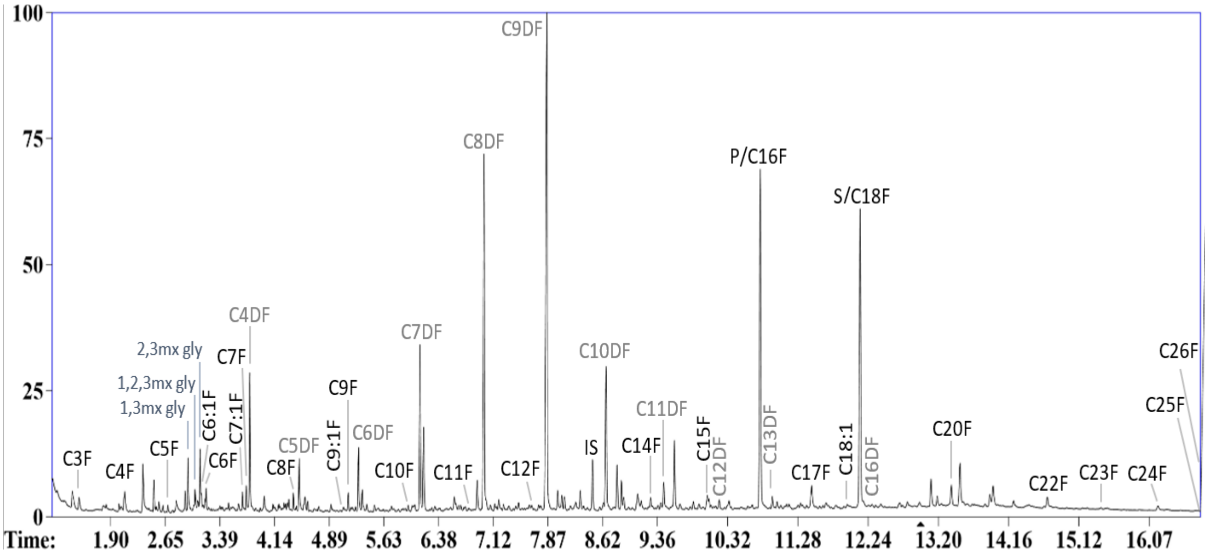

Figure 3.39: Total ion chromatogram of Py2 (brown paint, shinny exudate), sample derivatized with TMAH. "F" stands for fatty acids while "DF" for diacids, and "mx gly" identifies the glycerol derivatives.

For both samples Py1 and Py2 the highest peak belongs to azelaic acid (C9DF), followed in Py1 by the diacids C8DF, C7DF, C4DF, C10DF and the saturated fatty acids C16F and C18F, i.e. palmitic and stearic acid respectively. In Py2 after the C9DF peak, the next highest is the C8DF and the saturated fatty acids C16F and C18F. According to Jorrit van den Berg (2002), diacids are "the relatively stable end products of the oxidation of unsaturated fatty acids", for example, the azelaic acid is a C9 dicarboxylic acid formed upon the oxidation of unsaturated C18 fatty acids and indicates a high degree of oxidation during curing of the paint film (J. van den Berg 2002, 149, 212).

This "high content of dicarboxylic acids with respect to saturated long chain acids" is what distinguishes aged drying oils from non-drying fats (Bonaduce and Andreotti 2009, 308), and, in a mature drying oil, the content of azelaic acid, should be higher or at least equal to the content of palmitic acid (Bonaduce and Andreotti 2009, 308; Mills and White 1987, 142).

Based on the ratios described in the literature, for all samples, the A/P ratio fits within a drying oil while the values from the P/S indicate that it is linseed oil.

The main differences between Py1 (brown paint) and both Py2 and Py3 (glossy and soft exudate of the brown paint, respectively) are the higher amounts of palmitic acid (P/C16F) and stearic acid (S/C18F) in the Py2 and Py3 samples. Samples from the red paint and the glossy exudate from the red paint showed the same tendency, that the exudate has higher amounts of palmitic and stearic acid (see Figures C.9 and C.10 in Appendix C.9, page 307). A similar observation has been reported by Boon and Bronken in their study of dripping oil paints, noting that in a comparison of samples from a stiff (dry) paint and a dripped exudate, “Polar fatty acids and diacids are clearly more prominent” with an “abundance of saturated fatty acids in the exudate”. Boon and Bronken proposed that the polar fractions “can not be accommodated sufficiently in the paint mass and are separated according to a physical mechanism possibly after forming polar micelles i.e. acid groups at the surface and apolar aliphatic chain inside.” (Bronken and Boon 2014a).

No other features were identified in the chromatograms, which would point to the presence of resins, waxes or asphalt. These as discussed in Chapter 1 are materials that could be expected for paintings with alligatoring (see Chapter 1 and Chapter 6 for asphalt). The lack of evidence for resin in particular does not support the suspicion, which resulted from the shifted carbonyl band seen in FTIR, that the glaze-like binder in the top paint layers was made using an oil/resin mixture such as the gel medium Megilp.

3.3 Discussion

3.3.1 Unresolved features

Asphalt/Bitumen

The absence of asphalt markers in the paint samples will be further discussed in Chapter 6, as this research shows that the lack of analytical evidence does not mean that the material is not present.

Further work to determine the best techniques for identifying the presence of materials from the asphalt/bitumen/coal-tar family is necessary as the presence of any one of these compounds may help to explain the complexity of the current visual appearance of the paint.

Fluorescing surface in *O Cardeal D. Henrique…*

Despite the painting's overall fluorescence under UV radiation (see Figure B.9, Appendix B, page 261), and the fluorescent top layer visible in the cross-sections with OM in UV radiation (see section C.4, pages 281-284), that appeared to indicate the presence of a natural resin varnish layer, no resin was detected with Py-TMAH-GC/MS or Py-GC/MS (results not shown) in the samples analysed.

It should be noted that it is extremely unlikely for a 19th century history painting produced in the Academic style not to be varnished. A possible cleaning campaign to remove the original varnish layer cannot be ruled out since there are no condition/treatment reports for the painting. Nevertheless, the caution seen above, that an absence of evidence is not evidence of absence must be kept in mind, as the lack of a natural resin varnish coating on this painting would be highly unusual, but the lack of instrumental evidence for a specific material in a complex aged matrix may not be highly unusual.

There are other possibilities to explain the fluorescence at the surface of the painting which do not involve a natural resin varnish being present. For example, fluorescence has also been associated with medium rich surfaces[121], and as shown in section 3.2.3 the paint layers present strong fluorescence. Also, Bronken and Boon (2014) caution that the fluorescence of exuding materials "can be misinterpret[ed] as a local varnish" (Bronken and Boon 2014a).

During this research the fluorescence of several sources of asphalt (not shown) and of the paint reconstructions of "W&N Bitumen Oil Paint" (see Chapter 5) have also been investigated. Further research following a protocol that can account for relevant variables should be undertaken, but preliminary results have shown a strong fluorescence from natural sources of asphalt (such as Trinidad Lake Asphalt) under UV radiation.

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[121] Carlyle has recorded strong surface fluorescence in brown/black oil paint reconstructions which contain only linseed oil and pigment (Carlyle, personal communication, November 2022).

Large Particle in S19

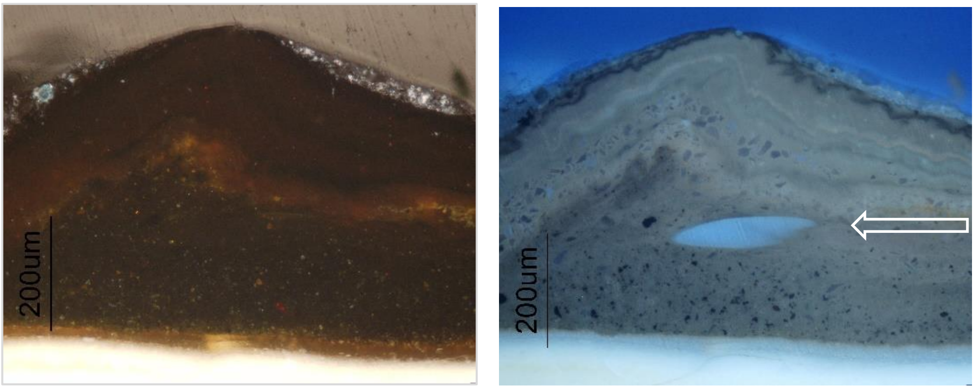

Figure 3.40: Detail from cross-section S19 in reflected light microscopy under cross-polarised light (left) and UV radiation (right). The white arrow points to the large fluorescent particle.

Due to it's anomalous appearance, large size (approximately 200 μm), and strong fluorescence in UV, the large particle (Figure 3.40, white arrow) seen in brown paint sample S19 was analysed with multiple techniques. EDX point analysis at three different points showed that its main constituents are N, S, C and O.

TOF-SIMS analysis gave ambiguous results, detecting a series of organic ions containing sulphur and nitrogen, and positive ion distributions for Pb^+, KSO_2H^+, Na^+ which suggested a structure inside the particle (such as mineral core surrounded by organic matter)[122]. In the search for evidence of asphalt in the samples, the signal was compared to asphalt/bitumen references and the same ions were found to be present.

Because the markers associated with asphalt/bitumen are also very common for other materials, no conclusion could be obtained solely from TOF-SIMS analysis. In fact, there are also other materials of interest such as proteinaceous compounds which do not produce specific markers. This is not only because protein itself degrades, but also because TOF-SIMS imaging is only able to detect amino acids fragments (which are fragments of fragments of the protein), since the technique itself results in most large molecules like proteins being broken down during or after the impact of the primary ions[123].

In an effort to further clarify the particle's composition, it was extracted from the embedded cross-section and analysed by μ-FTIR in transmission mode with a diamond cell[124]. The spectrum (Figure 3.41) shows a very low CH band and a very high amide band, pointing to a proteinaceous material.

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[122] Marques, R., Carlyle, L., De Viguerie, L., Pombo Cardoso, I., Cotte, M., Bouvier, C., Brunelle, A. 2021. *Unraveling complex cross-sections using FTIR imaging and TOF-SIMS analysis.* [Poster]. ICOM-CC Conference, 17-21 May 2021, Beijing.

[123] (Bouvier, C., and Brunelle, A., personal communication 2022).

[124] Probably due to a strong difference in hardness between the paint matrix and the particle, no ATR-FTIR map could be obtained of the area surrounding the particle.

The signal for Amide -CONH- is confirmed by the Amide I at 1653cm^{-1} (ν C=O), Amide II near 1537cm^{-1} (δ C-N-H), Amide III at 1452cm^{-1} (δ C-H), and ν N-H at about 3303cm^{-1}(Derrick, Stulik, and Landry 1999).

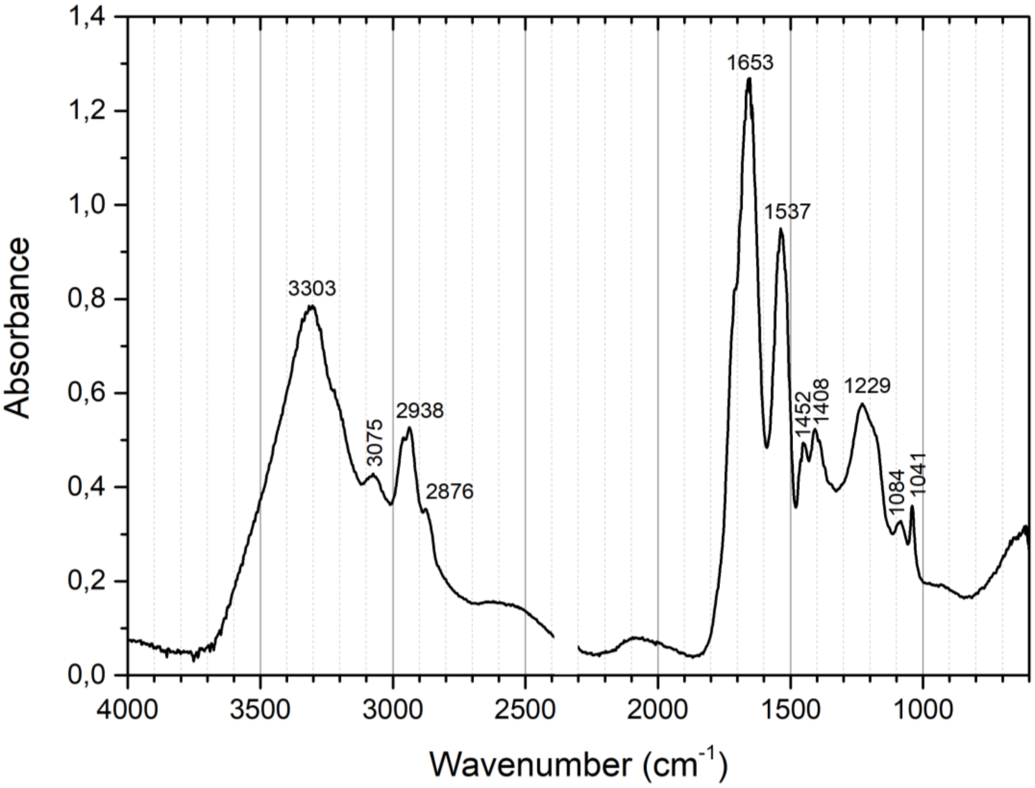

Figure 3.41: μ-FTIR spectrum from the large particle in S19.

Several sources of protein can find their way into a paintings composition, either intentionally or as contamination, such as paint brush hairs, animal-based fibres such as wool, and glue or egg (although both glue and egg have characteristic reference markers/signal which would likely be evident).

One hypothesis for the presence of protein in this sample, given the substantial presence of lake pigments, would be casein from milk used in the lake pigment manufacture which was used to provide calcium ions (Vitorino 2020, 29). Vitorino through her reconstructions of W&N 19th century cochineal lake pigments, has shown that protein is still detected by FTIR in the final pigment if during manufacturing the filtration step after the addition of milk is not performed (Vitorino 2020, 40). However the likelihood of the particle consisting of casein is held to be unlikely due to the particle's relatively large size.

Overall the presence of protein does not appear to be a constituent of the brown paint layer since it was not detected in the bulk paint with other techniques such as, μ-FTIR or PY-TMAH-GC/MS.

3.3.2 Paint defects - Alligatoring

Results from the examination and analyses of *O Cardeal D. Henrique…* show several features that can be associated with paint defects both in terms of the artist's technique and the materials present (see Chapter 1).

Regarding the painting technique, the canvas was reused and the current painting sits on top of a lead white - oil ground (Figure 3.42, 3), which was most likely non-absorbent. Oil paint over a non-porous surface can develop a higher proportion of oil at the paint surface as the lower layers cannot absorb it. There is also the presence of the oil-based translucent layer (further preventing absorption of the oil from the paint into the ground) which may have been applied as a sealing layer or to facilitate the spread of fresh paint over the greasy surface of a dried oil ground. It is notable that this layer (Figure 3.42, 4) remained in place and only the paint layers above it have distorted and contracted into paint islands. Another factor associated with the wrinkling and distortion in the upper layers are the many glaze-like paint layers with high binder to pigment ratios. All of this suggests that there is a surplus of oil binder which could have played an important role in the formation of the drying defects.

A scheme (Figure 3.42) based on cross-section S19 (Figure 3.17) shows the paint movement which appears to be consistent with the descriptions in the literature (see Table A.2, e.g. Thompson 1915; Walker and Hickson 1945; White 1986) that the mechanism of paint distortion is due to shrinkage.

The cross-sections from areas of alligatoring in *O Cardeal D. Henrique…* are showing a paint layering system that has been severely disrupted by being pulled into wavy layers likely due to the shrinkage of the top glaze layers (Figure 3.42, 6). The contraction of the top layers appears to have pulled the lower paint layers (Figure 3.42, 5), into paint islands with wrinkled surfaces. This presumes that the paint layers were ductile during this process.

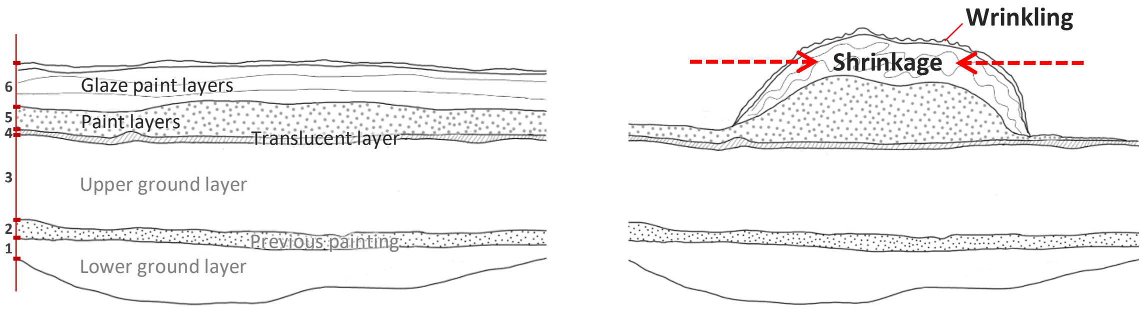

Figure 3.42: Scheme of the paint stratigraphy before (left image) and after (right image) the paint movement. The layers are identified as lower ground layer (1), paint layers from the previous painting (2), the non-absorbent upper ground layer (3), the translucent layer (4) which remains in place and does not get pulled away, and the paint layers (5, 6) where movement occurs with the contraction of the top glaze layers (6).

In terms of materials, the presence of significant quantities of lake pigments in paint passages most affected by alligatoring is notable: lake pigments are notoriously poor dryers and may have contributed to the breakdown of the paint layers (possibly along with the presence of asphalt/bitumen[125]). The gel-like behaviour of oil paints made with lake pigments had been addressed by 18th and 19th century sources which describe lake pigments "fattening" (becoming rubbery) in bladders and paint tubes. As early as 1758 this behaviour was described by Robert Dossie: "By fattening is meant a coagulation of the oil, that frequently happens on its commixture with several kinds of pigments…"[126]. He describes this state as "viscid or glutinous" and notes that "colours, in proportion to their tendency to fatten, are slow in drying; and when the oil once contracts this state, it will be a very long time before it will become duly hard and firm in the paintings" (Dossie 1758, I:6, as cited in Carlyle 2001, 151). For Vibert, writing near the end of the 19th century, this was due to the aluminium base of lake pigments, and he warned that once the paint reaches this state artists should not try to dilute them with "oils or essence" because "they will never dry thoroughly" (Vibert 1892, 74 as cited in Carlyle 2001, 151).

Shimazu (2015) addresses the effect of lake pigments in *La Descente des Vaches* by Théodore Rousseau, a painting suffering from paint defects, writing that the large amount of lake pigments with potassium aluminum sulfate (alum) as a substrate "might have contributed to poor drying conditions of oil components" because this material "has a characteristic feature of releasing protons by hydrolysis" making the paint more acidic, which can be hard to compensate for in dark paints (Shimazu 2015, 169). Van Loon et al. have expressed that pigments such as red lakes, vermilion and vine black are "paints that undergo a high degree of hydrolysis" and "produce many free mono- and di-carboxylic acids, resulting in soft films" as well as being "highly oil-absorbing, resulting in medium-rich paints" (van Loon, Noble, and Burnstock 2021, 222), which could be particularly relevant considering that the most affected areas are indeed mainly composed of organic pigments and poor drying pigments like carbon black or lake pigments.

As for vermilion, Languri had associated vermilion to drying defects since it is "a non-drying pigment" (Languri 2004, 164), but without a reference to corroborate this assessement. However, in 1980, Rasti and Scott had demonstrated that vermilion can accelerate the photo-oxidation of the oil in specific conditions. The authors showned that vermilion inhibits the rate of thermal, normal oxidation; except if exposed to UV radiation where the reverse is true and it sensitizes the oxidation process (Rasti and Scott 1980). The evaluation of paint films by Keune et al. established that "Vermilion and vine black result in films (…) [that are] closest in chemistry and consistency to the non-pigmented film. The films show a high degree of oxidation and contain diacids, but a low fraction of monoacids. These pigments have a low potential to interact with the oil paint medium components" (Keune et al. 2008).

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[125] As noted, in the case of *O Cardeal D. Henrique…* the presence of asphalt/bitumen could not be identified.

[126] Later on Dossie states that this defect is "apt to be found in lake" and if the lake pigment is "found to have this fault, it may be deemed utterly unfit for the use of colourmen." (Dossie 1758, I:63).

This is an interesting finding given the rich presence of vermilion and red lakes in the red paint in *O Cardeal D. Henrique…*.

Another clue lies in the composition of the oil, which the analyses showed has a high degree of oxidation and high amounts of fatty acids and diacis, indicating that the degradative oxidation was favoured over polymerisation. This confirms the previous observation that the pigments used may have enhanced the hydrolysis of the oil binder, providing further information about the degradation mechanism (Burnstock and K. J. van den Berg 2014, 7). Since the paint film has both a large amount of polar compounds, which are unlikely to form a stable network, and a lack of pigments which would be able to stabilise it. In addition to this abundance of polar compounds which are not stable in the paint, is the overall presence of metal carboxylates, dispersed or grouped in several regions: lead azelate in the translucent layer, lead monocarboxylates (such as lead palmitate or stearate) in some round-shaped regions and in the exudates. Monocarboxylates, being more mobile and less stable that lead azelate, have likely migrated within the aged paint layers and could be detected in all paint layers. As “monocarboxylic acids can only act as chain terminating units" (Boon and Ferreira 2006), high amounts of monocarboxylates also indicate an increase of polarity of the paint film, possibly preventing the formation of a stable 3D network. One has also to note the presence of aluminium soaps that could also contribute to this effect.

Similar chemical features have been reported for dripping paints from the 1950's, which to some extent can be used as a comparison to understand the process involved in the paint degradation in *O Cardeal D. Henrique…*. The importance of pigments for the stabilization of the paint was noted by Bronken and Boon, when analysing dripping paintings, reporting that the softer paints were mainly composed by "organic pigments and pigments, like cobalt blue or bone black" (Bronken and Boon 2014a). To some extent this seems to fit well with the paint composition of *O Cardeal D. Henrique…* where the presence of lake pigments is prominent and the glaze-like paint layers are medium rich. The high concentrations of diacids compared to saturated straight chain fatty acids (mainly P/C16F and S/C18F) and the series of oxidised S/C18F (oxy and hydroxy C18F) were described as an indication of the oxidation processes in the paint film. This failure to anchor the chemically changing medium as it is drying and ageing could explain an increase in fluidity of the paint film.

3.4 Conclusions based on paint material analyses

For the first time a full examination and technical analysis was performed on a painting by Marciano Henriques da Silva. The characterization of materials and techniques using a multi-analytical approach was fundamental for gaining insight onto the complex paint stratigraphies in *O Cardeal D.*

Henrique… but also revealed analytical difficulties and limitations that should be seen as future opportunities for research.

Imaging techniques such as ATR-FTIR Microscopy and TOF-SIMS have proven useful, not only in the identification of the materials but particularly for identifying their location within the paint structure. However precautions should be considered when interpreting TOF-SIMS results from complex paint stratigraphies. Since the data represents a large amount of information collected, the interpretation, particularly pertaining to organic ions which can come from a multitude of possible compounds in the paint samples, may be hampered by ambiguities worthy of further discussion. As shown in this case, although based on reference standards from a TOF-SIMS database (carried out in the LAMS laboratory on a wide range of paint materials), the identification of compounds is not necessarily unequivocal and detection limitations can create biased results.

Regarding the results of the painting *O Cardeal D. Henrique…*, the multi-analytical approach identified the presence of significant quantities of lake pigments in paint regions most affected by alligatoring, as well as metal carboxylates. In terms of degradation mechanism it can already be assumed that the deterioration of the painting is related to the abundance of polar compounds in the paint layers, the oil probably being heavily hydrolysed combined with a lack of pigments capable of stabilizing it. The unexpected presence of a stable lead azelate layer underlines further the complexity of the mechanisms at stake.

These factors may explain the alligatoring phenomenon to some extent, however a full characterisation of the organic compounds remain challenging and the analytical techniques used did not identify the presence of significant materials thought to be associated with alligatoring such as asphalt/bitumen. To better understand and interpret these results, a study of the British 19th century colourman, Winsor and Newton's pigment and paint production records was made to investigate and analyse their method of manufacture of Bitumen Brown oil paint. Based on the analyses of their production records reconstructions of 19th century asphalt/bitumen oil paint were prepared to understand how their Bitumen Brown paint was processed during preparation and to serve as analytical reference samples (see Part 2 - Chapters 4, 5 and 6).

PART II

WINSOR & NEWTON'S 19TH CENTURY BITUMEN OIL PAINT

Marques, Raquel, Leslie Carlyle, Laurence De Viguerie, Isabel Pombo Cardoso, and Jaap J. Boon. 2022a. 'Winsor & Newton's 19th-Century Bitumen Brown Oil Paint. Part I: A Critical Analysis of W&N Production Records'. In *Reflecting on Reconstructions, The Role of Sources and Performa-tive Methods in Art Technological Studies. Proceedings of the Eighth Symposium of the ICOM-CC Working Group ATSR, Held at the Cologne Institute of Conservation Sciences, 26-27 September 2019*, edited by Doris Oltrogge, Joyce H. Townsend, Anne Haack-Christensen, and Maartje Stols-Witlox, 49–64. ICOM-CC. https://www.icom-cc-publications-online.org/4607/Winsor--Newtons-19th-century-bitumen-brown-oil-paint-Part-I--a-critical-analysis-of-WN-production-records-

4

A CRITICAL ANALYSIS OF W&N PRODUCTION RECORDS

4.1 Abstract

"Alligatoring" or “Bitumen Cracking” describes an extreme paint defect which affects many 19th century oil paintings and was thought to be the result of employing bitumen or asphalt. The British colourman Winsor & Newton’s (W&N) 19th-century archive contains 25 production records for their “Bitumen for Oil Tubes”. While recipes for bitumen/asphaltum brown were published in 19th-century artists’ manuals, W&N’s records offer a unique source of detailed information on their commercially prepared product which differs substantially in ingredients and method of preparation from artists’ recipes. This chapter reports on W&N’s Bitumen oil paint production which reveals two separate steps, heat processing followed by the addition of a very high proportion of the gelled painter’s Medium, Megilp. In addition to raw materials, they incorporated other products that they were already making and selling. The W&N formulation, which became standardised in the 1850s, is compared with the published artists’ recipes. Based on the findings in Chapter 4, a production record from 1858 was reconstructed with historically appropriate materials and is described in Chapter 5.

4.2 Introduction

A significant number of 19th-century oil paintings exhibit severely disfiguring drying cracks and surface distortions. Reported to develop some years after completion, the problem has been associated with the use of bitumen, hence the name “bitumen cracking” (White 1986; Carlyle and Southall 1993;

Languri 2004; Costaras 2017). Paintings affected are found in many collections world-wide with no clear understanding of the materials and mechanisms which contribute to this phenomenon.

Despite the association with bitumen or asphaltum, (the terms were used interchangeably in 19th century Britain)[127], the actual ingredients and processing of bitumen-based oil paint has not been comprehensively studied. This chapter investigates the British colourman Winsor & Newton's (W&N) 19th century manufacture of their bitumen oil paint and compares it with recipes for bitumen or asphaltum brown published in British 19th century artist's manuals.

Because W&N's production records for a given product have multiple names, the convention has been adopted in this thesis of referring to a W&N product by one name, which is capitalised and appears in italics, for example *Bitumen* or *Strong Drying Oil*. Where the actual name in the record is referred to, it is placed in quotation marks.

Production records for W&N's *Bitumen* were accessed through the *Researcher's Edition of the W&N 19th-century Archive Database*[128] (Clarke and Carlyle 2005a; 2005b; Otero 2018; Carlyle 2020). The company combined other products in their formulation: *Strong Drying Oil*, *Double Mastic Varnish*, *Burnt Sugar of Lead* and *Deep Purple Lake*, all of which appear in separate production records (see Appendix D, pages 309-316).

Records are absent between 1846 and 1850 and the last production record is 1858 despite this product being listed in their sales catalogues until the end of the century (Carlyle 2001, 533). Gaps in the archive have also been identified by other researchers, for example Otero (2018).

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[127] On 19th century use see Carlyle (2001, 479). Terms such as "bitumen", "asphalt" and "tar" are still used interchangeably to describe "certain black, semi-solid mixtures of hydrocarbons" (Hsu and Robinson 2019, 6). In the USA bitumen produced by crude oil refining is known as "asphalt" or "asphalt binder" while outside the US it is called "bitumen" or "refined bitumen" (Hsu and Robinson 2019, 6; Hunter, Self, and Read 2015, 4); in Europe "asphalt" refers to a mixture of "bitumen and aggregate" (Hunter, Self, and Read 2015, 6). The Shell Company's Bitumen Handbook offers greater precision, referring to "bitumen" as a "refined bitumen, a hydrocarbon product produced by removing the lighter fractions (such as liquid petroleum gas, petrol and diesel) from crude oil during refining process." The handbook notes that the hydrocarbon product "should not be confused with natural or lake asphalt such as Trinidad Lake Asphalt, Gilsonite, rock asphalt and Selenice", because "these products are unrefined and not produced by refining of crude oil" and often contain "a high proportion of mineral matter (up to 37% by weight) and light components, leading to a higher loss of mass when heated." (Hunter, Self, and Read 2015, 4).

[128] The W&N 19th-century Archive Database project was initiated as part of the De Mayerne Programme funded by the Netherlands Organisation for Scientific Research (NWO). The Pilot Project which resulted was then developed further in the UK with a two-year Arts and Humanities Research Council (AHRC) Resource Enhancement Grant. The final Researchers Edition of this page-image database has been extensively described elsewhere (Clarke and Carlyle 2005a; 2005b; Otero 2018; Carlyle 2020).

W&N’s catalogues: bitumen and asphaltum products

In their catalogues from 1846 to 1900[129] both “Bitumen” and “Asphaltum” appear in their list of oil colours (Carlyle 2001, 533; W&N Archive Database: Catalogues). It is unclear whether these products differed; however, colourmen were accustomed to listing separate names for the same product[130]. By 1896 W&N identified them as synonymous (W&N Archive Database: Catalogues).

W&N also sold “Asphaltum in pots” under “Mediums and Varnishes” until c.1868 (Carlyle 2001, 337; W&N Archive Database: Catalogues)[131]. Salter’s comment that “It is common to call the solution in turpentine *asphaltum*, and the mixture with drying oil, *bitumen* …” (Salter 1869, 337–38) offers one explanation, and as will be seen the investigation of the production records has led to other possible interpretations.

4.3 W&N’s production records

Despite records being entitled “Bitumen for Oil Tubes” or just “Bitumen” the material called for is consistently listed as “Asphaltum”. While the archive contains other references to both terms, a clear distinction between the two was not found.

The asphaltum is described variously as “Foreign Asphaltum”, “Old Black Sort”, “Old Dark Sort”, “Egyptian Asphaltum” and “Original Egyptian Asphaltum”. By the 1850s that used most regularly was identified according to the supplier “S D” [Sarah Druke][132] from whom they purchased two kinds: the

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[129] W&N’s catalogue collection contains significant gaps and not all catalogues are dated (likely dates, designated with “*circa*”, were assigned according to the products being sold (Carlyle 2001, 277–78). As a consequence, it is usually not possible to establish a firm date of introduction, since the first appearance in a catalogue may be preceded by a large gap between it and the previous catalogue.

[130] “In trade catalogues several names are often given to one and the same pigment. This seeming superfluity is rendered necessary through some artists knowing a pigment by one name and some by another. Hence arises the value of a list of synonyms.” (Salter 1869, 145).

[131] “Liquid Asphaltum for water colours” (HSP131L01) was also found in the W&N archive however it did not contain asphaltum but refers to extracting colour from the madder root with potash then calcining the liquid to achieve a “fine deep brown tint” (it is unclear if other steps were involved in preparing this product for sale). In this case the term asphaltum is referring to a brown colour, not the material itself.

[132] The identity of S D was established by other references to an “S Druke” selling asphaltum (P2P115A). Thanks to the work of Jacob Simon and his *British Artists’ Suppliers 1650–1950* database, https://www.npg.org.uk/research/programmes/directory-of-suppliers.php (Simon n.d.), and to contributions by Sally Woodcock (Woodcock and Churchman 1997), much is now known about Sarah Druke and her business as a colour and materials merchant.

“Brown sort” bought in 1852 (V2P354)[133] and “Egyptian Asphaltum” bought in 1857 (V2P465)[134]. The company regularly mixed both types together in a single batch.

The archive database contains 25 production records for *Bitumen* oil paint[135]. By colour coding ingredients, changes in formulations are immediately visible (Table 4.1). In contrast to the early records which show a wide range of materials, by 1850 and through to 1858 the ingredients have been standardised.

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[133] The coding system designed for the *W&N 19th-century Archive Database* to identify page images and production records is used throughout this paper. Production records are identified by locator codes which indicate the beginning page for the recipe: e.g. V2 refers to the bound MS and P354 is the page (P) number. (The company used their own number codes placed in square brackets within their MS records, these refer to other materials and products in the archive. The database was designed to make the records designated by W&N’s own number codes easily accessible).

[134] Whereas “Egyptian Asphaltum” is not always associated with the name Druke, entries listing the “Brown Sort” consistently refer to S Druke, with one exception in 1855 where “Brown sort” appears without further information (V2P403).

[135] See Appendix D, Tables D.1 and D.2, pages 309-310.

Table 4.1: W&N *Bitumen* production records with ingredient colour coded. The standardisation of their formulation 1850-1858 is clearly visible. Each column represents one production record.

Asphaltum	■	■	■	■	■	■	■	■			■	■	■	■	■	■	■	■	■	■	■	■	■
Drying Oil	■	■		■	■	■	■	■	■	■	■			■	■	■	■	■	■	■	■	■	■
Turps		■	■	■	■	■								■	■	■	■	■	■	■	■	■	■
Double Mastic Varnish				■	■	■		■			■			■	■	■	■	■	■	■	■	■	■
Sugar of Lead												■	■	■	■	■	■	■	■	■	■	■	■
Purple Lake														■	■	■	■	■	■	■	■	■	■
Megilp							■	■						■		■			■	■	■	■	■
Dragon's Blood	■				■	■	■	■			■	■	■										
Japan Gold Size		■	■	■		■						■											
White Wax		■	■	■								■											
Burnt Copperas		■	■		■	■																	
Bitumen						■			■	■													
Linseed Oil			■									■	■										
Baker's Black Japan							■	■			■												
Beeswax									■	■	■												
Litharge												■	■										
Red Lead												■	■										
Venice Turpentine	■																						
Gum Mastic	■																						
Baker's Carriage Varnish							■																
Shellac	■																						
Boiled Oil	■																						
	1834	1844					1845				1846			1850	1851	1853	1855			1857		1858	
	W&N (1st set: from 1834 to 1846)													**W&N (2nd set: from 1850 to 1858)**									

W&N’s *Bitumen* was prepared in two steps (Figure 4.1): materials were first heat processed at their factory in Kentish Town (KT), then that product was sent to their premises in Rathbone Place (RP) in central London, where further ingredients were added prior to its being put into oil tubes (Figure 4.2).[136]

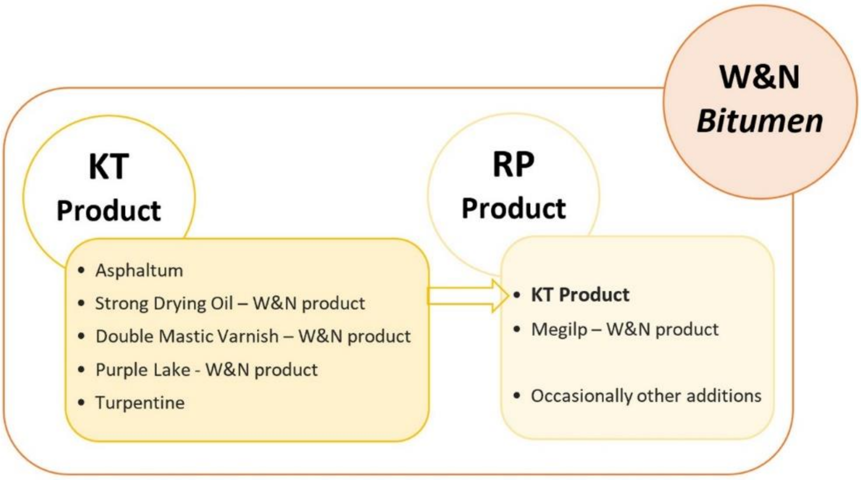

Figure 4.1: Summary of the steps in the production of W&N’s *Bitumen*.

Figure 4.2: a) Illustration of the Kentish Town factory (reproduced from Staples and Pavey 1984, 28), and b) Rathbone Place (reproduced from Harley 1975, 14)

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[136] In the archive “KT” refers to Kentish Town, the location of W&N’s purpose-built steam powdered factory (Harley 1975, 4), known as “The North London Colour Works” which opened in 1844 (Staples and Pavey 1984, 28). “RP” refers to “Rathbone Place” the commercial premises where they also undertook product preparations.

4.3.1 Step one: the Kentish Town product

The KT product was prepared in separate batches (“pots”) typically calling for 4 lbs of asphaltum at a time. Each batch took about 2 hours to prepare, with 4 batches produced in a day. A complete production run could consist of 12 batches over a total of 3 days (P2P116A[137]).

Table 4.2 compares the proportion of ingredients used in each batch once the formulation had become standardised between 1850 and 1858. The greatest variability is in the amounts of *Burnt Sugar of Lead* (lead acetate ground in oil) and *Purple Lake* (also ground in oil). The additions of larger amounts of lead acetate between 1851 and 1855 may reflect efforts to influence drying time as the records indicate this was a frequent concern. After 1857 the quantities were much reduced. In the last three records, the amount of *Strong Drying Oil* was increased, perhaps to compensate for the reduction in lead acetate. In the last two records, as the proportion of drying oil goes up, the amount of *Double Mastic Varnish* goes down; there is no explanation given.

There is a trend of increasing the proportion of *Purple Lake* between 1853 to 1857. In 1857 the increase was due to the *Purple Lake* being “not so strong as our usual kind, hence we were obliged to use more of it” (X7P081).

The use of “Turpentine” (or “*Turps*”) is very consistent throughout.

Table 4.2: Ingredients and amounts for a single batch of *Bitumen*, 1850 to 1858 (repeated records are not shown).

				Asphaltum	**Strong Drying Oil**	**Double Mastic Varnish**	**Burnt Sugar of Lead**	**Purple Lake**	**Turpentine (Turps)**	**R's Old Stout Asph.**	**Megilp**
Code	**Date**		**Name**	Pounds	Pints	Pints	Ounces	Ounces	Pint	Pints	
V1P074	1850	24/apr	Bitumen for Tubes	**4**	**8**	**6**	**8**	**3**	**1**		✓
V1P052	1851	11/mar	Bitumen	**4**	**8**	**8**	**32**	**4**	**1**		
V2P261	1853	August	Bitumen for Tubes	**4**	**8**	**8**	**24**	**3**	**1**		✓
X6P139	1853	14/nov	Bitumen	**4**	**8**	**8**	**32**	**6**	**1**		
V2P354	1855	27/mar	Bitumen	**4**	**8**	**8**	**24**	**5,6**	**1**		
V2P403	1855	27/oct	Bitumen	**4**	**8**	**8**	**24**	**6,1**	**1**		✓?
V2P465	1857	-	Bitumen 1st Batch	**4**	**8**	**6**	**16**	**6**	**1,25**		
X7P081	1857	March	Bitumen for Oil Tubes	**4**	**9**	**8**	**16**	**9**	**1**	**6**	✓
V2P493	1858	24/aug	Bitumen	**4**	**10**	**6**	**8**	**8**	**1**		✓
P2P115A	1858	Sept	Bitumen	**4**	**10**	**6**	**8**	**8**	**1**		✓

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[137] As indicated in footnote 133. For example: P2 refers to the bound MS, P116 is the page (P) number, and A is the side of the page where the recipe begins (some books have a single page number for both sides of the open book, A is the left page, B is the right page). For direct quotes or specific information, the exact page number is given since recipes often continue for multiple pages.

4.3.1.1 Ingredients: heat processing and the order of additions

In the early records, the asphaltum by itself was heated until it was liquid prior to the addition of drying oil (e.g. V1P307, 1844). After the 1850s it was always melted into the drying oil at the outset. Initially lead acetate was also included at this stage but later on it was added in a second step. In every record, additional drying oil was added gradually during heat processing while mastic varnish and purple lake were added separately at the end after the pot was removed from the fire. As shown in Figure 4.1 with the exception of the asphaltum and turpentine, the other ingredients had been prepared previously (see Appendix D, pages 309-316).

Records describe “heading up” and “beating down” the mixtures in the pot during heating. One record provides details, “and the whole boiled till it comes 3/4[th] of the way up the pot” and later, “boil up again same way till a white head shows” (1851, V1P052). This white head (foam) was reduced or “beat down” through stirring, but in some cases by removing the pot from the fire or removing some of the mixture with a ladle (X7P083).

An end point for evaluating the state of the mixture and its readiness for further additions was whether it would form “short strings”[138] (P2P115A).

Record X7P082 states that the mixture was cooked over an “open furnace” outside in the yard (Figure 4.3).[139] The fuel was primarily coke[140], with a smaller proportion of coal used when the coke is “getting to rather a dead looking heat”. The record states, “Don’t have too much flame in the fire …”.

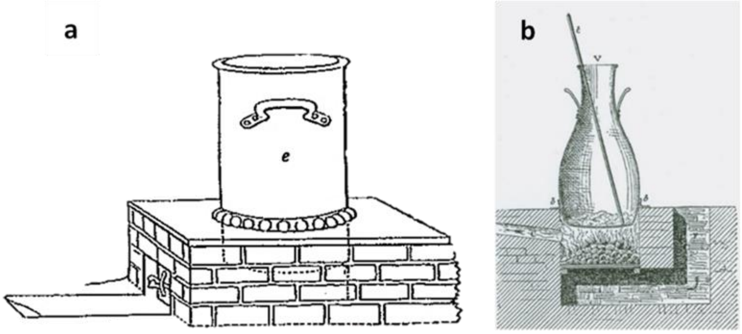

Figure 4.3: An impression of what the fire or furnace and some of the equipment may have been like can be gained from the detailed descriptions and diagrams provided by a) J. Wilson Neil in his treatise on varnish making (Neil 1833, 40), and from illustrations in b) Halphen's Couleurs et Vernis (Halphen 1895, 359).

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[138] The “string” is presumably formed at the end of a stirring stick (described as “an iron stirrer chisel pointed”, X7P082). A short string, will be the relative length of the drip before it breaks, with the remainder falling into the pot.

[139] In record V1P074 the yard is referred to as “the Chrome Yard” presumably also where chromate pigments were prepared.

[140] Coke is “a solid porous fuel that remains after some gases have been driven off from coal by heating; also a similar solid residue left by other materials (e. g. petroleum)” (Longman 1984, 284).

Aside from concerns that the mixture could boil up over the pot, there were also various cautions and warnings regarding the danger of fire. When adding mastic varnish, the mixture should be taken off the fire and the varnish “ought to be put in very carefully from the oil-pouring can used in varnish-making” (P2P116A), see Figure 4.4[141]. In a description of a three-legged iron pot being lifted off of an iron plate which sat over the fire, is the caution “lift the pot carefully out of the plate taking great care that the feet do not catch in the hole…” (X7P083). Numerous records also warn that the turpentine must be handled carefully, “for fear of the steam of the Turps catching fire” (V1P199).

Figure 4.4: Drawing of an oil-pouring can according to images available online.[137]

4.3.1.2 Pouring the mixture into pots

After the mixture of asphaltum, drying oil, and sugar of lead had been heat processed and a final satisfactory string was formed, the pot was taken off the fire for the incorporation of the mastic varnish and purple lake. Then the pot was lifted up over a muslin sieve[142] and its hot contents were poured through into “upright pots” which were filled entirely (X7P083). During the pouring the mixture “runs pretty freely” (X7P083). Dirt and insoluble matter were left behind, caught by the muslin.

This was the final step at KT, as one records instructs: “The whole put in Jars while warm & sent next day to RP -” (V1P237).

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[141] Accessed on 4 November 2019, available in: https://www.picclickimg.com/d/l400/pict/372474394253_/Vintage-Atlantic-1-Qt-Liq-Oil-Pouring-Can.jpg

[142] The record indicates that “A muslin sieve for straining (abt. 10 inches)” should be placed on “An iron varnish ladder” (X7P082). Although no description was given, in view of the risk of fire during varnish and oil preparation the use of an iron ladder rather than one made with wood would be prudent.

4.3.2 Step two: preparations at Rathbone Place

Further additions to the KT product were made at RP to thin the mixture and to influence its working and drying properties prior to being put into oil paint tubes (see Figure 4.5). Additions included one or more of their products: *Megilp*, *Burnt Sugar of Lead*, and *Strong Drying Oil* (see Appendix D).

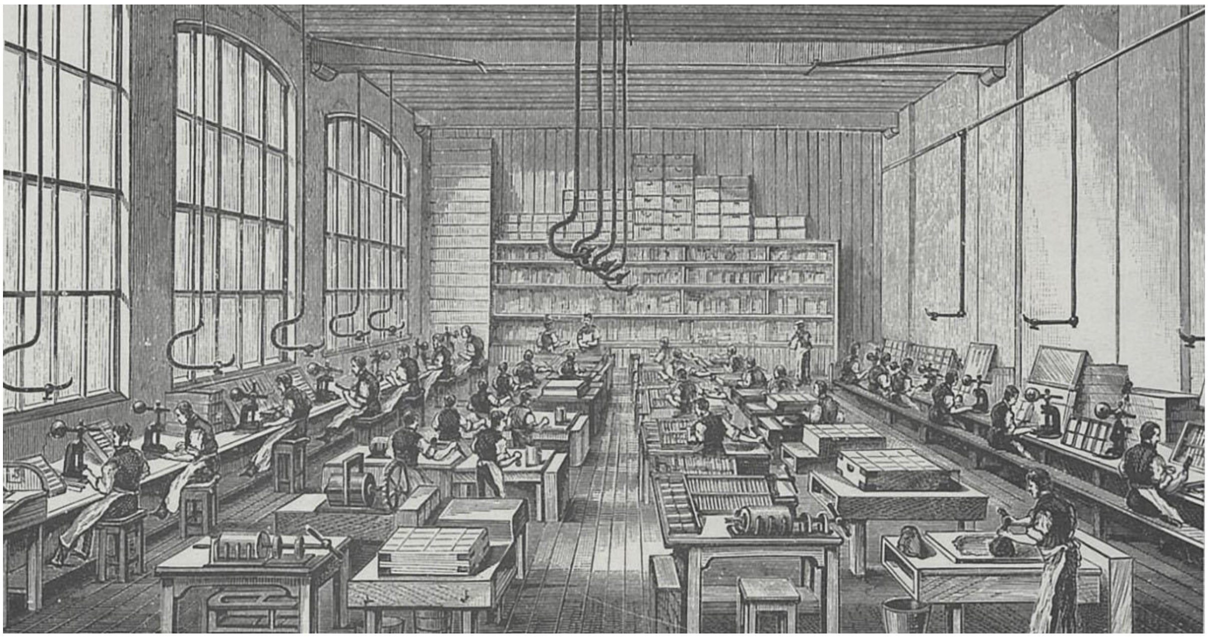

Figure 4.5: W&N's oil-colour tube filling room. Note the worker in the bottom right - on the table there appears to be a grinding slab possibly for further processing of materials prior to putting up in tubes. (reproduced from Staples and Pavey (1984, 29)).

The addition of megilp

The first reference to the incorporation of the painter's gelled Medium[143], "Megilp"[144] was in 1845 (V1P290). By the 1850s (Table 4.2), W&N's *Megilp* was a regular addition at RP in the proportion of one part KT product to one part *Megilp*, apparently for the same reason that it was a popular addition to oil paint since it allowed paints to "…'stand up' or keep their place in working" (Taylor 1890, 33). This echoes a note in V2P404 which states that *Megilp* is one of the essentials in making a good

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[143] In 19th century artist's manuals and handbooks, the term "Medium" (plural "Mediums") refers to an artist's material/product which was added to oil paint to modify its flow properties and appearance (Carlyle 2001, 101). This use of medium and mediums is still current today (https://www.winsornewton.com/na/mediums/oil-mediums/#product-info-mediums). Confusion arises with the general term "medium" with its plural form, "media". For this thesis, to distinguish the product called a medium/mediums, from the general term medium/media, the former has been capitalised. The same option was adopted in the HART Project Report (see Chapter 1 from Carlyle, 2023 (HART Project Report revised edition 2023).

[144] A gel formed by the addition of lead treated drying oil and mastic varnish (see Carlyle and Southall 1993; Townsend et al. 1998; Carlyle 2001; Pasco 2019). A range of gelled painters' Mediums was sold for addition to oil paint (Carlyle 2001).

"Bitumen" since it means that "…the Bitumen may retain shape & not run about". For W&N's *Megilp* production see Appendix D.5, page 315.

4.4 Analysis of the production records: summary of findings

4.4.1 W&N'S changing formulations and the quality of their Bitumen

Formula changes appear to be driven by drying and handling properties as well as colour. The quality of the KT product was evaluated at RP and if found lacking would be adjusted there, or in some cases, was returned to KT for further processing (V1P369). In the earliest records returned batches were re-heated and boiled to reduce the turpentine content and a pre-heated mixture of beeswax and *Strong Drying oil* was added (V1P256, V1P237). Usually, additions were made to improve drying, but in two records from 1845 the product was sent back because it was "…found to be too thin & dried too quickly" (V1P256).

At RP ingredients added to enhance drying included *Sugar of Lead* (V2P262); *Drying Oil* (V2P404);[145] and in one instance the pigment "Cappah Brown" (P1P279B). In another case a mixture of *Drying Oil* and *Megilp* was added to improve the KT product in relation to a competitor's *Bitumen* paint: "When so prepared for Tubes it is as much like Roberson's[146] Tube Bitumen as can well be conceived…[it] can be worked into for hours like Roberson's."(X7P086). The expected drying behaviour of W&N's *Bitumen* was made explicit: "Prepared Bitumen is required to keep wet & free working for 24 hours & then to dry off at once, not wanted to set & become sticky a long while."(P1P278B).

In terms of drying, the source of asphaltum was also influential: "The Brown Bitumen is not so good a dryer as the Egyptian" (P1P277B-278B). This observation led to the recommendation of a higher ratio of the Egyptian, as much as 3 parts to 1 (e.g. V2P493). Boiling time was also important: "Complained of as not drying well – I attribute it to Darling's[147] not having boiled it sufficiently" (V2P355).

Other factors affected drying, such as weather and time: "The weather being only moderately drying the Bitumen did not become dry on the *next day even when rubbed out very thin*"; "Bitumen always improves its drying properties by keeping" (X7P085). The amount of *Purple Lake* added was also held to influence drying (see below).

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[145] Drying oil was also added to thin the KT product (X7P085-86).

[146] The London-based British colourman Roberson was active from 1820 to 1939, see Woodcock (2020). W&N also compared their product's drying time to another competitor, Brown, reporting their product does "not dry sufficiently quick" as did Brown's (1844, V1P305). However, by 1845 their product "dried equally as well" as Brown's (V1P286). The colourman Brown was active in London between 1805 and 1854, see https://www.npg.org.uk/research/programmes/directory-of-suppliers/b/

[147] The database indicates the employee "Darling" was associated with 6 Bitumen records (1849 to 1855) and with 5 pigment records for watercolours and for the preparation of oxgall for pots.

Remarks on consistency indicate that thickness was desired in the KT product: “heat & cool down till it assumes a thick consistence” (V1P194). Handling properties such as retaining the shape of brush work and keeping the brown from running were conferred by the addition of high proportions of *Megilp* at RP, as already discussed.

Regarding colour, the earliest records report “[it] is a very fine tint even better than Brown’s” (V1P305) and a “fine colour not quite [so] red as Brown’s” (V1P286).[148] References to colour consistently begin with an evaluation of hue with terms such as “fullest colour”, “rich colour”, “richer tint”, followed by strength: “weaker in its colouring property”; “weak in colour”; and “strength of colour”. In a comparison with Roberson’s *Bitumen*: “The tint is exact & the strength of colour is the same…” (X7P086).

The source of the asphaltum was reported to influence both hue and tinting strength, for example the “browner kind” which was purchased from S. Druke in August 1852 “did very well as to colour being of a richer tint than the Egyptian but was weaker in its colouring property…” (V2P150).

Based on notes in the production records, *Purple Lake* was added for colour: in 1855 “*Common, Bag C*” purple lake provided “…a “[transparent] & good tint, but not quite so strong as the best” (V2P403). Too much could have a negative impact on drying, “And [next] time use the strongest Purple Lake [,] as this P L [Purple Lake] on [account] of using so much slakens (sic) its drying” (V2P404). In this case “strongest” likely refers to tinting strength since less of a higher strength pigment would be needed (lake pigments were notorious for being slow to dry, see Carlyle (2001, 51, 151)).

4.4.2 W&N’s asphaltum in pots and bitumen in tubes

In the absence of production records in W&N’s archive which refer to W&N’s “Asphaltum in Pots”,[149] the clue to the difference between it and *Bitumen* sold in oil tubes likely resided in their packaging. The KT product made with asphaltum was only ready for oil tubes after *Megilp* had been added at RP. Perhaps “Asphaltum in pots” represents the KT product alone which would presumably have been thicker and therefore more appropriate for sale in small pots. Artists could then add their own modifiers such as *Megilp* or another gelled Medium. Support for this interpretation comes from a letter dated 20 January 1823 by the artist David Wilkie (1785–1841) to his friend the amateur painter Perry Nursey,

> “I have desired Brown to send you a pot of asphaltum, this you are to use by mixing a portion with a palette knife with an equal portion of drying oil and a little japanner’s gold size – all three well mix together, then add to it, a portion of mastic varnish nearly equal to the whole, and mix them rapidly. This will make the

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[148] See foonote 144.

[149] Presumably “Asphaltum in pots” refers to small pots possibly similar in size to those used for Megilp in pots (Carlyle 2001, 278, 337). Records X3P309 & HSP127 indicate Megilp pots had a volume of between 47 to 60 ml.

> finest jelly and is the only way in which asphaltum can be used." (cited in Whitley 1928, II:44)

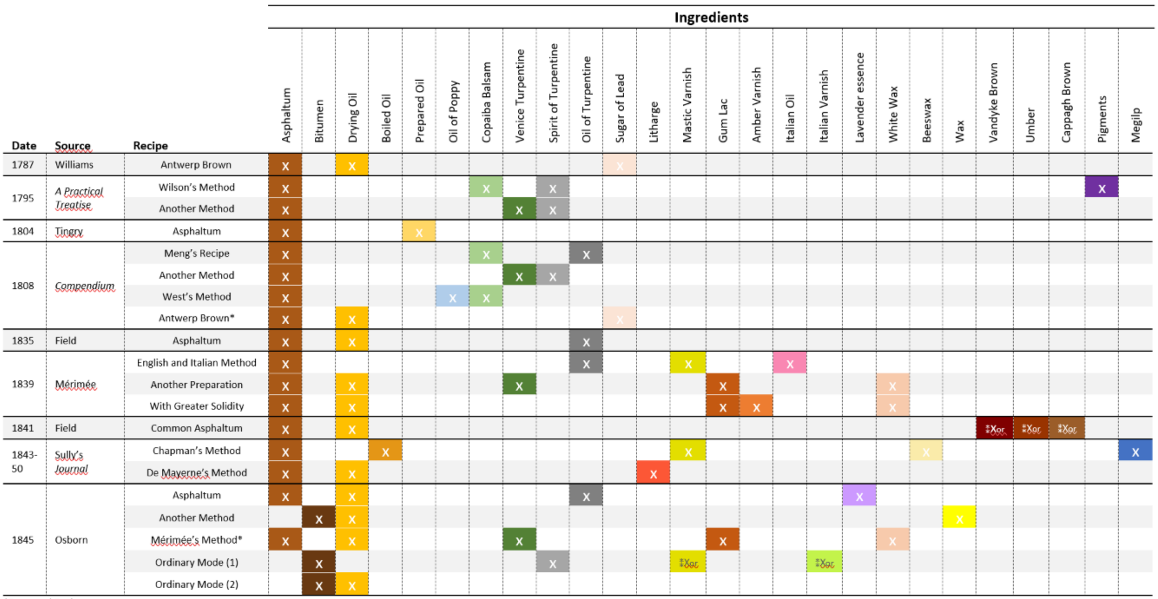
What remains unclear is whether "Asphaltum in pots" was a simple mixture of asphaltum in turpentine as stated by Salter (above), or the complex heat processed material produced at KT (see Conclusions and footnote 149).

4.5 Comparison of W&N's Bitumen with recipes in British artists' manuals

Oil painting manuals and handbooks published in Britain between 1750 and 1900 contain recipes for a transparent brown oil paint made with bitumen/asphaltum (see Carlyle 2001, 403–07, 479–82). Interestingly these instructions are limited to books published up to 1845, perhaps reflecting artists growing reliance on commercial products after this time.

A comparison was made of these recipes and of W&N's *Bitumen* formulations. While no exact recipe was found that could be related to a given production record, W&N's use of a wide variety of materials and the lack of one consistent formula prior to the 1850s is also reflected in the published sources (Table 4.3).

Table 4.3: Asphaltum/Bitumen recipes from artist's manuals with ingredients colour coded.



			Ingredients																									
Date	**Source**	**Recipe**	Asphaltum	Bitumen	Drying Oil	Boiled Oil	Prepared Oil	Oil of Poppy	Copaiba Balsam	Venice Turpentine	Spirit of Turpentine	Oil of Turpentine	Sugar of Lead	Litharge	Mastic Varnish	Gum Lac	Amber Varnish	Italian Oil	Italian Varnish	Lavender essence	White Wax	Beeswax	Wax	Vandyke Brown	Umber	Cappagh Brown	Pigments	Megilp
1787	Williams	Antwerp Brown	X		X								X															
1795	*A Practical Treatise*	Wilson's Method	X						X		X																X	
		Another Method	X							X	X																	
1804	Tingry	Asphaltum	X				X																					
1808	*Compendium*	Meng's Recipe	X						X			X																
		Another Method	X							X	X																	
		West's Method	X					X	X																			
		Antwerp Brown*	X		X								X															
1835	Field	Asphaltum	X		X							X																
1839	Mérimée	English and Italian Method	X									X			X			X										
		Another Preparation	X		X					X						X					X							
		With Greater Solidity	X		X											X	X				X							
1841	Field	Common Asphaltum	X		X																			‡Xor	‡Xor	‡Xor		
1843-50	Sully's *Journal*	Chapman's Method	X			X									X							X						X
		De Mayerne's Method	X		X									X														
1845	Osborn	Asphaltum	X		X							X								X								
		Another Method		X	X																		X					
		Mérimée's Method*	X		X					X						X					X							
		Ordinary Mode (1)		X							X				‡Xor				‡Xor									
		Ordinary Mode (2)		X	X																							

*Repeated Recipes;
‡ Xor = Materials given as options, either one could have been used in that recipe.

In terms of W&N´s standard ingredients in the 1850s, similarities are found in a recipe from the artist Thomas Sully (1783–1872) in his Journal 1843–50 (as cited in Hird 1978, 81), which is referred to as "Chapman's mode of preparing asphaltum. From Rome". Both involved melting asphaltum in a drying oil with the addition of mastic varnish, and both call for the addition of *Megilp* at the end. Sully reports that artists in Rome also added a small piece of beeswax, while in France the mastic varnish and beeswax was omitted (Carlyle 2001, 406).

The addition of Megilp by artists

In the 17 artists' recipes for bitumen/asphaltum brown there was only one specific reference to Megilp: Sully wrote, "with good magullip [*sic*] it works beautifully…" (Hird 1978, 81). However, in other sources discussing 19th-century oil paintings, there are mentions of Megilp in relation to the asphaltum mixture. For example the Redgraves describe Wilkie's additions to asphaltum: "About equal quantities of boiled oil, mastic varnish, and liquid asphaltum (asphaltum melted into the oil) were mixed together, forming a magylp [*sic*] that solidified or "stood up," as the painters called it, and this was the vehicle used throughout the picture, of course mixed with more asphaltum in the darks."[150] (Redgrave and Redgrave 1866, 594).

That there is a close association of Megilp with bitumen/asphaltum browns by the last decades of the 19th century is evident from this description: "That preparation usually sold under the name of Bitumen is only Asphaltum, with a little boiled oil, Mastic meguilp [*sic*], or wax, added. These ingredients give to it that consistency which we find when squeezed from the tube." (Muckley 1882, 72).

4.6 Discussion

This analysis of W&N's *Bitumen* oil paint manufacture reveals that the company strove to produce a rich brown that dried well, had good handling properties and compared favourably to their competitors' product. While they standardised the ingredients in the 1850s, nevertheless adjustments were still being made to the formula either at KT or RP according to a variety of factors, such as drying time (influenced not only by ingredients and processing, but also by the season or weather), and/or handling properties and colour. Therefore, a completely rigid adherence to a given formulation cannot be expected. The addition at RP of equal quantities of *Megilp* to the heat-processed mixture made at KT is a significant finding as *Megilp* itself was suspected of contributing to subsequent cracking which affected so many paintings from the period (Carlyle and Southall 1993).

Certainly W&N recognised problems with gelled Mediums like Megilp. In 1900 they write, "Gelatinized Mediums… have of late years been gradually dropping out of use…the pictures of a preceding generation, painted with secret nostra, are now in such a condition as to be destructive of all confidence in proprietary mediums" (Catalogue 1900, 105).

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[150] Wilkie's paintings are notorious for drying problems associated with descriptions of bitumen cracking, see Carlyle and Southall (1993) and Costaras (2017).

The role of the asphaltum itself in the development of drying problems is still unclear, especially as the identification of the source of asphaltum used by W&N was not possible with the information available. However, from their records it could be seen that the asphaltum source influenced the material properties of the final product. It is notable that their production records do not point to the use of the slow drying coal-tar substitute[151] in their *Bitumen* since this variety was reported to be soluble in turpentine, whereas W&N's required melting alone or in oil.

As a result of this analysis, the sporadic nature of drying problems reported for bitumen/asphaltum-based oil paint is easier to understand, since both W&N's records and the artists' recipes before 1850 show a wide variety of materials and a lack of uniformity in formulations. As well as the separate product, "Asphaltum in pots" required further additions by the artist to make it workable, which could explain the inconsistent occurrence of "bitumen cracking" in a single artist's oeuvre, and between one artist and another.

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[151] Osborn stated that the coal tar variety was "the only kind we have ever been able to procure in this country" (Osborn 1845, 88), meaning the USA, and Church writing near the end of the 19th century, stated the coal-tar source was "…now largely sold in lieu of the original and genuine product" (Church 1890, 209). The role of the coal tar source in bitumen cracking has yet to be examined. It should be noted that if "Asphaltum in pots", was truly only asphaltum dissolved in turpentine, that could point to it being a coal-tar substitute.

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Marques, Raquel, Leslie Carlyle, Laurence De Viguerie, Isabel Pombo Cardoso, and Jaap J. Boon. 2022b. ‘Winsor & Newton’s 19th-Century Bitumen Brown Oil Paint. Part I: A Critical Analysis of W&N Production Records’. In *Reflecting on Reconstructions, The Role of Sources and Performa-tive Methods in Art Technological Studies. Proceedings of the Eighth Symposium of the ICOM-CC Working Group ATSR, Held at the Cologne Institute of Conservation Sciences, 26-27 September 2019*, edited by Doris Oltrogge, Joyce H. Townsend, Anne Haack-Christensen, and Maartje Stols-Witlox, 49–64. ICOM-CC. https://www.icom-cc-publications-online.org/4608/Winsor--Newtons-19th-century-bitumen-brown-oil-paint-Part-II--the-reconstruction-

5

THE RECONSTRUCTION OF W&N'S *BITUMEN*

5.1 Abstract

This Chapter reports on the reconstruction of W&N's *Bitumen* oil paint based on their production record dated September 1858. It was chosen following a comprehensive analysis of the company's bitumen oil paint productions (see Chapter 4). Their product was prepared in two steps which took place first at their premises in Kentish Town and then at Rathbone Place. The two steps are described, with an evaluation of recipe instructions versus direct experience during the reconstruction. Where possible historically appropriate materials were used. Observations and supporting images of the behaviour of the products produced during application and initial drying are provided.

5.2 Introduction

The reconstruction of one of W&N's *Bitumen* oil paint formulations was made with two objectives: to provide insights into the processing methodology and conditions and to provide a material reference for chemical analysis. In the latter case, in order to establish what chemical markers will remain within a matrix of multiple ingredients after heat processing, and to establish the detection limits for ingredients.

W&N's production record from September 1858 (P2P115A)[152], entitled "Bitumen"[153] was chosen as it was amongst the most detailed in terms of ingredients, with documentation of all steps, and is representative in that it was the end point in a decade of adjusting quantities in an otherwise standard formulation.

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[152] The recipe and page numbering system in the *W&N 19th-century Archive Database* is used throughout and is explained in Chapter 4 (Marques et al. 2022a).

[153] Their recipes for this product were variously referred to as "Bitumen for Oil Tubes", "Bitumen for Tubes" or simply, "Bitumen" (see Chapter 4). For simplicity their product is referred to throughout as *Bitumen*. The same convention, of choosing one common name and placing it in italics was adopted for W&N's other products used in their *Bitumen* record.

Historically appropriate materials[154] were used where possible, i.e., Trinidad Asphalt, custom-extracted linseed oil, mastic resin, a reconstructed W&N purple lake pigment and pine turpentine (see Appendix E.3, Materials, page 319). However, laboratory grade materials were substituted in some cases, i.e. lead acetate (lead acetate trihydrate), litharge (lead(II) oxide) and red lead (lead tetroxide), mainly due to the toxicity and complexity of the reconstruction process.

Following W&N's practice, individual products used in their *Bitumen* were made up separately (see Appendix E.4, Reconstructions of W&N products, page 320). The details on their production records for these materials are given in the Appendix D.

At various points during the preparation of individual ingredients and throughout the production of both the Kentish Town (KT) and Rathbone Place (RP) products, small samples of material were removed for later analysis (Table 5.2). For a full description of the procedures at KT and RP see Chapter 4.

Original measures were converted to SI units and reduced to achieve amounts suitable for laboratory conditions (Table 5.1). A pilot reconstruction was carried out to test the equipment and procedures.

As detailed in Chapter 4, W&N heat processed asphalt with oil and various ingredients at their premises in KT then sent that product to RP for further processing before putting it into oil paint tubes.

Table 5.1: Conversion to SI units using conversion tables in Carlyle (2001, 545-47) and division into smaller quantities, of the selected W&N *Bitumen* record (P2P115A) from 1858. Highlighted in red are the amounts used for the W&N *Bitumen* reconstruction.

Asphaltum	SI	Strong Drying Oil	SI	Double Mastic Varnish	SI	Sugar of Lead	SI	Purple Lake	SI	Turpentine (Turps)	SI
Pounds	**g**	**Pint**	**ml**	**Pint**	**ml**	**Ounces**	**g**	**Ounces**	**g**	**Pint**	**ml**
4	1,814.4	10	5,682.6	6	3,409.6	8	226.8	8	22.,8	1	568.3
0.4	181.4	1	568.3	0.6	341.0	0.8	22.7	0.8	22.7	0.1	56.8
0.2	90.7	0.5	284.1	0.3	170.5	0.4	11.3	0.4	11.3	0.05	28.4
0.1	45.4	0.25	142.1	0.15	85.2	0.2	5.7	0.2	5.7	0.025	14.2
0.05	22.7	0.125	71.0	0.075	42.6	0.1	2.8	0.1	2.8	0.0125	7.1
0.02	9.1	0.05	28.4	0.03	17.0	0.04	1.1	0.04	1.1	0.005	2.8

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[154] Reconstructions of historical recipes for oil painting using historically appropriate materials has been referred to as a technique to achieve a degree of accuracy not obtainable with modern industrially processed materials (Carlyle et al. 2006). Any reference to "accuracy" is of course relative, and in this context represents an aspiration to find materials and techniques which approach those in use in the past as closely as is feasible (explored in Carlyle 2019; 2020; 2021).

5.3 Reconstruction of the Kentish Town product

Temperatures are not provided in the production records for the heat processing of ingredients at KT. Instead there are descriptions of the behaviour of the mixture that signal the point at which steps in the process are to be initiated: for example an increase in volume ("heading up"); the presence of foaming (a "white head"); and the formation of "short strings"[155] , As will be seen, these behaviours were not consistent with the performance of the reconstruction (perhaps due to the extreme differences in scale between the amounts in the reconstruction versus a full commercial production). To achieve the high temperatures required (over 300°C)[156] an outdoor gas furnace was constructed (Figure 5.1a–b).

Heat processing took place in a small cast-iron pot suspended in a retort stand. A custom-made glass stirring rod was substituted for the iron rod described in the production record. Two different infrared thermometers were used to cover the full temperature range 20°C to 320°C. Table 5.2 summarises the individual steps, quantities used and the time/temperatures throughout.

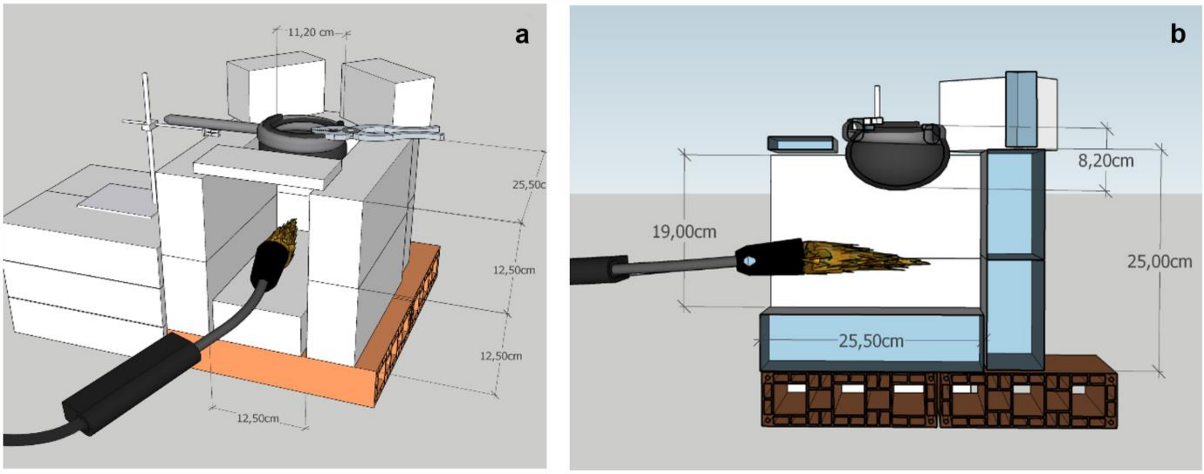

Figure 5.1: Gas furnace with fire-bricks (white) and clay bricks (base) with gas torch. a) Front view and b) in cross-section. Made in SketchUp Web (version 1.3, © Trimble Inc.).

Step 1 Melting the asphalt into *Strong Drying Oil*

The record specified using pieces of asphalt "about the size of small nuts" (P2P115A). For the reconstruction Trinidad Lake Asphaltum was broken into pieces (~0.5 to ~1 cm) using a ceramic mortar and

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[155] The "string" is presumably formed at the end of a stirring stick. A short string will be the relative length of the drip before it breaks, with the remainder falling into the pot.

[156] Actual temperatures for heat processing *Bitumen* were not given in the W&N records and were therefore based on previous experience during the reconstruction of copal oil varnishes (Carlyle 2005).

pestle. The asphalt (22.7 g) and *Strong Drying Oil* (35.4 ml)[157] were stirred together in the iron pot as heat was gradually introduced. The asphalt melted into the oil at ~104°C after 12 minutes (Table 5.2).

Step 2 Adding *Burnt Sugar of Lead* in oil

In the production record the asphaltum and drying oil mixture continued to be heated until it had boiled up ("head up") then it was taken off the heat and *Burnt Sugar of Lead* previously ground in oil was added "by degrees, for fear of coming over" (that is, over the rim of the pot). After 60 minutes of heating, at ~238°C, boiling was clearly evident but there was no obvious volume change. At that point the gas torch was extinguished.

When lead acetate ("Sugar of Lead") ground in oil was added in 3 portions of less than 1g at a time, intense bubbling and foaming occurred immediately. This procedure took approximately 4 minutes, afterwards the torch was reignited.

Step 3 The gradual addition of more *Strong Drying Oil*

The record states that the mixture was allowed to "head up again" and be "worked" (stirred) until "it strings in short strings". At that point 4 pints of *Strong Drying Oil* would be incorporated by adding 1 pint at a time on two occasions, with a final addition of 2 pints at once. Between additions, the mixture should "head up again till it strings short".

For the reconstruction, the small volume for each addition of drying oil (7.1 ml) did not appreciably lower the temperature of the mixture making the need to reheat and head up the mixture each time apparently unnecessary. Furthermore, the mixture was not forming short strings off the end of the stirring rod, so neither behavioural indicators were available to guide the time of heating between drying oil additions.

In the end, heating was stopped at 318°C when the mixture appeared to be getting too viscous.[158] To hasten cooling, the pot was taken off the furnace and left standing for approximately 3 minutes before the addition of *Double Mastic Varnish* (W&N recipe P2P113A, see Appendix E.4 page 320, and Chapter 4).

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[157] According to the calculated amounts, 28.4 ml of *Strong Drying Oil* should have been added at the beginning with the asphaltum. Based on previous experience (see footnote 156) this volume was judged to be too low, risking overheating at an early stage in the process. Therefore 35.4 ml was added instead.

[158] Or dangerously thick – the point at which hot oil can suddenly turn to a jellified mass (experienced by the authors in other experiments).

Step 4 Adding *Double Mastic Varnish*

Double Mastic Varnish (35.5 ml) was stirred into the hot mixture. Boiling and foaming were observed in keeping with the caution that "it ought to be put in very carefully" with "the oil-pouring can used in varnish-making" (P2P116A). For the reconstruction a long glass graduated cylinder (250 ml) was used to achieve distance while pouring.

Step 5 Adding *Purple Lake* in oil

A pint of *Double Mastic Varnish* was to be held back and added to the *Purple Lake* as "this makes it mix more certainly" (P2P116A). Therefore 7.1 ml of *Double Mastic Varnish* was first stirred into the *Purple Lake* in oil before it was added to the hot mixture.

Step 6 Decanting to the storage pot and adding turpentine

The next step was to pour the hot mixture through a muslin sieve into a fresh container. A fine stainless-steel sieve was suspended over a stainless-steel pot with the mixture being poured through in portions while stirring with the glass rod to encourage passage. The viscosity increased as it cooled with the final mixture in the pot becoming paste-like.

In the W&N production turpentine was used to wash out and clean utensils before it was added to the final mixture. Following this, 7.1 ml of pine turpentine, double rectified (see Appendix E.3, Materials, page 319) was used to rinse the iron pot, then passed through the sieve and stirred into the final mixture (somewhat increasing its fluidity).

Table 5.2: Summary of the KT product reconstruction (27 June 2019).

Time	T°C	Order of Addition	Ingredients	Quantities	Comments	Samples taken
11:17	30	1 3	Trinidad Lake Asphalt + Strong Drying Oil + Strong Drying Oil	22.7 g 35.5 ml	HEAT ON	
					Stirring is intermittent	
11:29	104				Asphalt melted	
11:46	157				Bubbles appear	
11:48	167				Bubbling pronounced	
11:53	198				Mixture smoking	**RS1**
12:17	238				Smoking intensely	

					HEAT OFF	
12:18	-	2	Sugar of Lead in Linseed Oil	2.8 g	Added by thirds (effervescent reaction)	
12:21	213				HEAT ON - Constant stirring from this point on	
12:35	~285	4	Strong Drying Oil	7.1 ml		RS2
12:36	~304	5 6	Strong Drying Oil + Strong Drying Oil	14.2 ml		
12:43	~304	7	Strong Drying Oil	14.2 ml		
12:46	318				Mixture quite viscous	RS3 (= KT-I)
12:49	275				HEAT OFF	
12:52	-	8	Double Mastic Varnish	35.5 ml	Stirring continues	
12:54	~180					RS4
12:58	-	9	Purple Lake in Linseed Oil + Double Mastic Varnish	2.8 g 7.1 ml	Stirred together then strained through sieve into a pot	RS5
13:07		10	Turpentine	7.1 ml	Poured into the pot, through the sieve & into the mixture	RS6
13:15					KT Product in Stainless Steel Pot, stirred with glass rod & with lid put on top.	RS7 (= KT)

5.4 Reconstruction of the Rathbone Place product

As noted in Chapter 4, throughout the 1850s the KT product was transported to RP where *Megilp*[159] was added in order to make their *Bitumen* ready for sale in tubes. In the 1858 record the proportion was 1:1 KT product to *Megilp*.

***Megilp* preparation**

W&N's formulation (P2P258A) involved a 1:1 mixture by volume of *Strong Drying Oil* and *Double Mastic Varnish*. Equal amounts of both (prepared previously for the KT product) were combined, given a slight stir with a glass rod, then put aside. A fairly firm gel resulted.

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[159] Production records indicate that other materials could be added at this stage, i.e. *Sugar of Lead*, or *Strong Drying Oil*, these additions were not called for in the 1858 record.

Adding *Megilp*

Equal parts by volume of the KT product and the *Megilp* were obtained using a stainless-steel measuring spoon. The mixture was ground together with a glass muller and grinding slab (stirring alone did not effect a homogenous mixture). Since artists could have added more Megilp on the palette prior to painting, another sample was made using 2 parts *Megilp* to 1 part of the KT product.

Figure 5.2: properties of the KT product prior to and after the addition of *Megilp* (RP product).

5.5 Observations during application

The KT product was a transparent, rich colour tending towards a black-brown but was viscous, sticky and stringy (Figure 5.2). Under the brush it was gritty and paste-like; however, within minutes the surface changed dramatically from an uneven granular matt coating, to a smooth surface with a high gloss. When brushed on to a 14-year-old reconstruction of a W&N oil ground (Carlyle et al. 2008) it exhibited crawling within 30 to 60 seconds (see KT in Figure 5.3a).

The addition of *Megilp* turned the intractable KT product into a viable light-brown paint: it flowed loosely and easily without being too fluid (Figure 5.2). While somewhat granular during brushing, it also exhibited flow after application, achieving a smooth, high gloss finish. No brush marks or ridges remained in the surface.

Changing the proportion of *Megilp* from 1:1 to 2:1 resulted in a looser, more fluid paint. The additional *Megilp* did make a visible difference to the crawling behaviour on the oil ground, showing severe crawling within 30 to 60 seconds, more pronounced in the 2:1 proportion (see RP2.1 & RP2.2

in Figure 5.3a). Note that extensive crawling did not occur when the same KT/RP products were applied to a modern commercially prepared artist's board.[160]

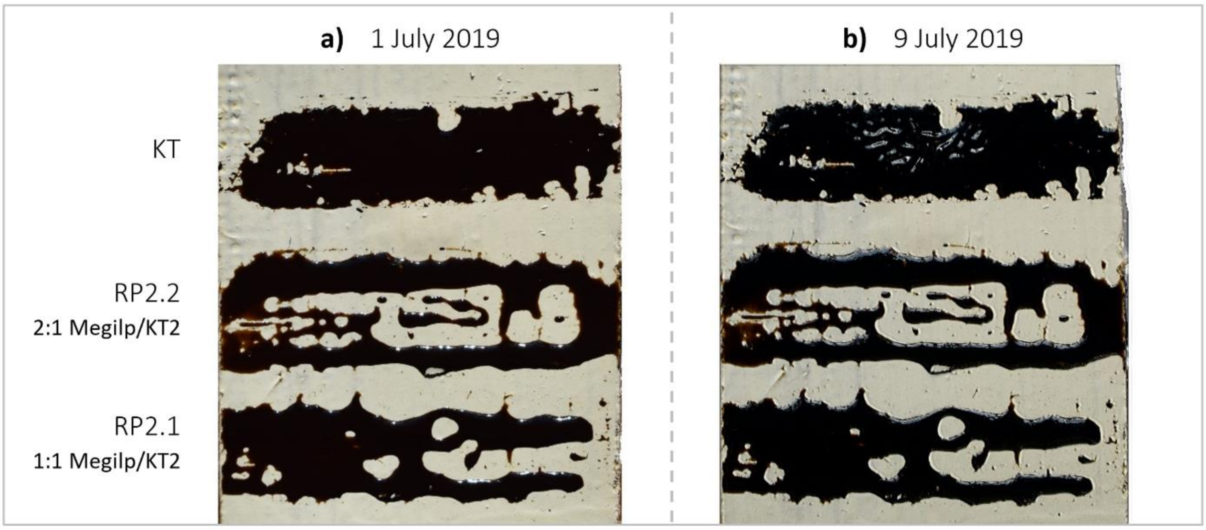

Figure 5.3: KT and RP product applied on a 14-year-old reconstruction of a W&N oil ground. a) immediately after being painted on the 1st of July and b) after a week.

5.6 Observations of initial behaviour

Wrinkling

Three days after being brushed onto a commercial artists' board the glossy surface of the KT product had developed micro-features: a fine cell-like structure with tiny lines between (Figure 5.4a). The top surface had developed a skin with the portion below still wet. A week later, within 24 hours, this sample suddenly developed severe wrinkling (Figure 5.4b).

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[160] Writers of 19th century British oil painting manuals complained of oil grounds (and paint) developing a "greasy surface" causing poor adhesion of subsequent oil paint (Carlyle 2001, 205–6). In hindsight the reconstructed oil ground should have been treated prior to use as suggested in the 19th century texts to remove/reduce the greasy layer.

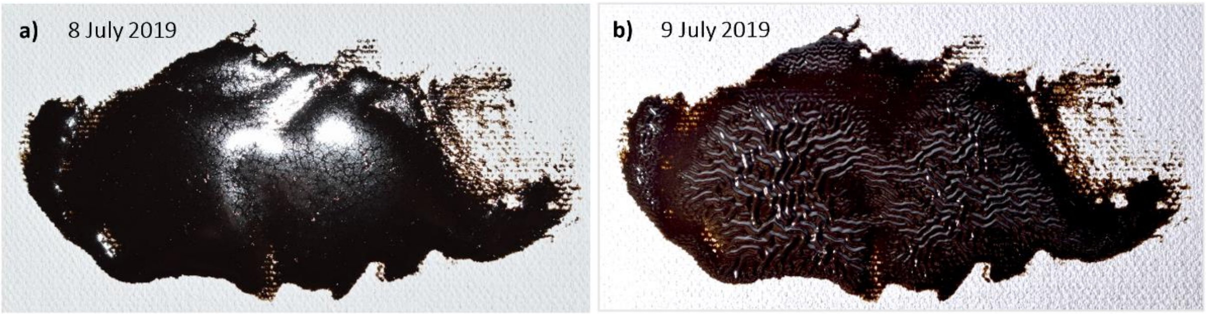

Figure 5.4: KT product applied onto an artist's board on the 1st of July. a) shows the micro-features on the glossy surface a week later; b) shows the severe wrinkling that happen within 24h.

Wrinkling, most prominently in the thickest areas, eventually occurred with some RP and all KT paint outs. The length of time it took varied according to the substrate and varied between the KT and RP products. KT samples applied to glass slides wrinkled after only three days and applied to the oil-ground substrate wrinkled after a week, while in the same period, no wrinkling was evident in the RP samples (see KT in Figure 5.3b). Observations with transmitted light of the KT paint-outs on glass after 10 months, showed a distinctive cell like structure (Figure 5.5), which indicates that the mixture separates in phases and is far from homogeneous.

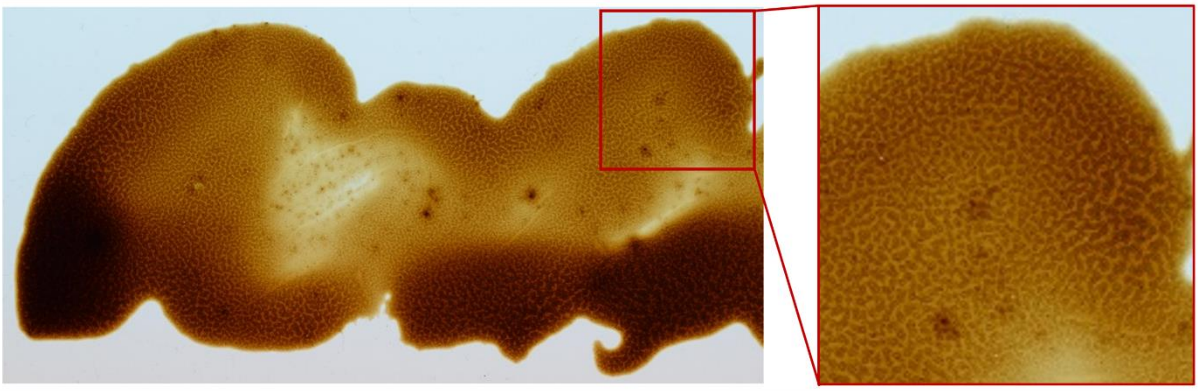

Figure 5.5: Distinctive cell-like structure visible on a KT paint-out on glass.

Drying

As noted in Chapter 4, W&N's goal for their *Bitumen* was a product that would "keep wet & free working for 24 hours & then to dry off at once" and that it should not "become sticky a long while" (P1P278B). Paint-outs from the reconstruction failed to dry after 24 hours, remaining sticky for at least 6 months, on all substrates. Our product would certainly have been sent back to KT for further processing.

5.7 Conclusions for Chapters 4 and 5

While the examination and analysis of W&N’s *Bitumen* paint formulations did not in itself lead to clear answers regarding the drying problems widely associated with the use of bitumen/asphaltum oil paint, it did contribute to a deeper understanding of the method and materials used for a commercial production, and insight into W&N’s concerns regarding the quality and durability of their product. However limited by factors such as the appropriateness of the materials and the scaled-down quantities, the reconstruction did result in an approximation that proved useful for determining whether chemical analyses of a complex heat-processed mixture could identify all materials present (see Chapter 6).

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DOI: https://doi.org/10.1016/j.microc.2022.107762.

6

TRACKING ASPHALT MARKERS IN BITUMEN OIL PAINT RECONSTRUCTIONS BY PY-TMAH-GC/MS AND PY-GCXGC/MS

6.1 Abstract

Bitumen brown oil paint reconstructions based on 19th century production records from the British colourman Winsor & Newton were analysed using thermally assisted methylation with tetramethylammonium hydroxide (Py-TMAH-GC/MS), and pyrolysis comprehensive two-dimensional gas chromatography (Py-GCxGC/MS). Reconstructions were compared with the starting material, Trinidad Lake asphalt (TLA), to determine how detectable this asphalt is after heat processing in lead treated linseed oil. The use of brown paint containing asphalt/bitumen (the names are used interchangeably) was blamed for severe film-forming defects in 18th and 19th century oil paintings, yet this material has rarely been identified in earlier studies of historical paintings. This research offers a possible explanation for the paucity of evidence as it reveals that asphalt markers identified in the TLA disappear in the first stage of reconstructing bitumen brown oil paint.

6.2 Introduction

A brown oil paint prepared from asphalt has been reported to be in widespread use in oil paintings, particularly during the 18th and 19th centuries (van der Loeff and Groen 1993; Bothe 2007). Prized for its transparent deep brown tone, it was employed on its own or in glazes on top of more opaque paint, however it gained a reputation for causing paint-film defects, such as severely disfiguring drying cracks and surface distortions which came to be referred to as “Alligatoring” or “Bitumen Cracking” (Carlyle and Southall 1993; Carlyle 2001; Languri 2004).

Despite the association with asphalt (or bitumen, the names were used interchangeably) only on rare occasions have chemical analyses of alligatoring proven those assumptions correct (van der Loeff and Groen 1993; Groen 1994; White 1986). This was thought to be due to the challenge of identifying asphalt in tiny samples from historical oil paintings. Further explanations pointed to different varieties of asphalt and the lack of precision in their identification in historical samples since this material can be sourced from many geolocations (Nissenbaum 1978). In addition, in the 19th century the use of an artificial asphalt produced from coal-tar was also reported (Carlyle and Southall 1993; Carlyle 2001).

Not only do asphalts in their natural form display highly complex chemical composition, this material was heavily processed prior to use as a brown pigment for artists and could have additional materials introduced during preparation and use (Bothe 2007; Carlyle 2001). Recently a series of production records for the British colourman, Winsor & Newton (W&N)’s “Bitumen” for Oil Paint were analysed and a representative production record was reconstructed using historically appropriate materials (Chapter 4 and 5).

With the aim of investigating how the preparation process (cooking, boiling and the addition of different materials) may influence the ability to detect the asphalt within the final paint product, an in-depth characterization of materials from each step of the reconstruction was carried out using Py-TMAH-GC/MS and Py-GCxGC/MS. The purpose was to track asphalt feature markers throughout the reconstruction of the bitumen brown oil paint.

6.2.1 Asphalt/bitumen characterisation

Natural asphalt or bitumen is reported to be composed of an n-heptane soluble fraction of hydrocarbon referred to as maltene (MAL) and an insoluble fraction of polycyclic asphaltene (ASP) the latter of which has a very high molecular weight. Both fractions are responsible for the properties of the material (Aydemir et al. 2013).

Asphaltenes are defined as the crude-oil fraction of bitumen and are soluble in aromatic solvents (e.g., toluene or benzene) but insoluble in aliphatic solvents (e.g., n-heptane, or n-pentane). In contrast, the maltene fraction is soluble in aliphatic solvents only.

The heaviest component in bitumen, the asphaltene fraction has a strong tendency to aggregate due to the attraction between its polyaromatic fused rings. In addition to the complex mixture of hydrocarbons and asphaltenes, natural asphalts also contain resins, NSO[161] compounds and complexed

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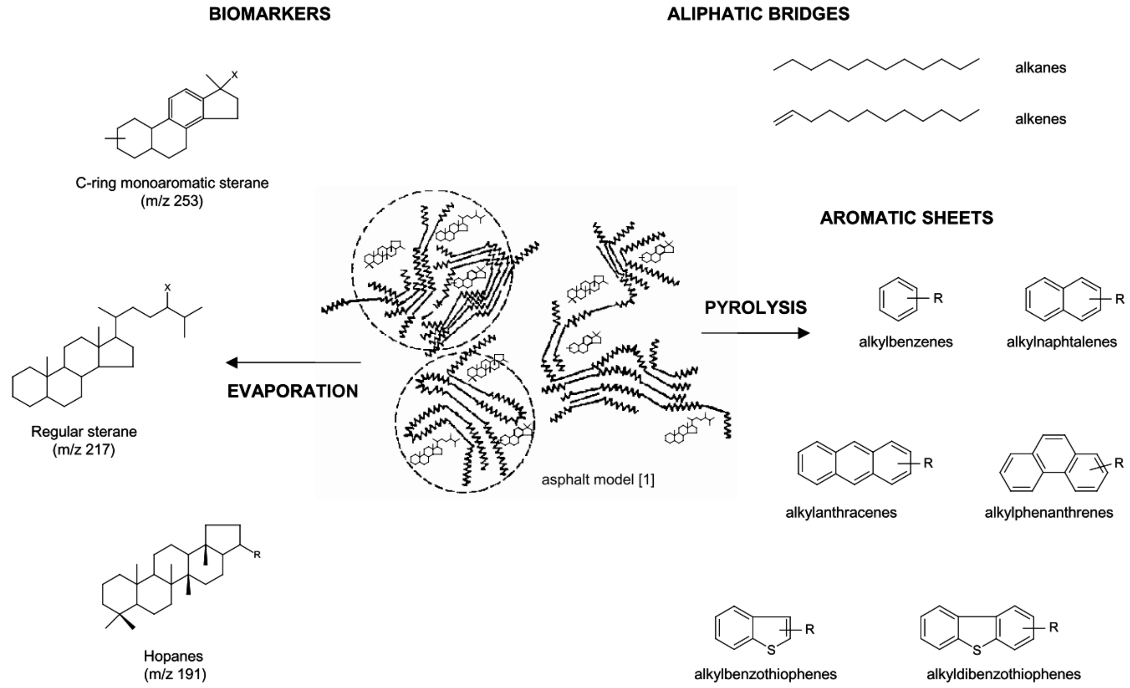
[161] Nitrogen, sulphur and oxygen compounds.

metals in the form of heteroatoms: mainly vanadium and nickel (Peters, Walters, and Moldowan 2005a; Yen 1990; Petersen 1984).

The rich chemistry of bitumen results in a diversity of intermolecular associations which in turn facilitates the formation of nanoscale to macroscale microstructures (Yu, Burnham, and Tao 2015). The "Yen-Mullins model" sheds light on the molecular and colloidal structure of asphaltenes in crude oils and with laboratory solvents: in sufficient concentration asphaltene molecules form nanoaggregates, then at higher concentrations these nanoaggregates form clusters (Mullins et al. 2012). The resulting structures are responsible for the physical and mechanical properties of bitumen.

Since the chemical and physical variations in natural asphalt are dependent on the geological source, as well as on the refining methods used, there is no single precise chemical structure or chemical composition of asphalt/bitumen.

Asphalts are therefore characterized by the percentage of carbon, hydrogen, trace NSO compounds and other elements present in the mineral matter. Its chemical composition is fundamentally related to its crude source and specific biomarkers for its depositional environment (Scheme 6.1). In earlier studies, Raymond White used the distribution of extractable hopanes as markers for asphalt compounds in artworks (White 1986; Mills and White 1987), then Languri (2004) developed an analytical methodology based on mass spectrometric techniques, such as Py-GC/MS, PY-TMAH-GC/MS and direct temperature-resolved mass spectrometry (DTMS), amongst others, for the characterization of a large number of biomarkers and marker compounds with the aim of detecting these markers in 19th century reference materials, model systems and historical paintings suffering from film-forming defects (Languri 2004). An asphalt sample from the 19th century Hafkenscheid collection was investigated with mass spectrometric techniques (Languri, van der Horst, and Boon 2002). Py-GC/MS revealed alkanes and alkenes, a number of alkyl-aromatic compounds and alkylbenzothiophenes plus a few compounds with hopane carbon skeletons, gammacerane and C-ring monoaromatic steroids. Asphalts contain many different sulphurised lipids but their detection requires chemical reduction techniques, which are hard to do on microsamples such as from paintings. The various alkylbenzothiophenes are however indirect indicators for the presence of (poly)sulphide bridges in asphaltic complex materials (Sinninghe Damste and de Leeuw 1990). The distribution of the pyrolysis products of asphalts were used by Languri (2004, chapter 5) to investigate how the asphalt markers are affected by paint manufacturing processes. The effects of roasting of asphalt, solvent extraction, addition to drying oils and their accelerated aging were investigated. Further changes in asphalt paint composition can result from oxidative conditions during natural aging of the painting, and due to exposure to solvent-based restoration treatments, which can extract solvent sensitive materials such as the maltene fraction. Languri however only investigated some of the effects of paint making in separate experiments.



Scheme 6.1: Reproduction of Languri's scheme, with "Yen's model" in the center surrounded by markers and biomarker molecules present in asphalt (Languri 2004). This schematic however underestimates the significance of sulphur bridges as cross links and the sulphurisation of lipid biomaterials (Kohnen 1991).

6.2.2 Py-TMAH-GC/MS and Py-GCxGC/MS

Pyrolysis gas chromatography/mass spectrometry (Py-GC/MS) offers a high degree of sensitivity for organic components in small samples of complex materials found in historical cultural objects. On-line pyrolysis does not require wet chemical workup, has a low sample requirement and has been successful in the characterization of oil derived constituents after chemical drying (e.g. J. van den Berg 2002; Bonaduce and Andreotti 2009). The addition of tetramethylammonium hydroxide (TMAH) allows on-line hydrolysis of ester bounds and methylation of acidic compounds and alcoholic moieties. Py-TMAH-GC/MS is therefore capable of analyzing fatty acids as methyl esters released from cross-linked as well as non-crosslinked materials (free- and esterified fatty acids), which makes separation and identification of more complex oxidised fatty acids a suitable approach (J. van den Berg 2002). Without TMAH, free fatty acids, acylglycerides and the fatty acids eliminated from the cross-linked network are much more difficult to separate effectively by gaschromatography. Elimination of fatty acids from a cross linked oil during pyrolysis can lead to an aromatised residual network that will produce various types of aromatic compounds at higher analysis temperatures (J. van den Berg 2002).

Pyrolysis-comprehensive two-dimensional gas chromatography (Py-GCxGC/MS) has recently been introduced in the study of cultural heritage materials for its analytical capabilities (Han, Daheur, and Sablier 2016; Han et al. 2021; 2022). This technique uses two capillary columns connected via a modulation system to optimize the complementary separation capabilities of columns of different polarities. It offers higher resolution, peak separation capacity, and selectivity and a lower detection limit for the analysis of volatile organic molecules (Tranchida et al. 2016). For this research it offered a complementary technique to Py-GC/MS alone as it ensures the detection of all targeted markers.

6.3 Experimental

6.3.1 Materials and Paint Samples

6.3.1.1 Materials

TMAH: Tetramethylammonium hydroxide solution, 25 wt% in H_2O. Linear Formula: $(CH_3)_4N(OH)$. Supplier: Sigma-Aldrich. 331635. https://www.sigmaaldrich.com/PT/en/product/sial/331635.

FA-C13 Internal Standard: Tridecanoic acid, analytical standard. Linear formula: $CH_3(CH_2)_{11}CO_2H$. Supplier: Sigma-Aldrich. 91988. https://www.sigmaaldrich.com/PT/en/product/sial/91988.

Asphalt: Trinidad Lake Asphalt (TLA) was selected as the asphalt source for the reconstructions because of its extensively characterized composition (e.g. Charles and Grimaldi 1996), it was readily available in small quantities and had been used in previous reconstructions of bitumen brown oil paint by Bothe (1999) and Izat (2001) (see Chapter 5). Supplier: Trinidad Lake Asphalt, Trinidad Epuré, Carl Ungewitter, Trinidad Lake Asphalt, GmbH & Co. KG, 28,195 Bremen, Bgm.-Smidt-Straße 56. Germany.

6.3.1.2 Bitumen brown paint samples

Reconstructions were made following the W&N production record for their bitumen brown oil paint dated 1858 (see Chapter 4 for analysis of the production records, and Chapter 5 for details on the reconstruction). The London based company first cooked ingredients together at their manufactory in Kentish Town (KT), then completed the recipe the next day at their premises at Rathbone Place (RP).

W&N incorporated other previously prepared products in their bitumen brown. These were made separately for the reconstruction following their production records for *Strong Drying Oil*, *Double Mastic Varnish* and *Purple Lake* pigment. The production record for their *Burnt Sugar of Lead* was not clear, therefore a laboratory grade lead (II) acetate trihydrate was used instead (Chapter 4 and 5). See Appendices D and E for more details on the materials and preparation procedures.

Following the steps in W&N's record, asphalt was first melted with their *Strong Drying Oil* (linseed oil previously cooked with litharge and red lead) while heating. Sugar of Lead (refined lead acetate ground in raw linseed oil) was then added with further cooking to a maximum temperature of 318 ^{o}C. After cooling, concentrated *Mastic Varnish, Purple Lake* pigment and Turpentine were added (resulting in the KT product). The next day, at room temperature a 1:1 proportion of the artist's gelled medium *Megilp* was ground into the mixture which resulted in their final product (the RP product). *Megilp* was sold by W&N and other British colourmen throughout the 19th century. It was a gel formed by mixing lead-treated linseed oil and mastic resin which was used to enhance the flow properties and transparency of artist's oil paint (Carlyle 2001; Pasco et al. 2022).

Samples were taken at different stages throughout the preparation before and after new materials were introduced (see Scheme 6.2). A reference sample of the Trinidad Lake asphalt (TLA) and three selected samples from the reconstruction (see Table 6.1) were analysed with Py-TMAH-GC/MS and Py-GCxGC/MS.

The "Bitumen" production record (P2P115A) dated September 1858 from W&N was reconstructed several times with analyses carried out on two separate reconstructions. Given the similarity in results, this chapter reports on only one reconstruction.

Table 6.1: Sample code and description of selected samples from the reconstruction of W&N's "Bitumen" (1858).

Sample Code	Description
KT-I	Kentish town **(KT)** initial **(I)** mixture: Strong Drying Oil + Asphalt (TLA) + Sugar of Lead after reaching ~318 ºC and cooking for 1h30min.
KT	Kentish Town (**KT**) product: which includes the mixture above with the additions of Double Mastic Varnish, Purple Lake pigment, and Turpentine. (total preparation time 2 hours).
RP	Rathborne Place (**RP**) final brown oil paint which includes the **KT** product with the addition of Megilp (1:1 strong drying oil : double mastic varnish) in a 1:1 proportion. This is the brown oil paint which was put into W&N's paint tubes.

Scheme 6.2: Schematic showing the sequence of samples taken during the production of W&N's Bitumen Brown oil paint with the time and temperatures reached.

6.3.2 Sample preparation for analyses

On-line: thermally assisted methylation. After adding 3 µl of tetramethylammonium hydroxide (TMAH) in methanol (5%) with tridecanoic acid (FA-C13) as internal standard (the concentration of FA-C13 is 16ug/ml), the sample is homogenized and then placed in a stainless steel cup (Frontier LabDisposable Eco-Cup SF).

6.3.3 Analytical procedures

Pyrolysis transesterification gas chromatography/mass spectrometry (Py-TMAH-GC/MS).

The pyrolysis unit used was a Frontier Lab 3030D pyrolyser mounted on a Thermo Scientific Trace 1310 GC / ISQ mass spectrometer combination. The analytical column was directly coupled to the pyrolyser via a home-made split device. A SLB5 ms (Supelco) column was used (length 20 m, int. diameter 0.18 mm, film thickness 0.18 µm). Helium was used as carrier with a programmed pressured flow of 0.7–1.2 ml/min and split ratio of 1:30. The pyrolysis temperature was 480 ºC. The temperature program was the following: 35 ºC (1.5 min), heating at 60 ºC /min to 100 ºC, heating at 14 ºC/min to 250 ºC, heating at 6 ºC/min to 315 ºC (2 min). The column was directly coupled to the ion source of the mass spectrometer. The temperature of the interface and the ion source was 270 ºC and 220 ºC, respectively. Mass spectra were recorded from 29 until 600 amu with a speed of 7 scans per second. Xcalibur 2.1, AMDIS 2.73 and GCMSsolution (version 4.45) software were used for collecting and processing of the data.

Pyrolysis-comprehensive two-dimensional gas chromatography/ mass spectrometry (Py-GCxGC/MS).

Py-GCxGC/MS analysis was conducted with a Shimadzu QP 2010 Ultra mass spectrometer (Shimadzu, Champs-sur-Marne, France) equipped with a two-stage thermal modulator ZX 2 (Zoex, Houston, USA). Pyrolysis was performed using a vertical micro-furnace-type pyrolyzer PY-3030D (Frontier Lab, Fukushima, Japan) directly connected to the injection port of the gas chromatograph. Before being placed in a stainless-steel sample cup, the samples were weighted with an XP2U Ultra Micro Balance (Mettler Toledo, Viroflay, France). Typical quantities of samples ranged from 25 to 80 µg. The sample cup was placed on top of the pyrolyzer at near ambient temperature and was introduced into the furnace at an optimized temperature of 600 ºC, and then the temperature program of the gas chromatograph oven was started. The pyrolyzer interface was held at 320 ºC. An Optima-5HT column (30 m × 0.25 mm I.D., 0.25 µm film thickness, Macherey-Nagel, Hoerdt, France) was used as the first dimension column and a Zebron ZB-50 (2.8 m × 0.1 mm I.D., 0.1 µm film thickness, Phenomenex, Le Pecq, France) was used as a second-dimension column and for the loop modulator system. The separation was carried out at an initial constant pressure of 300 kPa in the constant pressure mode, using Helium

Alphagaz 2 as carrier gas (Air Liquide, Bagneux, France). The ZX 2 two-stage thermal modulator employs a closed cycle refrigerator/heat exchanger to produce a − 90 °C cooled air jet regularly modulated with a pulsed hot air jet. The optimized modulation period for two-dimensional chromatogram collection was 6 s to 8 s with a programmed hot pulse of 0.350 s. The modulation time was optimized depending on the distribution of chromatographic peaks in the two-dimensional chromatogram. For the ease of reading, when a modulation time of 6 s was applied, a shift phase of − 2.0 s was applied during the treatment of data with the GC Image software. A multi-step temperature program was used for the hot jet set at 200 °C for 30 min and subsequently raised to 280 °C until the end of the acquisition. The oven temperature was initially held 1 min at 81 °C, and then ramped at 3 °C min − 1 to 325 °C, where it was held for 25 min. The total duration of GC analysis was ca. 107 min. The injector was held at 280 °C and used in split mode (1:30 of the total flow). The mass spectrometer was operated at 20,000 u.s − 1, with a scan range from 50 to 500 u, using electron ionization at 70 eV. The interface was kept at 300 °C and the ion source at 200 °C. Data processing of the 2D raw data was achieved using GC Image software, version 2.4 (Lincoln, Nebraska). Identification of components was performed by comparing the mass spectra of unknown components with reference compounds from the NIST MS library (2011) and interpretation of the main fragmentations.

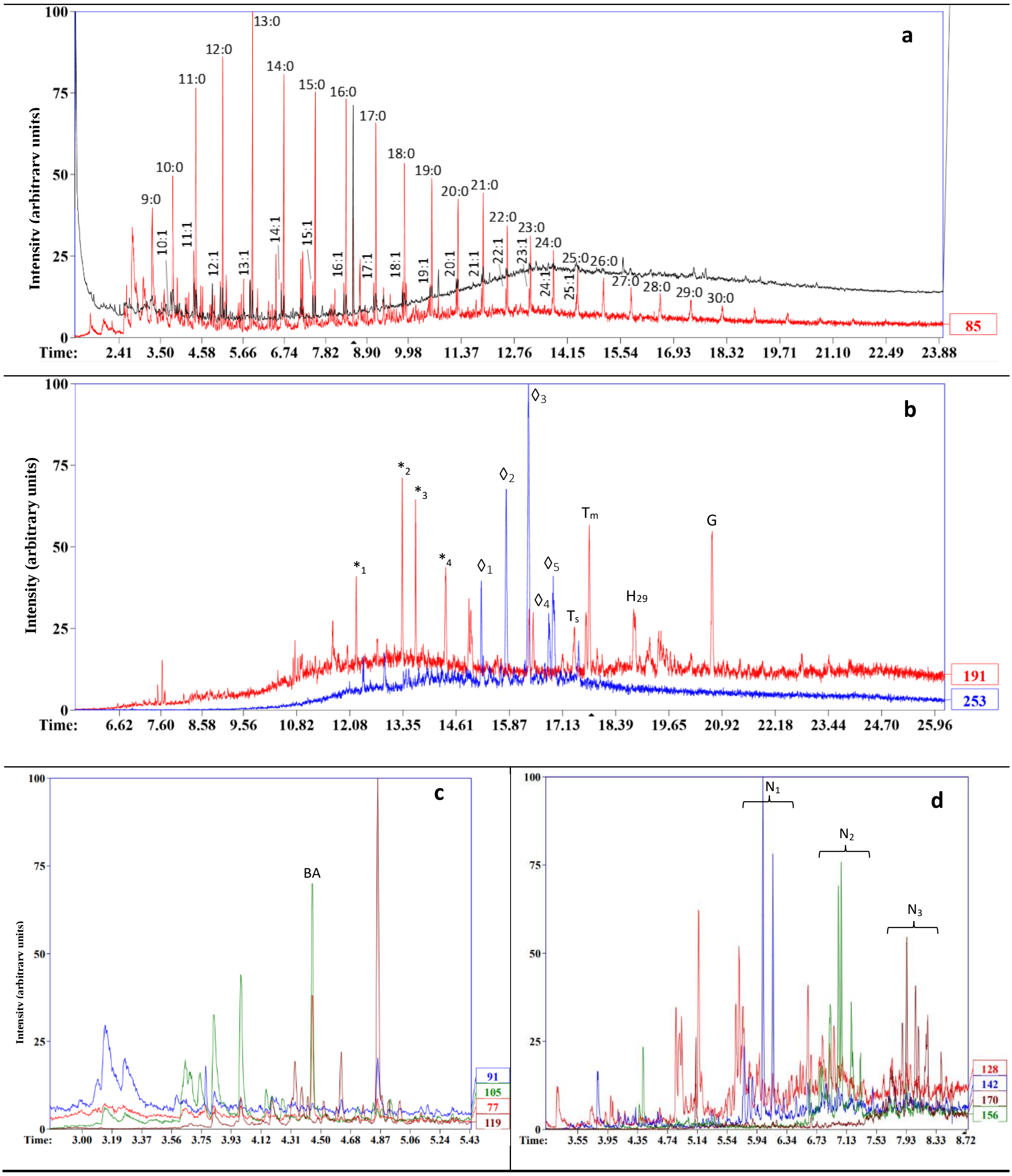
6.4 Results and discussion

6.4.1 Py-TMAH-GC/MS

6.4.1.1 Asphalt features in the Trinidad Lake asphalt reference sample

The raw Trinidad Lake asphalt (TLA) was characterized first to serve as the reference material using the same experimental conditions, which would be used later for samples from the individual steps in the reconstruction. Py-TMAH-GC/MS analysis showed a series of typical markers and biomarkers. These were defined as features to be tracked in the oil paint reconstruction samples (see Figure 6.1 and Table 6.2).

The markers identified were the aliphatic cross-links such as the homologous series of alkanes and alkenes, the aromatic sheet compounds such as the alkylbenzenes, alkylnaphthalenes and alkylbenzothiophenes and for the biomarkers the monoaromatic steroids, the hopane homologues (Ts, Tm, H29) and the gammacerane (see Scheme 6.1). Languri successfully identified these features in an asphalt sample described as “asphalt rich material (…) quite similar in its properties to the asphalt from the Dead Sea” and reported on their presence or absence in asphalt oil paint reconstructions and brown layers in paint samples from selected 19th century oil paintings with drying defects (Languri 2004).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75
50
25
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Time:
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3.50
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18.32
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21.10
22.49
23.88
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19:1
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21:1
22:1
23:1
24:1
25:1
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Intensity (arbitrary units)
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75
50
25
0
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7.60
8.58
9.56
10.82
12.08
13.35
14.61
15.87
17.13
18.39
19.65
20.92
22.18
23.44
24.70
25.96
*1
*2
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◊1
◊2
◊3
◊4
◊5
Tm
Ts
H29
G
191
253
c
Intensity (arbitrary units)
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75
50
25
0
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3.19
3.37
3.56
3.75
3.93
4.12
4.31
4.50
4.68
4.87
5.06
5.24
5.43
BA
91
105
77
119
d
100
75
50
25
0
Time:
3.55
3.95
4.35
4.74
5.14
5.54
5.94
6.34
6.73
7.13
7.53
7.93
8.33
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N2
N3
128
142
170
156

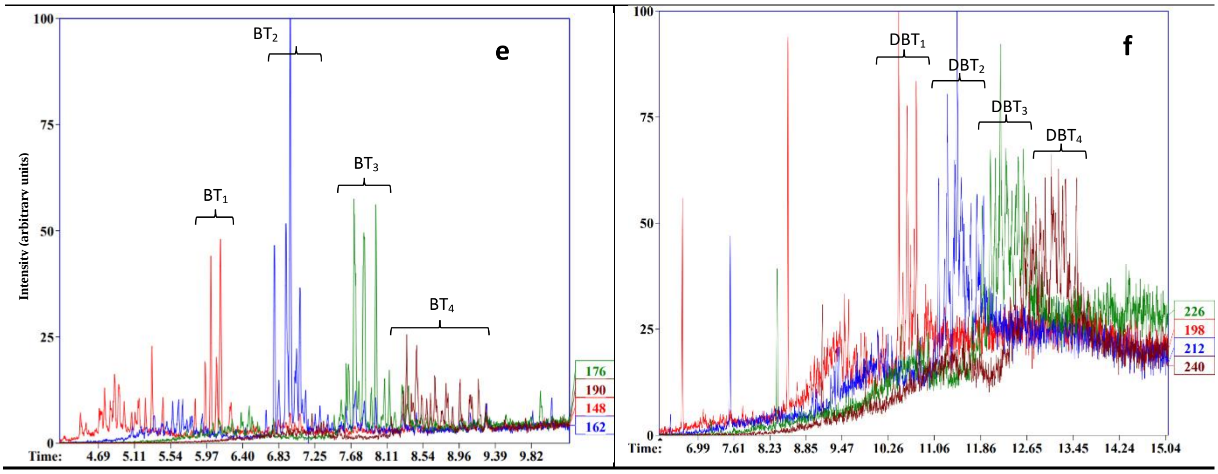


Figure 6.1: Mass chromatograms of TLA reference sample: a) Total ion chromatogram (TIC) (in black), alkanes and alkenes (*m/z* 85, in red), b) biomarker hopanes (*m/z* 191 in red) and C-ring monoaromatic steroids (*m/z* 253 in blue); Partial mass chromatogram of: c) alkylbenzenes (*m/z* 91, 77, 105, 119), d) alkylnaphthalenes (*m/z* 128, 142, 156, 170), e) alkylbenzothiophenes (*m/z* 148, 162, 176, 190) and f) alkyldibenzothiophenes (*m/z* 198, 212, 226, 240). Label information in Table 6.2.

Alkanes ranging from C9 to C30 and alkenes from C10:1 to C25:1 identified by mass peaks *m/z* 85 and 83 respectively have a right-skewed distribution and are a predominant feature in the TLA sample (Figure 6.1 a)). The acyclic isoprenoids, pristane and phytane were not detected. Their absence might be due to biodegradation processes which can alter or remove them completely (Peters, Walters, and Moldowan 2005a). Low values of pristane/phytane ratios in Trinidad Lake asphalts have been reported along with a predominance of even homologues of n-alkanes. This was seen to be pointing to “a severe reducing depositional environment of the marine organic matter of carbonate facies and bitumen immaturity” (Kayukova et al. 2016).

The labels used to identify each component in the following markers and biomarkers were based on the work of Languri (2004). Therefore the identification of the aromatic sheet compounds has been divided into four categories: the alkylbenzenes, the alkylnaphthalenes, the alkylbenzothiophenes and the alkyldibenzothiophenes.

For the alkylbenzenes a partial mass chromatogram with *m/z* 77, 91, 105 and 119 mass fragments shows a few peaks of interest (Figure 6.1 c)) however only the benzoic acid methyl ester (BA) was unequivocally identified. The alkylnaphthalenes are identified in Figure 6.1 d) for a range of peaks with *m/z* 142, 156, 170 respectively. This choice of a broader identification is due to the isomers present around the main peaks. The peaks for *m/z* 128 are present with a similar profile to the one observed in the literature (Languri 2004), however, the naphthalene peak was not unequivocally identified.

The same broader identification was made for the alkylbenzothiophenes with BT1, BT2, BT3 and BT4 representing a range of peaks with *m/z* 148, 162, 176 and 190 respectively (see Figure 6.1 e)). The presence of sulphur containing compounds such as the benzothiophenes and the dibenzothiophenes

(Figure 6.1 e) and f) respectively) are characteristic of the asphaltic nature of the sample and can be an indication for the geological origin of the asphalt (Languri 2004). Kohnen (1991) identified a large number of biomarker sulphur compounds and biomarker alkylthiophenes after desulpherisation using chemical workup of asphalts and kerogens from rocks (Kohnen 1991). Alkylthiophenes are therefore a marker for sulpherised organic matter when analytical pyrolysis is used.

The mass chromatograms of *m/z* 191 and *m/z* 253 (Figure 6.1 b)) show the characteristic fragment ions of the biomarkers hopanoid and steroid compounds identified in Table 6.2.

Using the mass chromatogram of *m/z* 191 four tricyclic terpanes and some tentatively assigned hopanoids were identified (see Figure 6.1 b) and Table 6.2). The assignment of 18 α(H)–22,29,30-trisnorneohopane (Ts) was based on the ion fragments 191 and 368, while the 17 α(H)– 22,29,30-trisnorhopane (Tm) had the *m/z* 191 and 370 (Languri 2004). Based on the relative retention time of the peak, and presence of fragments at *m/z* 191, 177, 398 (Subroto, Alexander, and Kagi 1991) the compound 17α(H),21β(H)-30-hopane (marked as H_{29}) was tentatively identified. The assignment of gammacerane (G) was based on the retention time and the mass spectra from Nytoft where the main ion fragments seen are *m/z* 191 and 412 (Nytoft et al. 2014).

The distribution of the C-ring monoaromatic steroids is easily detected using the mass chromatogram of *m/z* 253 (Figure 6.1 b) and Table 6.2). The peaks labelled $\lozenge_1$, $\lozenge_2$ and $\lozenge_5$ could be tentatively assigned to the C-ring monoaromatic steroids (MA) MA_{27}, MA_{28} and MA_{29} respectively based on their peak profile from the *m/z* 253 mass chromatogram (Figure 6.1b)) which have a distribution consistent with the data from the literature (Languri 2004; Peters, Walters, and Moldowan 2005b). Definite assignments of structures is however difficult and to achieve total certainty on this assignment it would be necessary to use standards along with the high-resolution capillary gas chromatography columns (Peters, Walters, and Moldowan 2005a; 2005b). For this reason, these compounds remained defined as C-ring monoaromatic steroid hydrocarbons in Table 6.2.

Table 6.2: List of feature compounds identified in the TLA reference sample, divided according to the classes of compounds with the respective retention time, label, formula and molecular weight. The presence (X) or absence (-) of these features in the reconstruction samples is indicated in the last three columns.

RT (min)	Label	Compound	Formula	M.W.	TLA	KT-I	KT	RP
Alkane (*m/z* 57, 85) & Alkene (*m/z* 55, 85)								
3.28	9:0	Nonane	C_9H_{20}	128	X	-	-	-
3.77	10:1	1-Decene	$C_{10}H_{20}$	140	X	-	-	-
3.82	10:0	Decane	$C_{10}H_{22}$	142	X	-	-	-
4.37	11:1	1-Undecene	$C_{11}H_{22}$	154	X	-	-	-
4.42	11:0	Undecane	$C_{11}H_{24}$	156	X	-	X	-
5.06	12:1	1-Dodecene	$C_{12}H_{24}$	168	X	-	-	-

5.12	12:0	Dodecane	$C_{12}H_{26}$	170	X	X	X	-
5.84	13:1	1-Tridecene	$C_{13}H_{26}$	182	X	-	-	-
5.90	13:0	Tridecane	$C_{13}H_{28}$	184	X	X	X	X
6.66	14:1	1-Tetradecene	$C_{14}H_{28}$	196	X	-	-	-
6.72	14:0	Tetradecane	$C_{14}H_{30}$	198	X	X	X	X
7.49	15:1	1-Pentadecene	$C_{15}H_{30}$	210	X	-	-	-
7.54	15:0	Pentadecane	$C_{15}H_{32}$	212	X	X	X	X
8.29	16:1	1-Hexadecene	$C_{16}H_{32}$	224	X	-	-	-
8.35	16:0	Hexadecane	$C_{16}H_{34}$	226	X	X	X	-
9.08	17:1	1-Heptadecene	$C_{17}H_{34}$	238	X	-	-	-
9.13	17:0	Heptadecane	$C_{17}H_{36}$	240	X	X	X	X
9.83	18:1	1-Octadecene	$C_{18}H_{36}$	252	X	-	-	-
9.87	18:0	Octadecane	$C_{18}H_{38}$	254	X	-	-	-
10.55	19:1	1-Nonadecene	$C_{19}H_{38}$	266	X	-	-	-
10.60	19:0	Nonadecane	$C_{19}H_{40}$	268	X	-	-	-
11.23	20:1	1-Eicosene	$C_{20}H_{40}$	280	X	-	-	-
11.28	20:0	Eicosane	$C_{20}H_{42}$	282	X	-	-	-
11.90	21:1	1-Heneicosene	$C_{21}H_{42}$	294	X	-	-	-
11.94	21:0	Heneicosane	$C_{21}H_{44}$	296	X	-	-	-
12.54	22:1	1-Docosene	$C_{22}H_{44}$	308	X	-	-	-
12.57	22:0	Docosane	$C_{22}H_{46}$	310	X	-	-	-
13.15	23:1	1-Tricosene	$C_{23}H_{46}$	322	X	-	-	-
13.16	23:0	Tricosane	$C_{23}H_{48}$	324	X	-	-	-
13.75	24:1	1-Tetracosene	$C_{24}H_{48}$	336	X	-	-	-
13.78	24:0	Tetracosane	$C_{24}H_{50}$	338	X	-	-	-
14.37	25:1	1-Pentacosene	$C_{25}H_{50}$	350	X	-	-	-
14.41	25:0	Pentacosane	$C_{25}H_{52}$	352	X	-	-	-
15.09	26:0	Hexacosane	$C_{26}H_{54}$	366	X	-	-	-
15.81	27:0	Heptacosane	$C_{27}H_{56}$	380	X	-	-	-
16.57	28:0	Octacosane	$C_{28}H_{58}$	394	X	-	-	-
17.37	29:0	Nonacosane	$C_{29}H_{60}$	408	X	-	-	-
18.20	30:0	Triacontane	$C_{30}H_{62}$	422	X	-	-	-
Tricyclic Terpanes (*m/z* 191)								
12.23	$*_1$	Tricyclic alkyl hydrocarbon (C_{21}?*)		290	X	-	-	-
13.33	$*_2$	Tricyclic alkyl hydrocarbon (C_{23}?*)		318	X	-	-	-
13.65	$*_3$	Tricyclic alkyl hydrocarbon (C_{24}?*)		332	X	-	-	-
14.35	$*_4$	Tricyclic alkyl hydrocarbon (C_{25}?*)		346	X	-	-	-

Hopanoids (*m/z* 191)								
17.41	T_s	18α(H)-22,29,30-trisnorneohopane	$C_{27}H_{46}$	368	X	-	-	-
17.45		25,28,30-trisnorhopane	$C_{27}H_{46}$	370	?			
17.76	T_m	17α(H)-22,29,30-trisnorhopane	$C_{27}H_{46}$	370	X	?	-	-
18.84	H_{29}	17α(H),21β(H)-30-nor-hopane	$C_{29}H_{50}$	398	X	?	-	-
Terpanes (*m/z* 191, 412)								
20.67	G	Gammacerane	$C_{30}H_{52}$	412	X	?		
Steroids (*m/z* 253, 231, 245)								
15.20	$\lozenge_1$	C-ring aromatic steroid hydrocarbon			X	-	-	-
15.80	$\lozenge_2$	C-ring aromatic steroid hydrocarbon			X	-	-	-
16.33	$\lozenge_3$	C-ring aromatic steroid hydrocarbon			X	-	-	-
16.80	$\lozenge_4$	C-ring aromatic steroid hydrocarbon			X	-	-	-
16.92	$\lozenge_5$	C-ring aromatic steroid hydrocarbon			X	-	-	-
17.68		Triaromatic steroid hydrocarbon		368	?			
Aromatics								
Alkylbenzenes (*m/z* 77, 91, 105, 119)								
4.44	BA	Benzoic acid methyl ester	$C_8H_8O_2$	136	X	X	X	X
Alkylnaphthalenes (*m/z* 128, 142, 156, 170)								
~ 5.70	N_1	C_1-naphthalene	$C_{11}H_{10}$	142	X	?	?	
~ 7.02	N_2	C_2-naphthalene	$C_{12}H_{12}$	156	X	-	-	-
~ 7.93	N_3	C_3-naphthalene	$C_{13}H_{14}$	170	X	-	-	-
Alkylbenzothiophenes (*m/z* 148, 162, 176, 190)								
~ 6.13	BT_1	C_1-benzothiophene	C_9H_8S	148	X	-	-	-
~ 6.97	BT_2	C_2-benzothiophene	$C_{10}H_{10}S$	162	X	-	-	-
~ 7.84	BT_3	C_3-benzothiophene	$C_{11}H_{12}S$	176	X	-	-	-
~ 8.50	BT_4	C_4-benzothiophene	$C_{12}H_{14}S$	190	X	-	-	-
Alkyldibenzothiophenes (*m/z* 198, 212, 226, 240)								
~ 10.50	DBT_1	C_1-dibenzothiophene	$C_{13}H_{10}S$	198	X	-	-	-
~ 11.50	DBT_2	C_2-dibenzothiophene	$C_{14}H_{12}S$	212	X	-	-	-
~ 12.40	DBT_3	C_3-dibenzothiophene	$C_{15}H_{14}S$	226	X	-	-	-
~ 13.00	DBT_4	C_4-dibenzothiophene	$C_{16}H_{16}S$	240	X	-	-	-

*based on (Peters, Walters, and Moldowan 2005a, 231).

N_1 = C_1 - methyl substitute; N_2 = C_2 – dimethyl substitutes; N_3 = C_3 – trimethyl substitutes

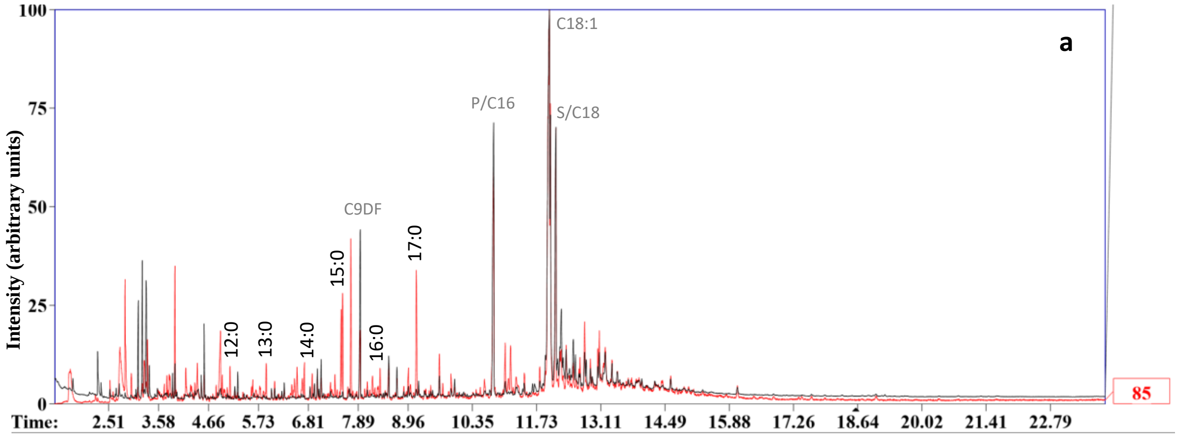
6.4.1.2 Asphalt features in the reconstruction

Results obtained from sample KT-I, which was taken after cooking the asphalt with the lead-treated linseed oil (*Strong Drying Oil*) to a top temperature of 318 ^{o}C, are detailed below, and clearly show the absence of markers and biomarkers from asphalt. As a result samples from KT and RP are not discussed further in this chapter since asphalt markers will also be absent in these samples. A summary of the results obtained for KT and RP using both Py-TMAH-GC/MS and Py-GCxGC/MS can be found in Table 6.2, and Table F.1 in Appendix F (pages 325-332).

Concerning the asphalt features (Figure 6.2), analyses revealed an almost complete absence of the alkanes and alkenes envelope with only C12 to C17 present. Using the mass chromatograms of *m/z* 191 no similar pattern to the TLA reference sample is observed in the KT-I sample. Only three peaks (with very low intensity) are present that match the retention time of the peaks identified in the TLA samples as Tm, H_{29} and G. However since these peaks in the KT-I sample present discrepancies when comparing their *m/z* values, a proper identification is unreliable. No peaks matching the TLA reference distribution of the C-ring monoaromatic steroids were detected using mass chromatography of *m/z* 253.

As suggested by previous thorough characterizations of differently processed linseed oil (J. van den Berg 2002; Bonaduce et al. 2012), aromatic compounds could also have been produced by the pyrolysis of the oil, despite the use of TMAH. This requires further investigation using Py-GC/MS of linseed oil processed by heating. Without TMAH, various alkyl aromatics are present in the Py-GC/MS of linseed oil paint (J. van den Berg 2002) which can be explained as thermal degradation of a residual substance after elimination of fatty acids from the oil paint network.

While only benzoic acid is present among the alkylbenzenes, in the alkylnaphthalenes (previously coded N_1-N_3) two main peaks from the N_1 group appear (with the same retention time but very little intensity). It is important to note that the alkylbenzothiophenes, which are important sulphur containing compounds characteristic of certain asphalts, have completely disappeared in the analytical data from the KT-I sample.



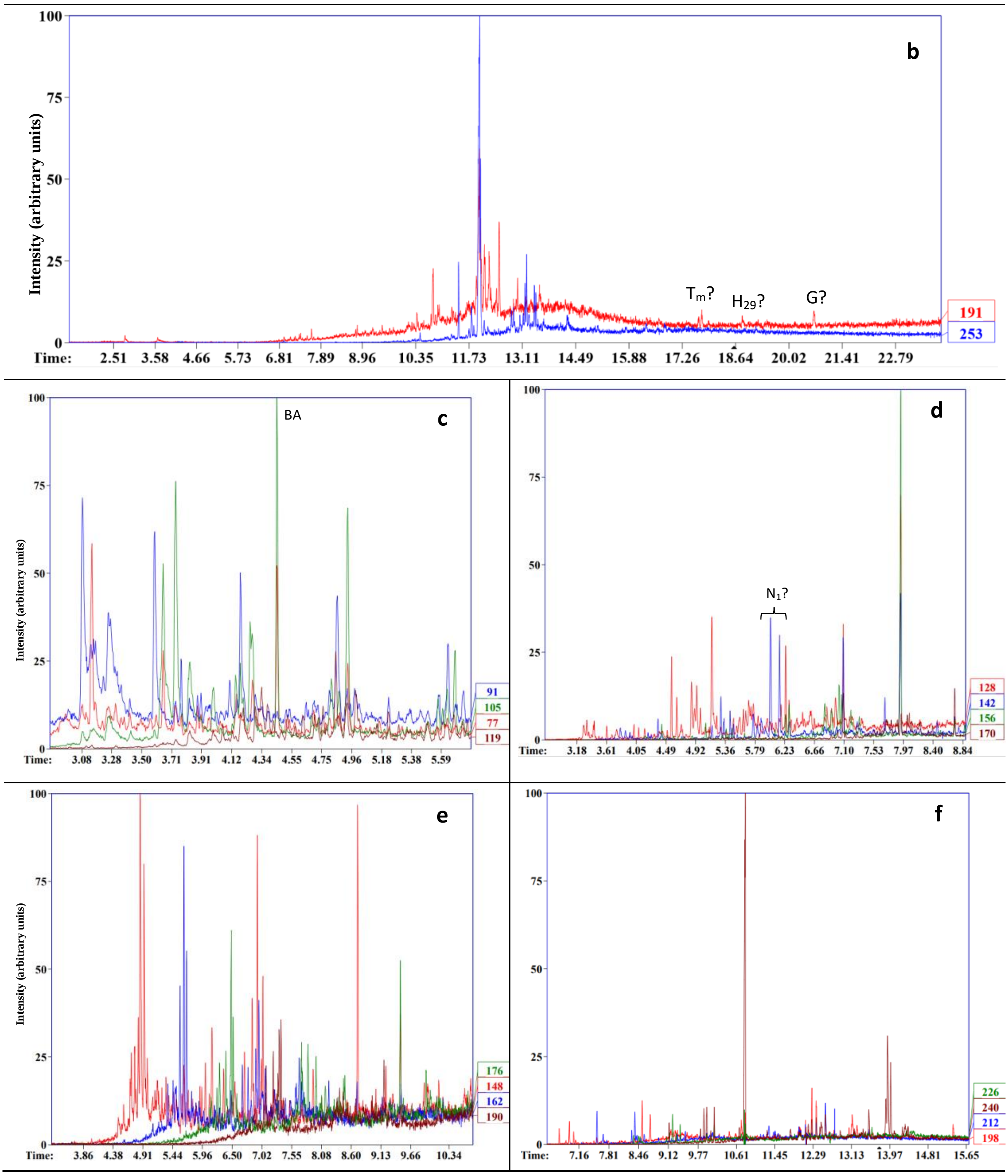


Figure 6.2: Mass chromatograms of sample KT-I: a) TIC (in black) and alkanes (*m/z* 85, in red), b) *m/z* 191 (in red) for hopanes and *m/z* 253 (in blue) for C-ring monoaromatic steroids; Partial mass chromatogram for comparison with Figure 6.1 of: c) alkylbenzenes (*m/z* 91, 77, 105, 119), d) alkylnaphthalenes (*m/z* 128, 142, 156, 170), e) alkylbenzothiophenes (*m/z* 148, 162, 176, 190) and f) alkyldibenzothiophenes (*m/z* 198, 212, 226, 240). Label information in Table 6.2.

Although the focus of the analysis is the tracking of the TLA features it is important to note that the main compounds present in the mass chromatogram of sample KT-I are fatty acids (determined by the *m/z* 74) identified in Figure 6.3. Clearly, the use of TMAH for derivatisation was the easiest means for exhaustively characterizing their presence. However, the predominance of the methyl esters may have obscured minor amounts of asphaltic components pushed below the detection limit. Nevertheless, as shown below, direct Py-GCxGC/MS analysis without TMAH still confirmed the absence of these compounds in KT-I.

In fact for the KT-I, KT and RP samples, saturated short and long-chain fatty acids (F) from C3F up to C27F and unsaturated C18 fatty acids could be observed along with short-chain diacids (DF) down to C4DF (Figure 6.3). The highest peak belongs to the C18 mono-unsaturated fatty acid, followed by the saturated fatty acids C16 and C18, palmitic and stearic acid respectively. Cooked at high temperature with lead compounds, these samples contain high amounts of oxidised C18 fatty acids, short fatty acids chains and glycerol compounds (gly), but a low amount of diacids when compared with naturally aged paint samples (J. van den Berg 2002).

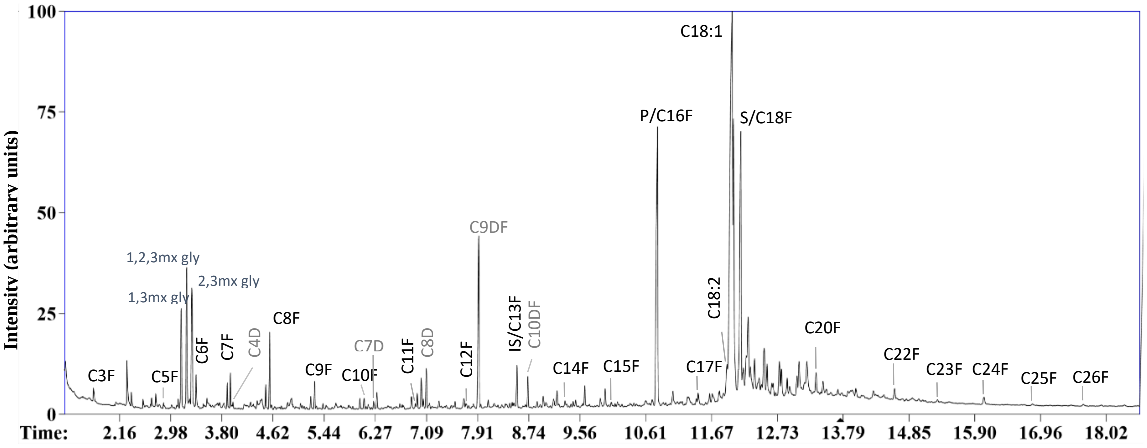


Figure 6.3: Total ion chromatogram of the KT-I sample derivatized with TMAH. “F” stands for fatty acids while “DF” for diacids, and “mx gly” identifies the glycerol derivatives.

6.4.2 Py-GCxGC/MS

6.4.2.1 Asphalt features in the TLA reference sample

Complementary to Py-TMAH-GC/MS, the same samples were analysed by Py-GCxGC/MS to determine whether this technique with its higher resolution and lower limit of detection, could help in the identification of asphalt in paint samples where the asphalt may be diluted by the paint production method. The reference sample of TLA was analysed in duplicate by direct Py-GCxGC/MS without derivatization since the targeted compounds detected above as potential markers for the TLA sample are not affected by methylation.

The series of markers and biomarkers previously observed with Py-TMAH-GC/MS were confirmed and refined thanks to the increased resolution provided by the bidimensional chromatographic separation.

Figure 6.4 reports the resulting total ion chromatogram obtained after pyrolysis at 600 ^{o}C of the TLA reference samples. Both the total ion chromatogram and the extracted ion chromatograms of the compounds of interest (as specified above, see 6.3 Experimental) were used for the characterization of components in the reference sample.

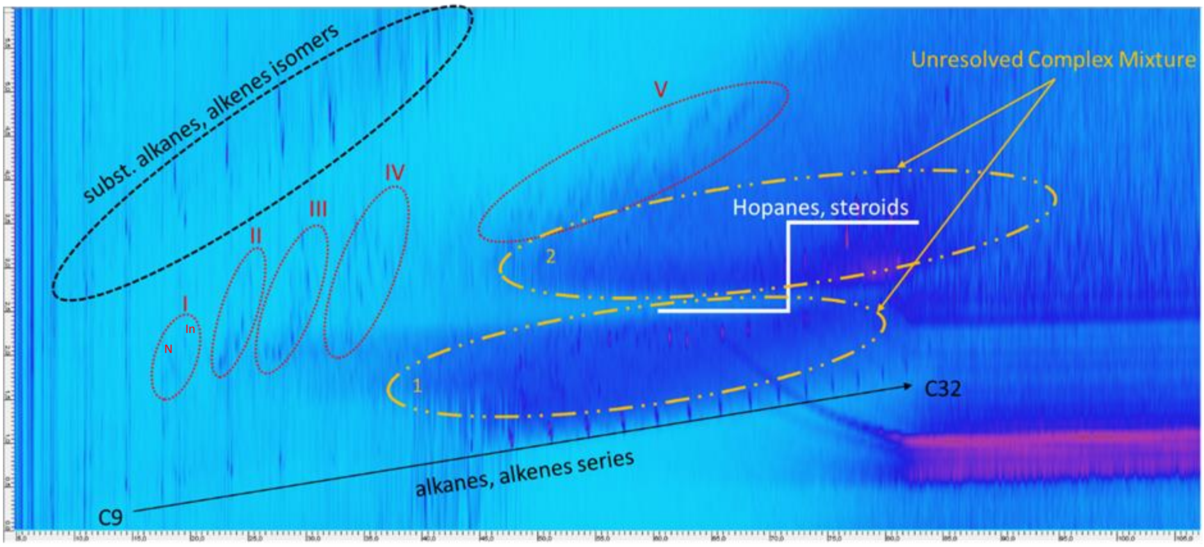


Figure 6.4: Total ion chromatogram of the TLA obtained by Py-GCxGC/MS for a reference sample of 39 µg (see experimental part for details). Families of compounds are circled in black, red and yellow. Inside group I, marked in red, are also reported naphthalene (N) and 1H-indene (In). The area in pink on the lower right side corresponds to the bleeding of the first column.

Three large areas of unresolved complex mixtures spanning from $^{1}t_{R}$ = 40 min to 90 min can be differentiated from the regular bleeding of the columns in the Py-GCxGC/MS chromatogram. This is responsible for the high level of background noise observed during the Py-TMAH-GC/MS experiments. Although the identification of the associated components is difficult, it can be stated that in area 1 circled in yellow (Figure 6.4) the peak distributions are attributable to hydrocarbons with a classical series of fragments at *m/z* 41, 43, 55, 57, 69, 71, 83, 85 etc. while in area 2 there are different fragmentation patterns with unclear significance. The 3D-view (Figure F., Appendix F, page 323) of the Py-GCxGC/MS chromatogram confirmed that most of the signal from the pyrolysis of the TLA reference sample lies in a series of linear hydrocarbons consisting of substituted alkanes or alkanes isomers; of hopanes structures; and of the unresolved complex mixture.

The families of compounds observed in Figure 6.4 outlined in black, red and yellow, will be the point of interest for tracking asphalt features in the reconstruction samples and are briefly detailed below and compiled in Table F.1 (page 325). They consist mainly of a series of alkanes/alkenes, a series of branched alkanes and isomers of alkenes, a series of hopanoid homologs and groups of compounds (I to V outlined in red). As will be seen below, the evolution of intensity of these compounds compared with the relative intensities of compounds from the unresolved complex mixture can be considered in the following samples. It is important to note that among the components detected during pyrolysis, few sulphur containing compounds were present. Some sulphur compounds were evident as methyl-substituted benzothiophenes. However no derivatives were observed of thiolanes, thianes, alkyl thiophenes, isoprenoid or steroid sulphides, which would be expected from asphalt (Sinninghe Damste and de Leeuw 1990). Extracted ion procedures were applied in an effort to select the relevant *m/z* fragments of these compounds in the mass spectra (Sinninghe Damste and de Leeuw 1990; Machado et al. 2011).

A series of alkanes and alkenes ranging from C9 (nonene) to C32 (dotriacontane) were observed as a predominant feature in the TIC (Figure 6.4). Their distribution showed disparities, while almost all the alkane homologs incremented in carbon number were detected, some of the associated alkenes were missing in the series, in particular for carbon chains exceeding C24 for which no alkene homologs were clearly separated from their alkane homologs or even present (Table F.1, page 325). In addition, a gap was present in the alkanes/alkenes series between the C14 and C18 homologs. In addition to this series of linear hydrocarbons, additional peaks assigned to substituted alkanes or positional isomers of alkenes and shifted in time in the second dimension (^2t_R = 3–6 s in Figure 6.4) are visible in the chromatogram.

Among the expected compounds of interest from the alkane series, neither phytane (*m/z* 282) nor pristane (*m/z* 268), were detected during pyrolysis of the TLA reference samples. This result corroborates well the data obtained with Py-TMAH-GC/MS.

Regarding the presence of fatty acids, only the n-hexadecanoic acid methyl ester was detected in both TLA reference samples in low quantity under the chosen conditions of analysis without the use of TMAH. However, traces of myristic acid methyl ester (C14) and stearic acid methyl ester (C18) could be observed in one of the TLA reference samples.

Among the expected biomarkers, a series of hopanes and monoaromatic steroids were observed (Table F.1, page 325). An extracted ion procedure, selecting the *m/z* fragments at *m/z* 191 and 253, present as base peak in the mass spectra, was applied to characterize the hopanes and steroids. Both series of these compounds are eluting among the unresolved complex mixture (in area 2 circled in yellow, Figure 6.4). For the general structure of these molecules see Appendix F.2 (Figure F.3, page 324). The hopane series can be differentiated into hopane and norhopane structures. Noteworthy, no steranes, which could be expected as markers in an asphalt (Peters, Walters, and Moldowan 2005a), were characterized during pyrolysis of the TLA reference sample.

The extracted ion procedure at *m/z* 91 revealed the presence of single aromatics: toluene and isomers of dimethyl-benzene. Extended search at *m/z* 105, 119 revealed the presence of substituted tri- and tetramethylbenzene homologues. No trace of benzoic acid was detected however this can be explained by the lack of methylation which is needed for its efficient detection. In contrast to the findings with Py-TMAH-GC/MS, structures with a base peak at *m/z* 128 and assigned to naphthalene and 1-methylene-1H-indene, respectively, were detected using Py-GCxGC/MS (Table F.1 in page 325).

Alkylbenzenes, akylnaphthalenes, and alkylbenzothiophenes previously detected with Py-TMAH-GC/MS were revealed in four groups of compounds, identified as I, II, III and IV in Figure 6.4. The first group I consists mainly of methyl-substituted benzenes, the previously mentioned naphthalene and substituted indene structures. Group II encompasses dimethyl substituted indene structures and methylated naphthalenes. Group III includes trimethyl substituted indene structures, dimethyl naphthalene isomers, and dimethylbenzothiophenes as well as their dibenzothiophene homologs. Group IV encompasses the higher homologs with trimethylated naphthalenes and trimethylated benzothiophenes. An additional group, identified as group V in Figure 6.4, consisted of a series of polycyclic aromatic hydrocarbons including phenanthrene to pyrene substituted structures.

6.4.2.2 Asphalt features in the reconstructions

Having established a full chemical fingerprint of the TLA reference sample using the findings above, sample KT-I from heating asphalt with lead-treated drying oil was investigated to determine any changes resulting during the manufacture of W&N's bitumen brown oil paint (Table F.1 in Appendix F, pages 325-332).

6.4.2.2.1 TLA features in sample KT-I

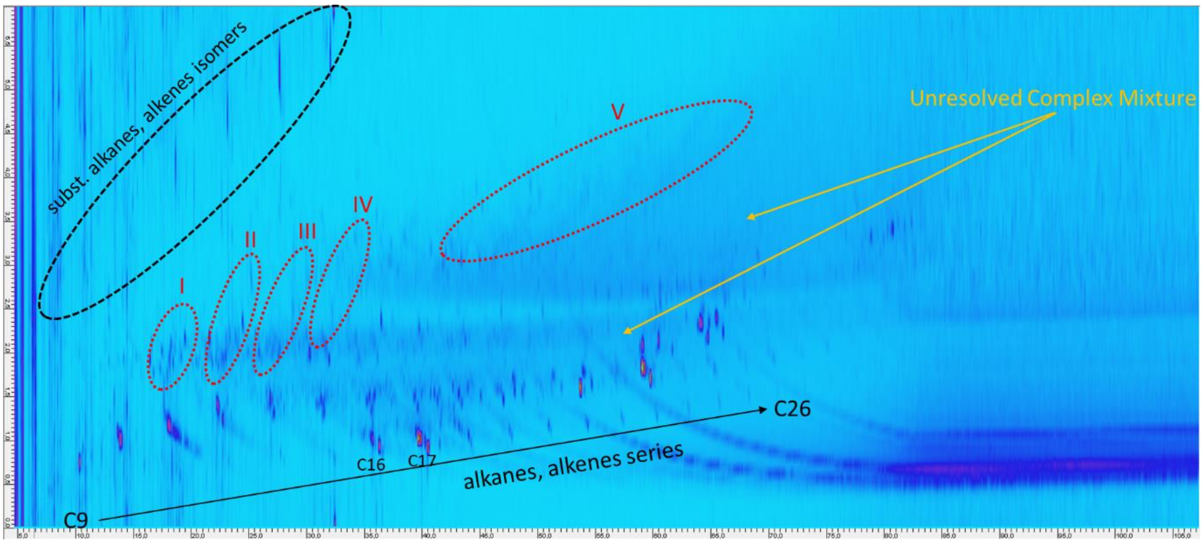


Figure 6.5: Total ion chromatogram of the KT-I sample obtained by Py-GCxGC/MS of 53 µg of sample. Families of compounds are circled in black and red.

Compared to the TLA reference sample, the unresolved complex mixture is significantly attenuated in the total ion current chromatogram from sample KT-I (Figure 6.5). The 3D-view of the Py-GCxGC/MS chromatogram confirmed this diminution in relative intensity when compared to the overall intensities of peaks assigned to the targeted compounds (Figure F. in Appendix F, page 324). In KT-I most of the signal is taken up by components from the addition of drying oil (see below). However patterns from the TLA reference sample were still detectable, specifically the series of linear hydrocarbons, substituted alkanes or alkanes isomers. Families of compounds which remain in KT-I are briefly detailed below and compiled in Appendix F, Table F.1, page 325.

A notable change in the series of alkanes and alkenes from C9 to C26 (longer than those detected by Py-TMAH-GC/MS which were limited to the C12-C17 homologs) was observed in KT-I compared to the TLA reference sample, in particular, an abnormally intense pattern of peaks assigned to 1-n-heptadecene/n-heptadecane structures was detected in the middle of the series around $^1t_R = 40$ min. This group of four components was attributed to heptadiene $^1t_R = 39.4$ min, isomer of 1-n-heptadecene, $^1t_R = 39.7$ min, 1-n-heptadecene $^1t_R = 40.2$ min and heptadecane $^1t_R = 40.5$ min, respectively. A similar pattern, however with comparatively lower intensities, was observed for the C16 homologs, with strong peaks associated to the 1-n-hexadiene and hexadiene, and with low intensity for the n-hexadecane. Interestingly the highest intensities of the C16 and C17 alkanes/alkenes homologs seen in KT-I had not been observed in the TLA reference sample since these compounds were missing. The presence of C16-17 hydrocarbons in the KT-I sample could result from the scission of alkyl chains of fatty acids during the pyrolysis process and are likely attributable to the addition of drying oil.

In the KT-I sample, additional peaks assigned to substituted alkanes or positional isomers of the alkenes and shifted in time in the second dimension ($^2t_R = 2.5–6$ s in Figure F. in Appendix F, page 324) appeared in the chromatogram which was similar to the TLA reference.

Among the expected biomarkers of asphalt, a series of hopanes and monoaromatic steroids were observed in the TLA reference during Py-TMAH-GC/MS analysis (Table 6.2). Application of the extracted ion procedure to the KT-I sample, selecting the *m/z* fragments at *m/z* 191 and 253 for the characterization of hopanes and steroids did not reveal their presence. Similarly, an extracted ion chromatogram (EIC) at *m/z* 230 for the detection of pyrene or terphenyls in the KT-I sample did not find these materials whereas they were detected in the TLA reference sample. Clearly, these compounds were no longer observed in the sample from the first step of the reconstruction.

Extracting the fragments at *m/z* = 91 showed more benzene and naphthalene homologs than had been observed in the TLA reference sample. At the beginning of the chromatogram for KT-I, for $^1t_R < 17$ min, these compounds correspond to unsaturated alkylbenzenes and dehydrogenated naphthalene (Table F.1 in Appendix F). Moreover new structures are observed, in particular a series of alkylbenzenes expanding to the undecyl-benzene $C_{17}H_{28}$, which could be related to radical condensation products and be explained by the addition of drying oil.

Application of the extracted ion procedure at the fragments *m/z* 119 in sample KT-I did not reveal the presence of group I components, tetramethyl-, benzene, observed in the TLA reference sample. Instead, EIC at *m/z* 119 showed mainly aromatic structures built around a substituted benzene ring (Table F.1 in Appendix F).

Similarly, benzothiophene based structures belonging to group I and group II were absent. In contrast, the 1H-Indene, 1-methylene-, 2-methylindene, 1H-Indene, dimethyl-, naphthalene structure were still present. The same applies for the dimethyl, indene (group II) which are still detected, while benzothiophene structures are absent.

However, EICs at *m/z* 142 for the KT-I sample showed that most of the compounds found during pyrolysis of the TLA reference sample, such as the benzocycloheptatriene structures, 1-H-indene structures, 1- or 2- methylnaphthalene (group II) were still present. Overall, group II provided almost the same number of components as those detected in the reference sample of TLA.

As observed for the benzothiophene based structure of group I, none of the dimethyl, benzothiophenes (EICs at *m/z* 162) were detected as representative compounds of group III. The same does not apply for most of the dimethyl, naphthalene homologs still prevailing in group III as well as the trimethyl, indene-based structures.

In a similar way, for group IV, only the substituted naphthalene (trimethyl-) remained while the main benzothiophene substituted homologs were missing. In general the presence of markers of asphalt are noticeably decreasing in the two last groups, IV and V, compared to the TLA reference. The most significant finding is that all sulphur containing compounds which had been observed in the TLA reference sample are absent in the KT-I pyrogram, (which was taken very early on in the preparation of the bitumen brown oil paint reconstruction, when the mixture contained only TLA, *Strong Drying Oil* and Sugar of Lead).

Whereas a significant number of compounds characterized during Py-GCxGC/MS analysis of the TLA reference sample were not detected in the KT-I sample, some compounds within the different groups defined earlier were still detected. At the same time, a new class of components, most likely introduced by the materials used in the reconstruction of bitumen paint, are observed in addition to these compounds: in particular, alkyl acids C5-C8, propenyl ester of alkyl acids C11-C21, and carbonylated compounds which were eluted in ${}^{2}t_{R}$ = 1–2.5 s (Figure 6.5).

Dilution of the asphalt in the oil paint mixture or chemical breakdown of the whole asphalt structure are proposed as possible explanations for the results of the Py-TMAH-GC/MS analyses. The Py-GCxGC/MS analyses results led to similar findings with greater emphasis on the second explanation, that a chemical breakdown of the asphalt structure was occurring: an assumption supported by the disappearance of the benzothiophene homologs.

To understand the effect of temperature (during paint manufacturing) an additional TLA sample heated to 318 °C was analysed with Py-GCxGC/MS (see Table F.1 in Appendix F). Contrarily to the results observed with the TLA reference sample, the heated TLA had predominantly alkyl homologs C14-C18 which could likely be attributed to the thermal degradation of alkyl bridges of the asphaltene structure in the asphalt sample. However, the marker compounds (hopanes, monoaromatic steroids and groups I-V) were still observed in the heated TLA sample with no noticeable change in their distribution except an increased number of aromatic homologs in group IV-V. Therefore, the temperature of cooking does not appear to cause the disappearance of sulphur compounds, or induce significant differences in the compounds distribution detectable by Py-GCxGC/MS. Considering the TLA processing and the materials added in the first step of the reconstruction (KT-I), the interaction with the drying oil and respective lead driers appear to be dominant factors for the absence of asphalt features.

6.5 Conclusion

In summary, the analysis of the TLA reference sample with both techniques showed specific markers and biomarkers that could be used to identify the presence of the original TLA in the reconstruction samples:

- An homologous series of alkanes and alkenes, with Py-GCxGC/MS identifying additional peaks assigned to substituted alkanes or positional isomers of alkenes;
- Monoaromatic steroids;
- A series of hopanoid homologs (which can be differentiated into hopane and norhopane structures);
- The pentacyclic triterpenoid gammacerane;
- Compounds issued from the aromatic sheet structure of asphaltene such as the alkylbenzenes, alkylnaphthalenes and alkylbenzothiophenes, further characterized with Py-GCxGC/MS and reported as five groups of compounds:
  - Group I: mainly methyl-substituted benzenes, the previous naphthalene and substituted indene structures.
  - Group II: dimethyl substituted indene structures and methylated naphthalenes.
  - Group III: trimethyl substituted indene structures, dimethyl naphthalene isomers, and dimethylbenzothiophenes as well as their dibenzothiophene homologs.
  - Group IV: higher homologs with trimethylated naphthalenes and trimethylated benzothiophenes.
  - Group V: series of polycyclic aromatic hydrocarbons including phenanthrene to pyrene substituted structures.

Interestingly, few sulphur containing compounds were present, such as, methyl-substituted benzothiophenes, and no derivatives of thiolanes, thianes, alkyl thiophenes, isoprenoid or steroid sulphides were observed.

The unresolved complex mixture is more easily discerned with Py-GCxGC/MS in the TLA reference sample. Although it remains visible throughout samples from the reconstruction this mixture became noticeably attenuated at each stage with a marked diminution in relative intensity. Given the mineral content in the TLA sample, it is possible that large complex organo-metallic compounds play a role in this unresolved complex mixture. However, it is important to note that supplementary analysis of other sources of asphalt or bitumen (not discussed here) do not show this unresolved complex mixture and therefore this should not be considered a “feature” to track asphalts in oil paintings.

The main conclusion from this study is that with both analytical techniques, the main TLA markers have already disappeared in the first step of the reconstruction (sample KT-I), and those remaining, such as the series of alkanes, are insufficiently characteristic to make an unequivocal attribution for asphalt. This finding is extremely important for any conclusions based on analyses using Py-TMAH-GC/MS or Py-GCxGC/MS of 19th century paintings suffering from film-forming defects thought to have been associated with the use of asphalt.

The use of the highly sensitive technique of Py-GCxGC/MS in this study illustrates that the difficulty in identifying asphalt markers in historical paint is not simply due to its dilution during paint production, rather these findings indicate that in the case of Trinidad Lake asphalt at least, the original asphalt markers disappear during heating and processing in a drying oil consisting of linseed oil cooked with litharge and red lead.

In this case it is thought that the asphalt could be undergoing reduction due to the loss of sulphur bridges, possibly favoured in the presence of lead, which results in the chemical breakdown of the asphalt and the disappearance of thiophenes visible in the original material. Further chemical study on the effects of lead oxide on polysulphides and bound sulphurised lipids would be relevant to better understand this process, and further study with other elemental techniques could help clarify if sulphur is still present in the samples.

GENERAL DISCUSSION, CONCLUSIONS AND FUTURE RESEARCH

The aim of this research was to contribute to the knowledge of 19th century oil paintings suffering from alligatoring. For that, a multi-disciplinary approach was carried out.

The critical analysis of published sources (Chapter 1), focusing on the perception of the problem, provided context for alligatoring and revealed a narrow view of the problem and fragmented literature on the subject. Particular emphasis was given to the bias created by the perceived connection between appearance and cause, resulting in an association of paint film defects in brown paint with the use of asphalt/bitumen. As demonstrated, the assumptions based on the visual perception alone were not necessarily confirmed through material evidence. This concentration on the single question of the presence or absence of asphalt/bitumen inhibited investigations of other materials that may play an important role in the degradation mechanism.

With few exceptions (e.g. Frame 2022), the literature survey demonstrated the confusion between cause and effect, whereby the paint defect was persistently assigned to bitumen brown paint without material evidence to establish the connection. The revelation that asphalt not being detected relates more to the analytical methodology employed than to the actual absence of the material became a guiding thread throughout the analysis and characterization of *O Cardeal D. Henrique*... This then culminated with the production and analysis of W&N's Bitumen Oil Paint reconstructions.

The documentary research on the artist (Chapter 2) contributes significantly to a comprehensive understanding of his life and work. This research clarified Marciano's biographic information and placed the Portuguese artist in the larger context for the problem of severe alligatoring in 19th century paintings. The exploration of Marciano's training and early painting experience identified important connections with other contemporary artists (for example with the painter Ary Scheffer, who also created paintings that developed severe alligatoring) and highlighted his mobility (traveling to Paris, London and Rome), which is likely related to his choice of materials and techniques and therefore to the technical problems encountered in his paintings. A total of 64 paintings were identified, only 14 were located. This discrepancy could indicate that many more of his paintings suffered from paint defects and may not have been preserved for that reason.

The full examination (Chapter 2) and technical analysis (Chapter 3) of the painting *O Cardeal D. Henrique*… was carried out using a multi-analytical approach. This investigation determined several variables in terms of the artist technique (e.g. reused canvas) and materials present (e.g. lake pigments) that may be associated with the paint defects. It also revealed analytical difficulties and limitations that are important considerations and should be recognised as opportunities for future research.

Further research is necessary to develop a full picture of the degradation mechanism evident in *O Cardeal D. Henrique…*, however one outcome of this research is that the degraded paint is characterised by an oil binder with a high degree of oxidation, rich in polar fatty acids as diacids, combined with a lack of the pigments that are capable of stabilizing the paint. The presence of the translucent lead azelate layer above the ground underlines the complexity of the possible mechanisms for degradation. Through OM observations of the cross-sections it appears that this layer which remains intact, signals a point after which the subsequent layers are free to distort and pull the paint into paint islands. It remains unclear what role this layer has within the paint stratigraphy and the formation of the paint deformations; but the excess of oil in the paint system and the possible role of metal carboxylates have to be highlighted.

It is possible that additional materials, such as asphalt, might be contributing to the phenomenon. Despite this investigation with state of the art analytical techniques, the full characterisation of the organic compounds remains challenging and emphasises the relevance of the reconstructions prepared in Part II.

A particularly significant contribution from this doctoral research, detailed in Part II, was the research carried out on the Winsor & Newton's 19th century Archive Database, a unique resource that, for the first time, allowed the exploration of the commercial production of 19th century asphalt/bitume oil paint formulations.

Access to the *Researcher's Edition of the W&N 19th-century Archive Database*, allowed the analysis of the 25 production records for W&N's *Bitumen* oil paint and a comparison with recipes for bitumen or asphalt brown published in British 19th-century artist's manuals (Chapter 4). The discovery that the wide variety of materials and a lack of uniformity in formulations found in artist's recipes were echoed in the W&N records before 1850 provides new knowledge regarding the extent of variations in bitumen brown paints which, in turn, explains the sporadic nature of drying problems reported for asphalt-based oil paint (interestingly despite the production records being for *Bitumen* oil paint the raw ingredient was always asphalt).

An important finding from the analysis of W&N's *Bitumen* oil paint manufacture is that the company standardised the ingredients in the 1850s but that they still carried out adjustments in materials and proportions from the "standard" ingredients in order to produce a consistently rich brown that dried well, had good handling properties and compared favourably to their competitors' product.

Access to the W&N Archive database allowed, for the first time, a reconstruction of W&N's production of their bitumen brown oil paint (Chapter 5). Not only did the reconstruction, using the HART research model provide insights into the processing methodology itself, it also provided the first ever material reference for chemical analysis of a commercial product with known ingredients.

Observations of the paint reconstructions during application and initial drying provided some characteristics seen in the widely described "bitumen cracking" in oil paintings such as the severe wrinkling observed within one week. Another important observation was the formation of a distinctive cell-like structure demonstrating that the mixture separates in phases and is far from homogeneous.

The paint reconstructions contributed a critical finding. As reference samples for the analytical detection of asphalt using thermally assisted methylation with tetramethylammonium hydroxide (Py-TMAH-GC/MS), and pyrolysis comprehensive two-dimensional gas chromatography (Py-GCxGC/MS) the reconstruction demonstrated that (at least with the Trinidad Lake asphalt), the original asphalt markers disappear during heating and processing in a drying oil consisting of linseed oil cooked with litharge and red lead. It also established which chemical markers from TLA remained within this paint matrix of multiple ingredients after heat processing, and how these are insufficiently characteristic to make an unequivocal attribution for asphalt.

Conclusion

This research contributes new knowledge in the analysis and interpretation of 19th century paintings suffering from paint defects and explains the lack of evidence of asphalt in the results reported in the literature. This work demonstrates the fundamental importance of understanding artist's materials in the context of their preparation and use, and illustrates why materials cannot simply be evaluated and analysed in their original state as raw materials. Although analyses of the raw ingredients can provide useful information, because processing for use can result in significant chemical alterations, they are of limited value in their raw state. As this work show, chemical analysis of the starting materials for asphalt containing brown paint can result in unreliable markers which do not persist after processing. The impact of heat processing and mixture of ingredients necessary to produce an asphalt paint was enough to prevent the detection of distinctive markers from the raw asphalt source in complex 19th century brown paint formulations and very likely in 19th century paintings.

Future Work

Concerning *O Cardeal D. Henrique*… an important question remains in terms of the characterization of the lake pigments present in the painting, particularly the possible brown/yellow lakes. As no further information could be obtained with TOF-SIMS, further clarification on the dye's chromophore would require other analytical techniques such as micro-spectrofluorimetry or high-performance liquid chromatography (HPLC). The latter technique requires extraction methods to separate the dye from the oil binder. The role of the lake pigments in the paint film defects identified in *O Cardeal D. Henrique…* is a rich area for future research, as these notoriously poor driers have not received systematic attention in relation to drying problems in oil paint films.

Regarding the mechanism for the alligatoring, the gel-like state of lake pigments in oil should be investigated, particularly the influence of the lake substrate, the aluminium hydroxide which is a gelatinous material in aqueous solution (e.g. Sato and Sato 1996; J. Kirby, Spring, and Higgitt 2005; Vitorino 2020, 13; Zhuang et al. 2020) during precipitation of the lakes. Another factor for consideration is the role of the loss of volatile materials and low molecular weight fragments during extended reactions occurring in the paint film which may be related to the extreme shrinkage response apparently evident in *O Cardeal D. Henrique….* possibly exacerbated by the complex paint stratigraphies in this painting.

To follow up on the possible relationship between paint material exudates found on *O Cardeal D. Henrique…* and fully dried 20th century oil paintings exhibiting a mobile phase (paint dripping), analysis of samples from *O Cardeal D. Henrique*… using direct temperature-resolved mass spectrometry (DTMS) to look for the polar compounds previously identified at *m/z* 152, 155 and 280 (Boon, Hoogland, 2014) in 20th century oil paint drips (exudates) could further our understanding of unstable dried oil paint systems.

These elements would help build a comprehensive scheme for the degradation mechanism. Reconstructions of paint layers of similar composition, or model systems (with a high content of fatty acids/diacids) could also be investigated after artificial ageing to gain insight on the exact role of these different materials, and to reveal whether those materials can be responsible for such degradation.

The reconstructions of W&N's *Bitumen* oil paint are a valuable resource that should continue to be investigated. Deeper consideration of the heating source, and the time and temperature of cooking is needed to obtain greater control and monitoring of these variables. Another area deserving further attention is the issue of scaling down the reconstruction recipe. Industrial chemists are well aware of the effect of scale on their processes which will impact reaction times and properties of the final product (Carlyle et al. 2011).

Analyses showed that the original markers from TLA do not disappear simply by heating the raw material to the temperatures reached during the reconstructions. The next step is to understand if the markers remain after heating the TLA with other components in the production record. Of primary interest is the role of linseed oil alone or with lead driers to examine the possible role of lead in the chemical breakdown of the asphalt.

Also being currently investigated as a promising technique in the search for asphalt/bitumen is Electron paramagnetic resonance (EPR). EPR of vanadyl porphyrins and carbonaceous radicals (present in the asphaltene fraction of bitumen) has been recently used in a non-destructive way to unambiguously identify the presence of bitumen in Egyptian embalming materials (e.g. Dutoit et al. 2020). This approach, successful for archaeological artifacts, shows potential for the analysis of complex 19th century oil paint samples where processed asphalt/bitumen might be present.

In terms of painting's conservation, interesting perspectives should also be highlited. Further work collecting reference paintings for "The Alligatoring in Oil Paintings Survey", a database of images of affected paintings which was designed and populated during this research, would provide a wider understanding of the scope and visual impact of this problem. This information would determine the extent of the problem, the countries of origin for the paintings and the date range involved. This work would facilitate communication amongst those who have identified the problem in their own collections and for the dissemination of information on the phenomenon. Making the Database available online for crowdsourcing should also be considered, as it would increase the reach of the project to encompass paintings collections all over the World.

Another avenue for future research is to study the perceptions of audiences, both professional and public when they encounter alligatoring in an oil painting. The understanding of what is being perceived and how the defect alters our perception of paintings with the problem has not been a topic of comprehensive research. The Alligatoring in Oil Paintings Survey could provide a starting point in this study.

Finally, interesting ethical questions regarding the preservation of severely affected paintings deserve consideration. Paintings affected by alligatoring offer a rich resource for studying degradation phenomena but the severe distortions produced in their imagery compromises their existence as viable and exhibitable artwork, which in turn is likely to compromise their continued preservation.

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A

Appendix to Chapter 1

A.1 Sources selected

Table A.1: Overview of the number and type of sources selected, divided by the field of literature.

№	Type of Source	Reference/Published Source
Conservation and Restoration Literature		
43	Articles	(Keck 1969; Jesseli 1981; Wolbers 1983; Shank 1984; Buckley 1986; Kirby Talley 1986; White 1986; Massing 1988; Svoboda and van Vooren 1989; Erhardt, von Endt, and Tsang 1990; Jones 1990; Schmitt 1990; Hill Stoner 1990; Carlyle 1993; Swicklik 1993; van der Loeff and Groen 1993; Groen 1994; White and Kirby 1994a; Townsend et al. 1995; Bucklow 1996; Carlyle 1996; Southall 1996; Woodcock 1996; Theurer 1998; Townsend et al. 1998; Boon, Townsend, and Jones 1999; Bucklow 1999; Jones, Townsend, and Boon 1999; White 1999; Dubois 2000; van der Werf et al. 2000; K. J. Van Den Berg et al. 2002; Carlyle et al. 2002; Languri, van der Horst, and Boon 2002; Languri and Boon 2005; Languri, Boon, and Boitelle 2005; Carlyle, Boon, Haswell, and Witlox 2008; Morrison 2010; Van Zuien 2012; Gent, Morrison, and von Aderkas 2015; von Aderkas, Gent, and Peggy 2021; Pasco et al. 2022; Frame 2022)
14	Books	(Redgrave and Redgrave 1866; M. de Macedo 1885; Stout 1950; Eastlake 1960; Mills and White 1987; Mayer 1991a; 1991b; Bothe 1999; de Willigen 1999; Kirsch and Levenson 2000; Carlyle 2001; Carlyle et al. 2006; Doherty and Woollett 2009; Mayer and Myers 2011)

12	Book Chapter/Section	(Harley 1975; Carlyle and Southall 1993; Townsend 1995; Katz 1998; Pey 1998; Harley 1982; Bothe 2007; Boon and Hoogland 2014; Bucklow 2021; Schmitt 2012; Costaras 2017; Carlyle 2020)
10	Thesis/Dissertations	(Hodge 1987; Carlyle 1991; Grimm 1999; Mourato 2000; Izat 2001; Languri 2004; Grober 2006; Rae 2010; Shimazu 2015; Pasco 2019)
Paint and Coating Industry		
7	Books	(Sabin 1904, 1927; Cruickshank Smith 1912; Walker and Hickson 1945; Spence and Haynie 1972; Hess and Hamburg 1979; Schweitzer 2006; Koleske 2012)
1	Book Chapter/Section	(Stoner 2006)
1	Article	(Thompson 1915)
Other Sources		
8	Books	(Macedo 1951; Asphalt Institute 1989; Callu 1994; Wess, Olsen, and Haring Sweeney 2004; Peters, Walters, and Moldowan 2005a; 2005b; Eastaugh et al. 2008; Hunter, Self, and Read 2015)
3	Book Chapter/Section	(Yen 1990, 2000; Petersen 2000)
7	Articles	(Macedo 1950a; 1950b; Zander 1995; Charles and Grimaldi 1996; “Lake Asphalt of Trinidad and Tobago (1978) Limited” 2009; 2012; Mullins et al. 2012; Hsu and Robinson 2019)

A.2 Terminology

Table A.2: Descriptions of the term Alligatoring in published sources from the Paint and Coating Industry literature and the Conservation and Restoration literature, spanning from 1904 to 2015.

Alligatoring	Published Source
Paint and Coating Industry Literature	
“(…) the paint is cracked and the cracks have opened to a considerable width, frequently a quarter of an inch, in a reticulated pattern suggestive of alligator-leather. These cracks are at first minute; then the paint or varnish on the interspaces contracts, drawing slowly apart, until the cracks become wide bare strips. In nearly all cases this is due to the use of rosin varnish, either by itself or as a considerable ingredient in a paint.”	(Sabin 1904, 98) (Sabin 1927, 127, 455)
“The term alligatoring as applied to paint is an American one and has crept into use in popular paint literature. It is a descriptive term used to describe the appearance	(Cruickshank Smith 1912, 27)

presented by a paint, varnish or enamel film when it has become cracked in such a way as to resemble the markings on an alligator’s back. Unfortunately, the same term is also used to describe a particular variety of wrinkling or ridging, and as there is a sufficiency of English words available to describe either phenomenon it would appear to be desirable to eliminate the term “alligatoring,” which is by no means a suggestive term to people who rarely see alligators.”	
““Checking" and "alligatoring" consist in the development of fine interlacing lines on the surface of a paint, that is, lines embracing areas, which, if small, are called checks, and which, if large, have the appearance of alligator skin. It would appear that the phenomena of checking and alligatoring are closely related and are probably due to the same general cause." “Now in all cases the outer coats of varnish and paint tend greatly to shrink in volume and to become progressively harder and more coherent, thus producing two possible effects. One of these is the rupturing of this outer coat with consequent alligatoring or checking. The other possible effect is that the outer coat becomes thinner without rupturing. Which of these effects occurs depends upon the under coat. If the under coat is soft, the outer coat in oxidizing and shrinking will draw up and slip over it with consequent rupturing. If the under coat is sufficiently hard, the outer coat does not slip over it but simply becomes thinner by shrinkage and no rupturing occurs. / This is the general explanation of the alligatoring of varnish and paint. It is also shown whenever a paint is applied over another that inherently will not dry hard, as in the case of a harder paint applied over an asphaltum one (…) or in the case of a harder paint applied over a yellow ochre one (…) Very extreme examples of checking or alligatoring occur where a non-volatile mineral oil has been used in an under coat.” “From the writer’s experience the causes of checking are identical with the causes of alligatoring. (…) If alligatoring takes place, it simply means that the under coat is relatively much softer than the outer coat. If checks occur it means that this difference in the hardness of coats is not so great as in the case of alligatoring, but the difference is in degree, not in kind.”	(Thompson 1915, 137–38)
“Alligatoring consists of the development of interlacing lines over relatively large areas on a paint film, giving the appearance of alligator’s skin (…). One cause of alligatoring is the application of a hard-drying coat of paint or varnish over a comparatively soft undercoat (for example, a flat white paint applied over a bituminous coating). (…) Alligatoring may begin as checking or cracking but the break tends to grow wider at the bottom as well as at the top. The top coating contracts, thus exposing portions of the undercoat. In the typical extreme case of alligatoring, the "islands" of coating between interlacing breaks have not only contracted in area but have increased in thickness and, consequently, often have become wrinkled. Alligatoring may be caused by the application of successive coats of incompatible	(Walker and Hickson 1945, 112–13)

paints or by the application of paints or enamels over resin-impregnated surfaces (…)”	
“Film rupture resulting from the application of a brittle film over a more flexible coating.”	(Spence and Haynie 1972, 18)
“*Crocodiling* or *Alligatoring* is a drastic type of crazing (see checking, p.262). producing a pattern resembling the hide of a crocodile.” “This term is used for pronounced wide cracks over the entire surface but the cracks do not reach the substrate; they may affect a single layer of film only. The failure resembles alligator skin (…) Alligatoring may begin as checking or cracking but the break tends to grow wider at the bottom as well as at the top. The top coating contracts, thus exposing portions of the undercoat. In the typical extreme cases of alligatoring, the 'islands' of coating between interlacing breaks have not only contracted in area but have increased in thickness and consequently often have become wrinkled.”	(Hess and Hamburg 1979, 82, 262)
"Cracking, checking, alligatoring. These types of failures develop with the aging of the paint film. Shrinkage within the film during aging causes cracking and checking. Alligatoring is a film rupture, usually caused by application of a hard, brittle film over a more flexible film."	(Schweitzer 2006, 51)
“All coal tar paints “alligator,” more or less, in the sun. The paint will look like an alligator skin, and hence, the name alligatoring. This alligatoring is a surface defect. It is brought about by the hardening of the upper layer of the film, stimulated by the sun’s rays. This causes the upper layer to contract, crack, and slip over the lower stratum which is still soft.”	(Stoner 2006, 9–2)
Conservation and Restoration Literature	
"Breaks in the paint layer caused by failure of the film to withstand the strain of its own contraction during the drying process. / Paint applied over an unstable film like bitumen and covered over with a thick layer of varnish often splits open into wide rifts from the pull of drying. This has been called "alligator crackle" or "alligatoring". / Two patterns of cracks out of many that may develop in paint which shrinks more on the top surface than in the under part of the film."	(Stout 1950, 41)
"In extreme cases of shrinkage cracking, especially where media containing oil varnish or asphalt underlie the surface paint, the pattern resembles that of an alligator skin or the bark of a tree. The cracking is often called 'alligatoring' (Fig.12). In advanced cases of alligatoring the 'islands' of paint between interlacing breaks have not only contracted, but have increased in thickness and consequently have frequently wrinkled [15]. This has sometimes been described as 'scurf and scab' formation (Fig. 13)."	(Keck 1969, 15)
"(…) of all [Richard] Wilson's paintings only one early example shows the cracking or 'alligatoring' characteristically associated with the use of asphaltum"	(Harley 1982, 151)

“As a result the surface skin will dry and contract during hardening pulling the lower, softer layers into the characteristic 'islands' - that is, crocodiling and wrinkling will occur."	(White 1986, 66)
“The cracking usually appears as an "alligator" design of fine lines with sharp edges, occasionally quite deep, but more often a surface effect. Cracks from this cause are liable to occur soon after the drying of the paint.” "The typical poppy oil crackle under normal painting conditions is likely to result in an elongated alligator pattern with ragged edges along the short sides of the pattern; the fissures are usually wide enough to reveal the ground underneath."	(Mayer 1991a, 209–10)
“**alligatoring** or **alligator cracks** a form of CRACKLE that appears on paintings in a pattern resembling the design of alligator hide.”	(Mayer 1991b, 12)
"The more extreme drying defects, perhaps caused by the tarry bitumen derived from the distillation of coal, can result in wrinkled and torn paint that looks like an alligator skin (...), or shiny islands of one colour floating meaninglessly on paint of quite another colour"	(Carlyle and Southall 1993, 23)
"The wrinkling, alligatoring and crow's foot cracks are clear signs of problems with the drying of the paint." “(...) certain aspects of the painting technique (...) include the droplets in and on the paint film, indicating problems with wetting, the coarse alligatoring and finer crow's foot cracks, due to slow drying of the dark painting containing asphaltum, the wrinkling of the paint film (again, indicative of problems with drying), and the use of fast-drying, thin opaque layers.”	(van der Loeff and Groen 1993, 101–2)
"Certain pigments still did not dry successfully even with the aid of a heat-bodied oil. Asphaltic or bituminous pigments are notoriously bad driers, encouraging long-term cold flow of the paint film; this results in a characteristic craquelure or 'crocodiling'."	(White and Kirby 1994, 71)
"(…) drying cracks that appear like gleaming scars between wrinkled patches, making the paint look like an alligator skin."	(Southall 1996, 118–19)
"The non-drying and thermoplastic properties of asphaltum, (…) had disastrous effects on the paint layer if it was used in the underlying layer of a quick-drying layer. The result was 'alligator cracks', shrinkage and wrinkling."	(Pey 1998, 499)
“In some of [Albert Pinkham] Ryder’s paintings, these fissures are wide and deep, often with slightly raised lips along their edges. Sometimes the drying cracks exhibit a severe shrinkage pattern of mounds and valleys known as “alligatoring,” so named because the paint surface has something of the appearance and texture of alligator hide.”	(Grimm 1999, 52)
“The current rule for artists is “fat on lean”- meaning that slower-drying, thicker paint should be applied over thinner and leaner paint. When an artist ignores this rule the rapidly drying upper paint can pull apart the still tacky paint below, causing disfiguring cracks known variously as traction craquelure, drying craquelure,	(Kirsch and Levenson 2000, 155, 159)

shrinkage craquelure, or alligatoring. Such cracking can also be caused by paint additives that inhibit drying, such as bitumen (asphaltum). Bitumen was most commonly used by British and American painters during the eighteenth and nineteenth centuries; paintings from that era regularly exhibit dramatic craquelure." "An extreme drying effect probably caused by the presence of bitumen in the paint caused a wide fissure in the upper paint layer. The result, know as alligatoring, exposes the layers below."	
"If significant amounts of resins or other complex materials are mixed with the paint, large, disfiguring drying cracks may develop, imparting a texture to the surface of the painting that resembles reptile skin (hence the term *alligator cracks*)."	(Doherty and Woollett 2009, 24)
"Alligatoring is a more advanced form of drying crack where islands of poorly dried and disfigured paint are surrounded by networks of wide cracks which reveal the underlying paint layer."	(Rae 2010, 46)
"The surface shows many small and relatively large drying cracks, so-called 'alligator cracks', especially in the dark painted areas (…). The upper paints have become islands of paint resulting from contraction of surface paint layers (…). The large cracks in particularly expose the colors of underlying paints, and seriously change the tonality, the color harmony and the composition (…)"	(Shimazu 2015, 121–22)

Table A.3: Descriptions of the term *Bitumen cracking* and its variants in published sources and the Conservation and Restoration literature, from 1988 to 2022.

Bitumen Cracking	**Published Source**
Conservation and Restoration Literature	
"'bituminous' craquelure", "When prepared with a drying oil bitumen can absorb any amount of oil and the result is a rich transparent brown paint pleasing to use but which never dries completely, and the paint layer forms drying cracks which may continue to develop into abnormally wide cracks."	(Massing 1988, 90, 101)
"Both bitumen shrinkage and the much smaller form under discussion [micro-cissing] are examples of drying-cracks, which are known also as 'early', 'modern', 'immature', 'contraction' or 'ductile' cracks. Although found in a variety of patterns and networks, they are characterised by wavy, irregular edges, which are rounded in profile, and in most instances by a visible substrate at the bottom of each crack. This substrate is either a lower layer of paint which has remained intact or the ground or priming layer.", "Drying cracks, (…) need not be general in either a painting or a period. This is because they are formed during the complex drying of the oil paint film, the composition of which varies not only at different periods but also within a single picture."	(Jones 1990, 50)
"So-called bituminous cracks have almost mythological status as being the cause of disastrous cracking in British 18th and 19th century paintings. Certainly, the presence of a variety of brittle fractures of paint or glazes, early shrinkage cracks, 'crocodiling' and wrinkling indicate a serious departure from sound technique. / However, the possibilities of their causes are manifold. The materials employed, (…) and inappropriate use of these materials, (…) and the reality of adulteration by manufacturers are all potential sources of behavioural defects. "	(Izat 2001, 1)
"Bitumen has often been held responsible for paint film defects, such as extreme cracking, wrinkling, discolouration and creeping - so much so that the term 'bitumen cracking' has become common parlance to describe a cracked, brown paint layer, and the term 'bituminous' to describe any paint passage that possesses those characteristics."	(Frame 2022)

A.3 Previous reconstructions

Table A.4: Summary of the reconstructions performed by Boitelle, Bothe, Izat and Grober in terms of recipes followed, sources of "asphalt" and variations in the paint application.

Boitelle (1999)*	**Bothe (1999)**	**Izat (2001)**	**Grober (2006)**
Recipes	Recipes	Recipes	Recipes
• Williams, 'Antwerp Brown', 1787 • Mérimée, 'English Method', 1939 • Mérimée, 'Other Method', 1939	• Nunes, 1615 • De Mayerne, 1620 • Dossie, 1764 • Williams, 'Antwerp Brown', 1787 • Anonym, 1795 • Bouvier, 1827 • Mérimée, 1839 • Jaennicke, 1878 • Niederländer, 1893 • Asphaltlack, Kremer Pigmente 1997**	• Anon, *Compendium*, 'Another Method' • Tingry, 'Asphaltum', 1804 • Mérimée, 'English and Italian Method', 1939 • Sully, 'Chapman's Method from Rome' • Osborn, 'Asphaltum', 1845	• Nunes, 1615 • De Mayerne, 1620 • Anon, 1795 (likely 'Another Method' due to the addition of Copaiba balsam)*** • Bouvier, 1827 • Mérimée, 1839 (likely 'Another Preparation' due to the addition of Venice Turpentine)*** • Merrifield, 1849 • Sully, 'Chapman's Method from Rome', 1834
Source of "Asphalt"	Source of "Asphalt"	Source of "Asphalt"	Source of "Asphalt"[162]
• VEGA asphalt (provided by Shell Oil Company)	• TLA[ii] (53-55% bitumen content) • Asphalt with a 99% bitumen content [ii]Trinidad Épuré from Carl Ungerwitter Trinidad Lake Asphalt GmbH	• Trinidad Lake Asphalt (TLA)[i] • Coal Tar [i]TLA from Wells (Trinidad Lake Asphalt) Limited, Nutfield Road, Merstham, Redhill, RH1 3ES	• Kiefernholzteer (Pine Tar?) • Kiefernholzteerpech (Pine Tar Pitch?) • Steinkohlenteer (Coal Tar?) • Steinkohlenteerpech (Coal Tar Pitch?) • Gemisch aus Steinkohlenteer und natürlicher Asphalt [TLA][ii] (Mixture of Coal Tar and Natural Asphalt ?) • Teerölfeststoffgemisch (Tar oil solids mixture ??)
Variations	Variations	Variations	Variations
• 3 Recipes • 1 source of Asphalt • Paint outs cured for 8-10 months before artificial light-aging for 3 months (equivalent to	• 10 Recipes • 2 sources of Asphalt • 8 variations in sequence of layering: 2 ground layers, 2 paint layers (one oil, other tempera) alternating with the	• 5 Recipes • 2 sources of "Asphalt" • Fat and lean ground layers; White and coloured ground layers; Layer sequence; Thick and thin application of the	• 7 Recipes • 6 sources of "Tar" • 4 variations in layer sequence: 2 ground layers and alternating oil paint/tar paint (as undercoat or final glaze).

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[162] According to Mills and White, both "Tars" and "Pitches" are products from the pyrolysis of wood, coal or resin, and differ in the sense that while tars are a distilled product, pitches are undistilled (Mills and White 1987, 48).

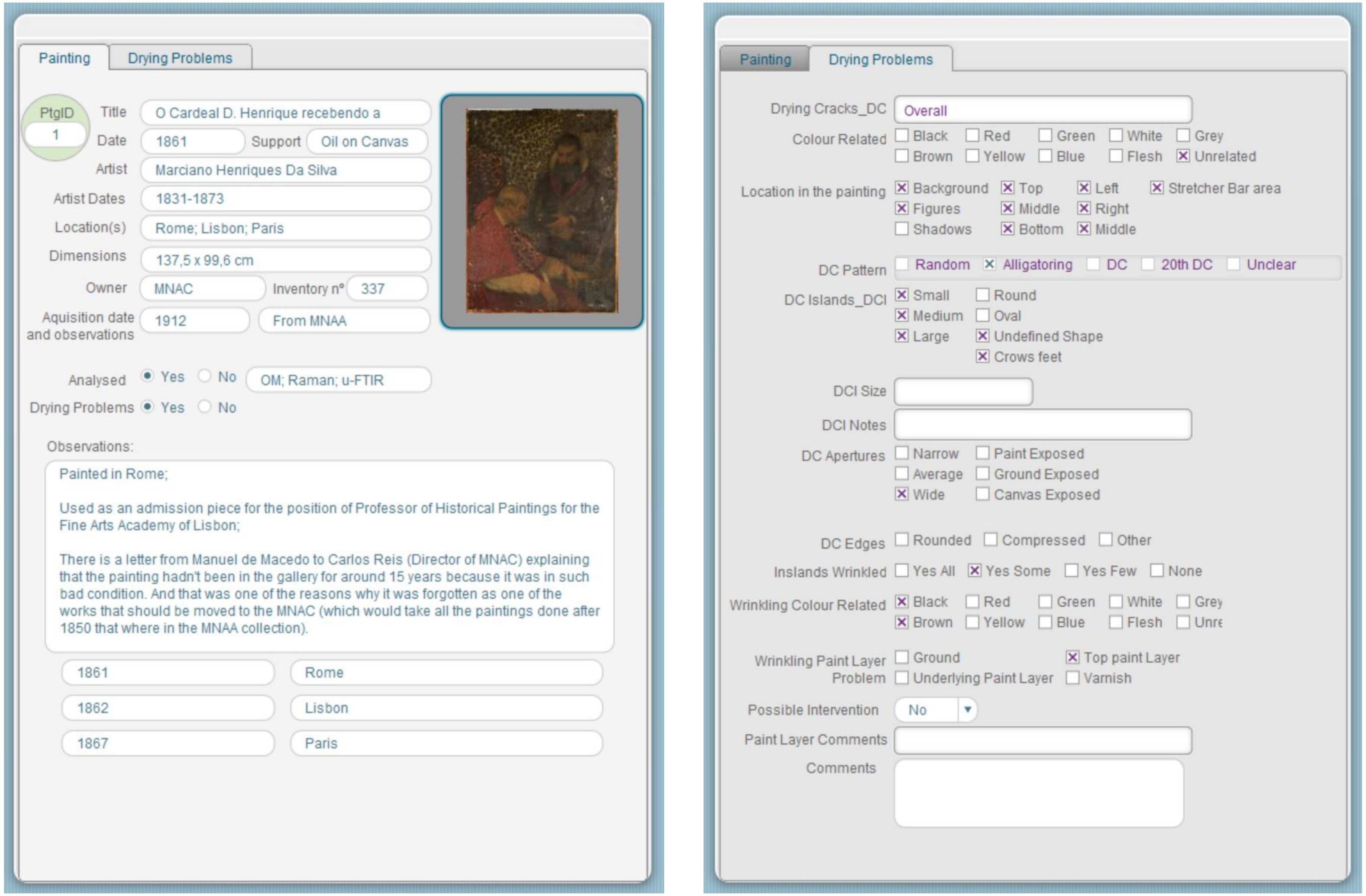
40years in museum conditions)	asphalt paint layer (as undercoat or final glaze) - 3 variations for aging (normal conditions: daylight and dark, artificial aging)	asphalt and coal tar paint layers; having dry or touch dry layers prior to application. Overall 64 variations, 32 for each material (TLA & Coal Tar).	- 2 repetitions of each for normal and artificial aging.

* According to the descriptions in (Languri 2004, 124; Languri, Boon, and Boitelle 2005).

** Not an actual recipe, but a ready to use Asphalt lacquer from Kremer (#79850).

*** According to the designations in the "Asphaltum Recipes" from Carlyle (2001, 403-04).

A.4 The Alligatoring in Oil Paintings Survey



PtgID: 1

Title: O Cardeal D. Henrique recebendo a

Date: 1861 Support: Oil on Canvas

Artist: Marciano Henriques Da Silva

Artist Dates: 1831-1873

Location(s): Rome; Lisbon; Paris

Dimensions: 137,5 x 99,6 cm

Owner: MNAC Inventory nº: 337

Aquisition date and observations: 1912 From MNAA

Analysed ● Yes ○ No OM; Raman; u-FTIR

Drying Problems ● Yes ○ No

Observations:

Painted in Rome;

Used as an admission piece for the position of Professor of Historical Paintings for the Fine Arts Academy of Lisbon;

There is a letter from Manuel de Macedo to Carlos Reis (Director of MNAC) explaining that the painting hadn't been in the gallery for around 15 years because it was in such bad condition. And that was one of the reasons why it was forgotten as one of the works that should be moved to the MNAC (which would take all the paintings done after 1850 that where in the MNAA collection).

1861	Rome
1862	Lisbon
1867	Paris

Drying Cracks_DC: Overall

Colour Related: ☐ Black ☐ Red ☐ Green ☐ White ☐ Grey ☐ Brown ☐ Yellow ☐ Blue ☐ Flesh ☒ Unrelated

Location in the painting: ☒ Background ☒ Top ☒ Left ☒ Stretcher Bar area ☒ Figures ☒ Middle ☒ Right ☐ Shadows ☒ Bottom ☒ Middle

DC Pattern: ☐ Random ☒ Alligatoring ☐ DC ☐ 20th DC ☐ Unclear

DC Islands_DCI: ☒ Small ☐ Round ☒ Medium ☐ Oval ☒ Large ☒ Undefined Shape ☒ Crows feet

DCI Size:

DCI Notes:

DC Apertures: ☐ Narrow ☐ Paint Exposed ☐ Average ☐ Ground Exposed ☒ Wide ☐ Canvas Exposed

DC Edges: ☐ Rounded ☐ Compressed ☐ Other

Inslands Wrinkled: ☐ Yes All ☒ Yes Some ☐ Yes Few ☐ None

Wrinkling Colour Related: ☒ Black ☐ Red ☐ Green ☐ White ☐ Grey ☒ Brown ☐ Yellow ☐ Blue ☐ Flesh ☐ Unre

Wrinkling Paint Layer Problem: ☐ Ground ☒ Top paint Layer ☐ Underlying Paint Layer ☐ Varnish

Possible Intervention: No

Paint Layer Comments:

Comments:

Figure A.1: Database page fields in FileMaker Pro 12, for the overall painting's information and the "Drying Problems" details.

Table A.5: List with the identified 62 artists and respective 137 paintings suffering from paint defects (85 showing alligatoring).

Artist (Artist's dates)	**Nº of paintings**	***Painting title* (date)**
Achille-Etna Michallon (1796-1822)	1	*The Death of Roland, in 778.* (1819)
Albert Pinkham Ryder (1847-1917)	6	- *Curfew Hour.* (1882) - *Landscape*. (1897-98) - *Moonlight Marine.* (1870-90) - *Siegfried and the Rhine Maidens.* (1888-91) - *The Toilers of the Sea.* (1880-85) - *Under a Cloud.* (c. 1900)
Alexandre-Gabriel Decamps (1803-1860)	3	- *The Bell-Ringers.* (1841) - *L'école Turque.* (1846) - *Enfant et Mouton [Enfant donnant a manger a un mouton].* (1847)
Alphonse de Neuville (1836-1885)	1	*Le Cimetière de Saint-Privat, 18 août 1870.* (1881)
Anne-Louis Girodet de Roussy-Trioson (1767-1834)	2	- *Scene from the Deluge.* (1806) - *Pygmalion in Love with his Statue, also know as Pygmalion and Galatea.* (1819)
Anonyme français (entourage de Théodore Géricault)	1	*Portrait of an Artist in his Studio.* (1820)
Anton Raphael Mengs (1728-1779)	1	*Self Portrait.* (1774)
Ary Scheffer (1795-1858)	5	- *The Souliot Women.* (1827-28) - *Eberhard, comte de Wurtemberg, dit Le Larmoyeur, pleurant la mort de son fils.* (1834-36) - *La Mort de Théodore Géricault (1791-1824).* (1824) - *Portrait présumé de la princesse Louise d'Orléans (Palerme, 1812 - Ostende, 1850).* (1833) - *Le Prince de Talleyrand.* (1828)
Auguste Flandrin (1804-1842)	1	*Savonarole prêchant à San Miniato à Florence.* (1840)
Camille Roqueplan (1803-1855)	1	*Les Puritains d'Écosse.* (1837)
Charles Gleyre (1806-1874)	1	*Lost Illusions, also known as Evening.* (1843)
Charles-André, dit Carle Vanloo (1705-1765)	1	*Rest on the Hunt.* (1737)
Claude-Marie Dubufe (1790-1864)	1	*Portrait de Madame Leullion de Thorigny.* (1840)
Claudius Jacquand (1803-1878)	1	*Thomas Morus grand chancelier d'Angleterre.* (1827)
Claudius Lavergne (1814-1887)	1	*Le Miracle des roses de sainte Élisabeth de Hongrie.* (1845)
[Sir] David Wilkie (1785-1841)	11	- *Bathsheba at the Bath.* (1817) - *The Bag-Piper.* (1813) - *A Roman Princess Washing the Feet of Pilgrims.* (1827) - *Prince Charles of Leiningen.* (c.1824-30) - *The Entrance of George IV at Holyroodhouse.* (1822-30) - *The First Council of Queen Victoria.* (1838) - *The Guerilla's Departure.* (1828) - *The Guerilla's Return.* (1830) - *The Penny Wedding.* (1818) - *The Preaching of Knox before the Lords of the Congregation.* (1832) - *William IV (1765-1837).* (1832)
Élisabeth-Louise Vigée-Lebrun (1755-1842)	1	*Madame Vigée LeBrun and her Daughter, Jeanne-Lucie, known as Julie (1780-1819).* (1786)
Eugène Delacroix (1798-1863)	23	- *The Murder of the Bishop of Liege.* (1829) - *Battle of Poitiers, also known as King Jean at the Battle of Poitiers (19 September 1356).* (1830) - *Hamlet and Horatio in the Cemetery.* (1839) - *Hamlet and Horatio in the Cemetery.* (1859) - *Saint George Fighting the Dragon, also known as Perseus Delivering Andromeda.* (1847) - *Jewish Wedding in Morocco.* (1839) - *Women of Algiers in their Apartment.* (1834) - *Dante and Virgil in the Underworld, also known as Dante's Boat.* (1822)

		- *The Prisioner of Chillon.* (1834) - *Jewish Musicians from Mogador (Morocco).* (1847) - *Le Naufrage de Don Juan.* (1840) - *Pietà, Esquisse.* (1841-43) - *Hamlet and Horatio in the Cemetery.* (1835) - *Disciples et Saintes Femmes Relevant Le Corps de Saint Étienne pour l'ensevelir.* (1847-1853) - *La Chasse aux Lions.* (1855) - *Médée Furieuse.* (1838) - *Cléopâtre et le paysan.* (1838) - *Le Kaïd, Chef Marocain, Visitant une Tribu, ou EncoreL'Offrande Du Lait.* (1832) - *Chevaux arabes se battant dans une écurie.* (1860) - *Combat du Giaour et du Pacha.* (1835) - *Femme nue au perroquet [Femme caressant un perroquet].* (1827) - *Apollon vainqueur du serpent Python.* (1850) - *Rébecca enlevée par le Templier pendant le sac du château de Frondeboeuf, dit aussi L'Enlèvement de Rébecca.* (1858)
Fleury Richard (1777-1852)	2	- *Jeune fille à la Fontaine.* (1825) - *Le Tasse et Montaigne.* (1821)
François-André Vincent (1746-1816)	1	*Portrait of Three Men.* (1775)
François-Joseph Heim (1787-1865)	1	*King Charles X Distributing Awards to the Artists at the End of the Salon of 1824, in the Grand Salon at the Louvre.* (1827)
Gerrit Dou (1613-1675)	1	*The Young Mother.* (1658)
Gustave Caillebotte (1848-1894)	1	*Raboteurs de parquet.* (1875)
Gustave Courbet (1819-1877)	1	*Un enterrement à Ornans.* (1849-50)
Hortense Haudebourt-Lescot (1785-1845)	1	*Portrait de Daniel-François-Esprit Auber (1782-1871).* (?)
Jean Restout (1692-1768)	1	*L'Exaltation de la sainte croix.* (1748)
Jean-Auguste-Dominique Ingres (1780-1867)	3	- *Presumed Portrait of Auguste François, painter and naval officer (died in 1812), also known as Talma's Nephew.* (1805) - *The Composer Luigi Cherubini (1760–1842) and the Muse of Lyric Poetry.* (1842) - *Antiochus et Stratonice.* (1840)
Jean-Baptiste Greuze (1725-1805)	2	- *Septimius Severus Reproaching Caracalla.* (1769) - *Self-Portrait.* (?)
Jean-François Millet (1814-1875)	1	*The Washerwoman.* (1853-54)
Jean-Honoré Fragonard (1732-1806)	2	- *The High Priest Coresus Sacrifices Himself to Save Callirhoe.* (1765) - *The Bolt.* (1769)
Jean-Jacques Henner (1829-1905)	5	- *La Liseuse.* (1880-90) - *La Vérité (recto); Études de femmes (verso).* (1898-1902) - *Églogue.* (1879) - *Portrait de jeune fille.* (1859-64) - *Rêve.* (c. 1900)
Jean-Paul Laurens (1838-1921)	1	*L'Excommunication de Robert le Pieux.* (1875)
Jean-Siméon Chardin (1699-1779)	1	*A Chemist in his Laboratory. Portrait of the Painter Joseph Aved (1702-1766), a friend of the artist.* (1734)
John Everett Millais (1829-1896)	2	- *The Good Resolve.* (1877) - *The Martyr of the Solway.* (1871)
Joseph Siffred Duplessis (1725-1802)	1	*Portrait of Joseph-Marie Vien (1716-1809), painter.* (1784)
Joseph-Nicolas Robert-Fleury (1797-1890)	1	*Saint Bartholomew's Day Massacre (August 1572).* (1833)
[Sir] Joshua Reynold (1723-1792)	1	*Self-portrait Wearing Spectacles.* (c. 1788)
Louis Cretey (1635- 1721?)	1	*La Vision de saint Jérôme.* (1681-83)
Louis Tocque (1696-1772)	1	*Portrait of Louis Galloche (1670-1761), painter.* (1734)
Lucien Mélingue (1841-1889)	1	*Le prévôt des marchands Étienne Marcel et le dauphin Charles.* (1879)

Marciano Henriques Da Silva (1831-1873)	2	- *O Cardeal D. Henrique recebendo a notícia da morte de D. Sebastião.* (1861) - *Retrato de Bulhão Pato.* (1871)
Marie Taglioni (1804-1884)	1	*Portrait de la danseuse.* (c. 1840)
Marie-Françoise Constance Mayer – Lamartinière (1778-1821)	1	*Le rêve du bonheur (The Dream of Happiness).* (1818-19)
Nicolas Anne Dubois ? (?)	1	*Hallali du cerf dans les grandes écuries de Chantilly le 13 Septembre 1776.* (1780)
Nicolas Vleughels (1668-1737)	1	*Apelles Painting Campaspe.* (1716)
Niels Simonsen (1807-1885)	1	*An Arab Family in the Dessert.* (1847)
Pascal Dagnan-Bouveret (1852-1929)	1	*Le Pain bénit.* (1885)
Paul Baudry (1828-1886)	1	*Charles Garnier.* (1868)
Paul Delaroche (1797-1856)	1	*Portrait d'Horace Delaroche, fils du peintre.* (1838)
Paul Dubois (1829-1905)	1	*Tête de femme.* (?)
Paul Mathey (1844-1929)	1	*Auguste Rubé (1815?-1899)Painting a set for the Opera.* (1877)
Petrus Van Schendel (1806-1870)	1	*Sainte Marie-Madeleine en prière.* (1846)
Pierre-Paul Prud'hon (1758-1823)	15	- *Portrait of Marie-Marguerite Lagnier (1786-1840).* (1796) - *Portrait of Napoléon François Charles Joseph Bonaparte (1811-1832), King of Rome, known as The King of Rome Sleeping.* (1811) - *The Wedding of Hebe and Hercules.* (1810) - *The Soul Breaking the Ties that Bind it to Earth.* (?) - *Portrait of Madame Jarre, née Hébert.* (1821-22) - *Portrait of the Empress Joséphine (1763-1814).* (1805-09) - *L'Enlèvement de Psyché [The Abduction of Psyche].* (1808?) - *Justice and Divine Vengeance Pursuing Crime.* (1806-08) - *Christ on the Cross, with Mary Magdalene and the Virgin Mary at his Feet.* (1822) - *Portrait de Madame Anthony et de ses fils.* (1796) - *Georges Anthony, maître de poste à Gray.* (1796) - *L'Abondance.* (?) - *Hommage à la Beauté.* (1808) - *Le sommeil de Psyché.* (?) - *Jeune Zephyr se balançant au dessus de l'eau.* (1814)
Prosper Marilhat (1811-1847)	1	*Souvenir de la Campagne de Rosette.* (c. 1835)
Richard Redgrave (1804-1888)	2	- *Gulliver Exhibited to the Brobdingnag.* (1836) - *The Governess.* (1844)
Robert Fowler (1853-1926)	1	*Women of Phoenicia.* (1879)
Théodore Chassériau (1819-1856)	1	*Arabian Horsemen at a Fountain in Constantine.* (1851)
Théodore Géricault (1791-1824)	4	- *The Woman with Gambling Mania.* (1820) - *The Raft of the Medusa.* (1818-19) - *The Wounded Cuirassier.* (1814) - *Cheval Sortant de L'Écurie.* (c. 1824)
Théodore Rousseau (1812-1867)	1	*The Descent of the Cattle in the Haut-Jura Mountains.* (1834-35)
Tintoret (Jacopo Robusti, dit) (1518-1594)	1	*La Vierge et l'Enfant avec sainte Catherine, saint Augustin, saint Marc et saint Jean-Baptiste.* (1549-50)
Victor Orsel (1795-1850)	1	*The Infant Moses presented to Pharaoh.* (1830)
William Hilton the Younger (1786-1839)	3	- *Editha and the Monks Searching for the Body of Harold.* (c. 1834) - *Study of a Monk's Head for 'Editha and the Monks'.* (c. 1834) - *Sir Calepine Rescuing Serena*. (c. 1831)

B

Appendix to Chapter 2

B.1 Information on the Artist

B.1.1 Records of baptism and death

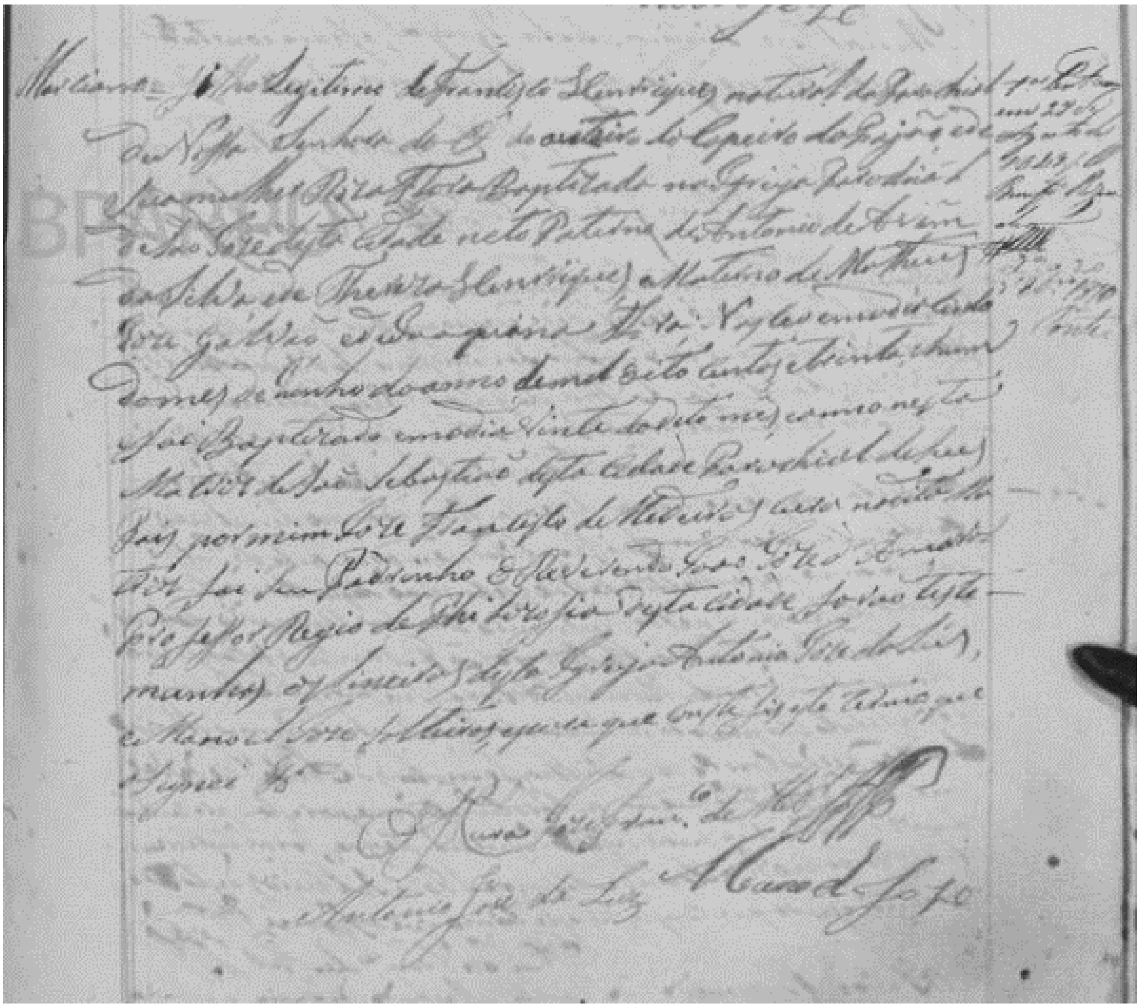


Figure B.1: Marciano Henriques da Silva record of baptism. Available at: http://culturacores.azores.gov.pt/biblioteca_digital/SMG-PD-SAOSEBASTIAO-B-1828-1835/SMG-PD-SAOSEBASTIAO-B-1828-1835_item1/index.html?page=95 (accessed 10th of May 2022)

Transcription from Figure B.1

Marciano filho legítimo de Francisco Henriques natural [do Parochial]
da Nossa Senhora do Ô do [?] de
sua mulher Roza Flora Baptizado na Igreija [Parochial?] [?]
São José desta cidade neto Paterno de Antonio de [Aviem?]
da Silva e de Thereza Henrique[s] Materno de Matheus
Jozé Galvão e[?] Joaquina Flora; Nasceu em [dia cinco?]
do mês de Junho do anno de mil oito centos e trinta e um e
foi Baptizado em dia vinte do [dito] mês [como nesta]
[Matriz] de São Sebastião desta Cidade Parochial [de seus
Pais] por mim Jose Francisco de Medeiros [?]
foi seu Padrinho o Reverendo João José d'Amaral
[?]

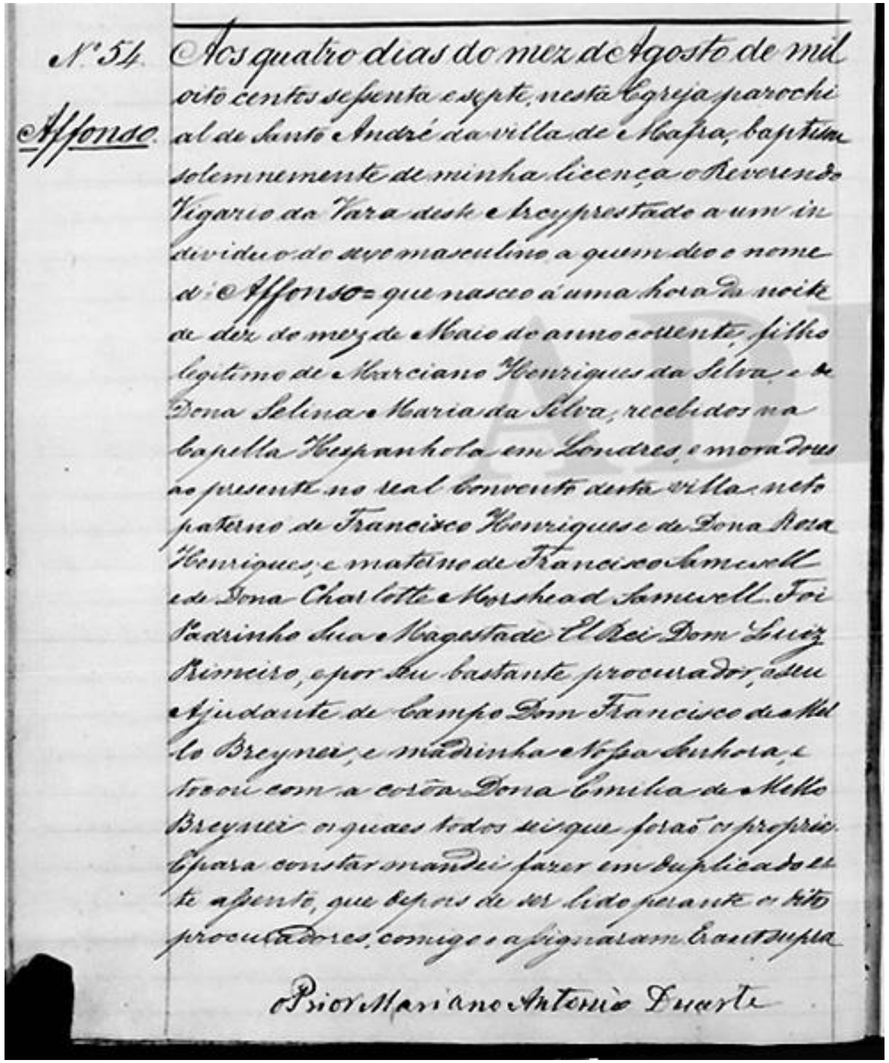


Figure B.2: Affonso's record of baptism, son of Marciano Henriques da Silva. Available at: http://digitarq.arquivos.pt/viewer?id=4824796 page 26 (full code: PT-ADLSB-PRQ-PMFR09-001-B9_m0026.TIF) (accessed 10th of May 2022).

Transcription from Figure B.2

N.º 54 *Aos quatro dias do mez de Agosto de mil*
Affonso *oito centos sessenta e septe, nesta Igreja parochi*
al de Santo André da villa de Mafra, baptisou
solemnemente de minha licença o Reverendo
Vigario da Vara deste Arcyprestado a um in
dividuo do sexo masculino a quem deo o nome
d' = Affonso = que nasceo á uma hora da noite
de dez do mez de Maio do anno corrente filho
legitimo de Marciano Henriques da Silva e de
Dona Selina Maria da Silva, recebidos na
Capella Hespanhola em Londres, e moradores
ao presente no real Comvento desta villa. neto
paterno de Francisco Henriques e de Dona Roza
Henriques; e materno de Francisco Samwell
e de Dona Charlotte Morshead Samwell. Foi
Padrinho Sua Magestade El Rei Dom Luiz
Primeiro, e por seu bastante processador, o seu
Ajudante de Campo Dom Francisco de Mel
lo Breyner; e madrinha Nossa Senhora, e
tocou com a corôa Dona Emilia de Mello
Breyner os quaes todos sei que forão os proprios.
E para comstar mandei fazer em duplicado es
te assento, que depois de ser lido perante os [ditos]
procuradores, comigo [e?] assignaram [?].
o Prior Mariano Antonio Duarte

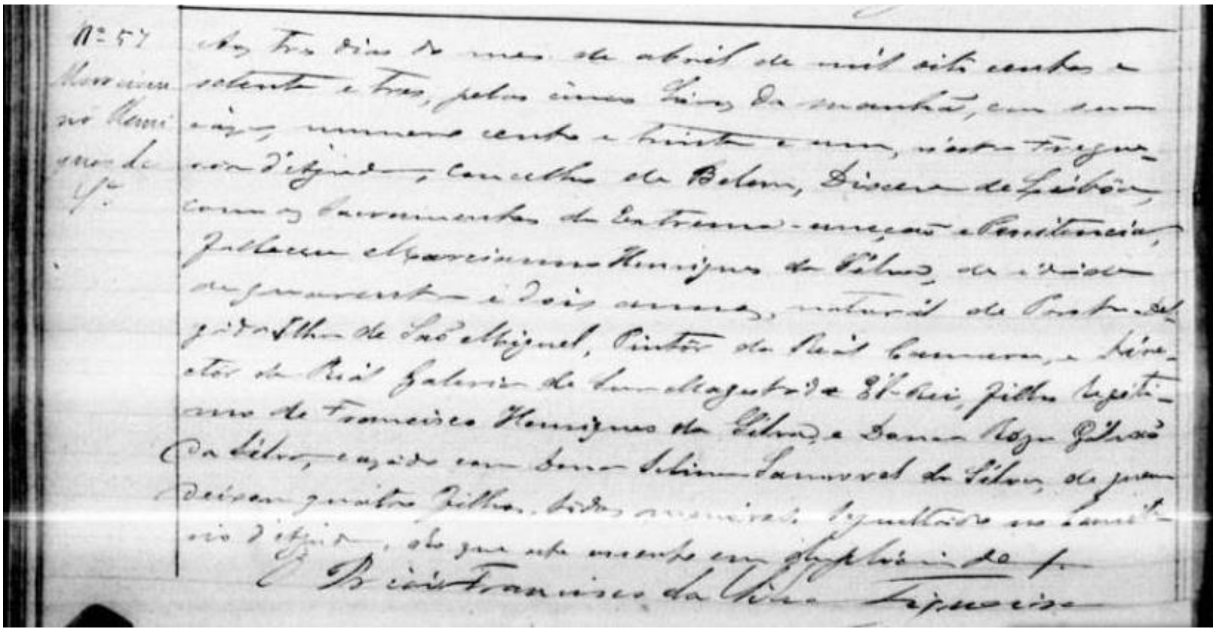
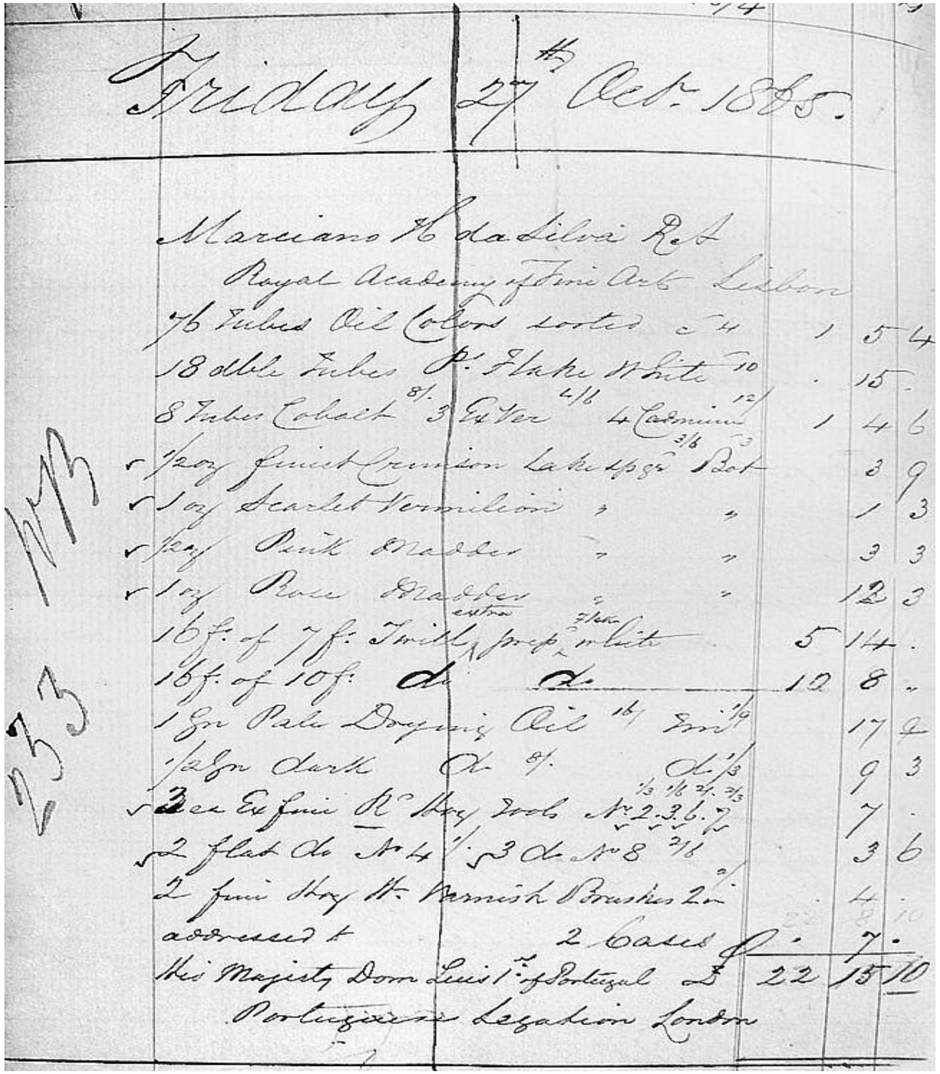


Figure B.3: Marciano Henriques da Silva record of death. Available at: https://digitarq.arquivos.pt/viewer?id=4812453 page 683 (full code: PT-ADLSB-PRQ-PLSB01-003-O13_m0683.TIF) (accessed 10th of May 2022).

	Transcription from Figure B.3
nº 57	Aos tres dias do mes de abril de mil oito centos e
Marcian	setenta e tres, pelas cinco horas da manhã, em sua
no Henri	casa, numero cento e trinta e um, nesta Freguesia
ques da	d'Ajuda, Concelho de Belem, Diocese de Lisboa
Sª.	com os Sacramentos da Extrema-unção e Penitência
	faleceu Marciano Henriques da Silva, de idade
	quarenta e dois annos, natural de Ponta Del
	gada, Ilha de São Miguel, Pintor da Real Camara, e Dire
	ctor da Real Galeria [do Paço da Ajuda?] de El-Rei, filho legiti
	mo de Francisco Henriques da Silva, e Dona Roza [?]
	da Silva, casado com Dona Selina Samwel da Silva, de quem
	deixou quatro filhos [?]

B.1.2 Artist Supplies



	Friday 27th Oct. 1865.			
	Marciano H da Silva RA			
	Royal Academy of Fine Arts Lisbon			
	76 Tubes Oil Colors sorted [assorted] [c ^{4} ?]	1	5	4
	18 dble Tubes P. Flake White [^{10}]	.	15	.
	8 Tubes Cobalt $^{8/.}$ 3 Ex Ver [Extract of Vermillion] $^{4/6}$ 4 Carmim $^{12/}$	1	4	6
✓	1/2 oz finest Crimson Lake sp gr^{d} [specially ground] $^{3/6}$ Bot [bottle] ^{3}		3	9
✓	1 oz Scarlet Vermilion " [ditto] " [ditto]		1	3
✓	1/2 oz Pink Madder " [ditto] " [ditto]		3	3
✓	1 oz Rose Madder " [ditto] " [ditto]		12	3
	16 f. [feet] of 7 f. [foot] Twill $^{\text{extra}}$ prep $^{\text{Flake}}$ White	5	14	.
	16 f. [feet] of 10 f. [foot] do [ditto] do[ditto]	10	8	"
	1 Gn [gallon] Pale Drying Oil $^{16/}$ Tin $^{1/9}$		17	~~9~~
	1/2 Gn [gallon] dark do[ditto] $^{8/}$ do[ditto] $^{1/3}$ 1/3 1/6 2/ [2]/3		9	3
✓	3 [ea] [each?] Ex [extra] fine R^{d} [round] Hog Tools N$^{r.}$ 2. 3. 6 [/ unclear]		7	.
✓	2 flat do[ditto] N$^{r.}$ 4 $^{1/.}$ 3 do [ditto] N^{r} 8 $^{2/6}$		3	6
	2 fine Hog H. [hair] Varnish Brushes [$^{2/.}$ unclear]		4	
	addressed to 2 Cases	.	7	.
	His Majesty Dom Luis I[$^{st.}$] of Portugal £	22	15	10
	.Portuguese [Legation?] London			

Figura B.4: Image (left) (Ferraz 2017b, 285) and transcription (right) of the Roberson's account book (HKI MS. 106-1993, p. 194a) with the record of Marciano's purchase.

B.1.3 Marciano's Paintings and Exhibitions

Table B.1: Compiled information on Marciano's paintings.

	Painting	Date	Dimensions	Inventory n.	Current Location
1	*Figuras*	Before 1849			
2	Portrait of *Senhora*	Before 1849			MCM, Azores
3	Portrait of the father of *Cândido Fortunato Sales*	1849			
4	*Um pastor tocando flauta*	Before 1849			
5	*O filho pródigo*	Before 1849			
6	*O Senhor da Apresentação*	Before 1849			
7	Portrait of *Frei Henrique*	Before 1849			
8	*Um preto mendigo*	Before 1849			
9	*Um cão ao colo duma dama*	Before 1849			
10	*Corpo de dama*	Before 1849			
11	*Adoração de Jesus*	Before 1849			
12	*Cabeça de Turco – estudo*	ca. 1847	55 x 41 cm	MCM5346	MCM, Azores
13	Self-portrait	1849	49.5 x 39 cm	MCM5347	MCM, Azores
14	Painting sold for 100 guineas in Paris				
15	Portrait of *Marquês de Sousa Holstein*	1857-1863?			
16	Portrait of *João de Sousa Lobo*	1857-1863?			
17	Portrait of the English sculptor *Gattey*	1857-1863?			
18	Portrait of a Goan Priest *Miguel da Cunha*	1857-1863?			
19	*O Cardeal D. Henrique recebendo a notícia da morte de D. Sebastião*	1861	137.5 x 99.6 cm	MNAC 337	DCR/FCT-NOVA, as a long term loan from MNAC
20	*Tasso na véspera de morrer/ Os últimos dias de Tasso*	1862	156 x 225 cm	MCM5202	MCM, Azores
21	*A Capela de Trisulti*	1857-1863?			
22	*Santa Rosalinda Portuguesa da Cartuxa*	1857-1863?			
23	*Recordação de Plombara*	1857-1863?			
24	Sketch of *O beija-mão de Inês de Castro*	1860			
25	(Sketch of) *Coroação de D. Inês de Castro*	1861-?			
26-30	5 landscape paintings (painted in Capri)	1859			
31	*La Vendetta*	1857-1863?			
32	Portrait of *Celina Maria*	ca.1860-1862	36 x 30 cm	MCM5011	MCM, Azores

33	*A Inocência*	1864?			
34	*A Saudade*	1864?			
35	*Os Apeninos*	1864?			
36	Portrait	1865?			
37	Portrait of *Mariana da Câmara*	1866?			
38	Portrait of *José Maria Alves Branco*	1866?			
39	Portrait of *D. Francisco de Melo Breyner*	1867?			
40	*O rancheiro do Asilo de Mafra*	1867			
41	*O moiro/ Um mouro*	1867	90 x 72 cm	PNA 4117	PNA, Lisbon
42	*Filippa de Vilhena entregando as espadas aos filhos para libertarem Portugal*	1868			
43	*A Vingança de Viriato*	1867?			
44	Portrait of *Celina Maria Silva*	ca. 1867	59.5 x 49 cm	MCM05203	MCM, Azores
45	*O velho soldado* (study)	1867?			
46	Self-portrait	1867			
47	*Mulher de Perfil*	1864	55.6 x 46.2 cm	PNA 2814	PNA, Lisbon
48	*Busto/Cabeça de velho*	n.d.	27 x 19 cm	PNA 2887	PNA, Lisbon
49	*Um filósofo*				
50	*Nossa Senhora com o Menino ao colo*	1868			
51	Portrait of *Inês Dulan*	1871	75 x 63 cm	MCM5012	MCM, Azores
52	Portrait of *Senhor Scholdtz*	n.d.	76 x 64 cm	MCM5010	MCM, Azores
53	*Um negro / Retrato de um escravo - Tio Paulo*	n.d.	43.5 x 36 cm	MCM5188	MCM, Azores
54	Portrait of *Bulhão Pato*	1871	65 x 54 cm	MCM5201	MCM, Azores
55	*Cabeça de Bispo*	Before 1868			
56	Portrait of *Eduardo Dulan;*	Before 1868			
57	Portrait of *António da Câmara Medeiros;*	Before 1868			
58	Portrait of the 2nd Dean of Ponta Delgada High School	Before 1868			
59	*Cristo e a Adúltera*				
60	Portrait of *Visconde de Castilho*				
61	Portrait of *Pinheiro Chagas*				
62	Sketch with *O Calvário*				
63	*Cabeça de Cristo*				
64	*Cabeça de Guerreiro*				
+	Other religious scenes (left in Italy)				

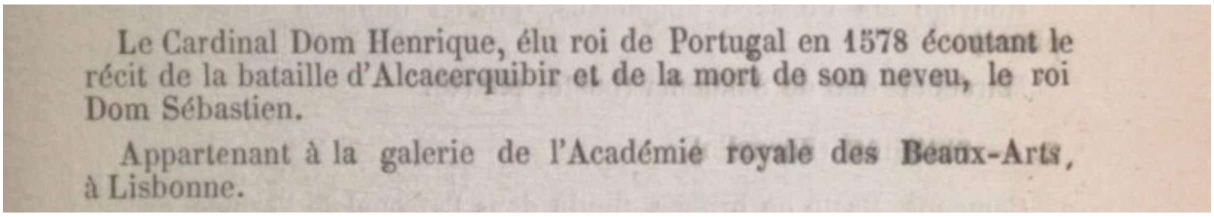
B.2 Information on the Painting

B.2.1 The painting's title

The painting's title undergoes slight variations depending on the sources consulted, being more or less descriptive of the painting's subject, always with the focus on the main figure, the Cardinal D. Henrique. The are also some spelling variations in the words "Cardeal"/"Cardial" and "Kibir"/"Quibir" due to old Portuguese spellings.

Interestingly, the shorter title is found in Marciano's letter to the Marechal Saldanha dated 16th of June of 1863, where the artist calls the painting "*Cardeal Rei D. Henrique"* (as cited in D. de Macedo 1951, 14).

According to Macedo, in 1867 for the "Exposition Universelle de Paris" the artist extended the title to give the French a Portuguese history lesson (Figure B.5Figure B.), "*Cardeal D. Henrique, eleito Rei de Portugal em 1578, escutando a descrição da batalha de Alcácer Kibir e da morte de seu sobrinho o Rei D. Sebastião"*[163] (D. de Macedo 1950b, 145).



Le Cardinal Dom Henrique, élu roi de Portugal en 1578 écoutant le récit de la bataille d'Alcacerquibir et de la mort de son neveu, le roi Dom Sébastien.

Appartenant à la galerie de l'Académie royale des Beaux-Arts, à Lisbonne.

Figure B.5: Painting information, title and provenance, in the catalogue of the "Exposition Universelle de Paris" in 1867.

The reference to the place of the battle in the North of Africa is also present in the titles used by Francisco José Rezende (contemporary to the painter) with "*O cardeal D. Henrique recebendo a noticia da batalha de Alcacer-Quivir e da morte de El-Rei D. Sebastião*"[164], and by Diogo de Macedo in "*O Cardeal D. Henrique recebendo a notícia da morte de D. Sebastião na Batalha de Alcácer Quibir*" (D. de Macedo 1950a, 17).

Two sources emphasise the second figure of the painting, as being the nobleman Jorge Serrão:

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[163] Cardinal D. Henrique, elected King of Portugal in 1578, listening to the description of the battle of Alcácer Kibir and the death of his nephew King D. Sebastião.

[164] Letter by F. J, Rezende. Porto 7 de novembro de 1867 from "O Commercio do Porto" - Porto/12.11.1865 - B.P.M.P.", "Documento n.º 159" as reproduced in Cor e melancolia, vol. III (Mourato 2000, 235).

- *"Cardial Rei escutando a relação que lhe fez um fidalgo portugês da morte de D. Sebastião"* (D'Athaide 1915, 149)
- *"O Cardeal D. Henriques, eleito Rei de Portugal em 1578, escutando a descrição da batalha de Alcácer-Kibir e da morte de seu sobrinho o Rei D. Sebastião, que Jorge Serrão lhe relata"* (D. de Macedo 1951, 20–21)

In one of Macedo's description of the painting, the location of D. Henrique is also mentioned, as being the city of Alcobaça in Portugal:

- *"O Cardeal D. Henrique recebendo em Alcobaça a notícia da morte de D. Sebastião"* (D. de Macedo 1950b, 144)

Finally, two different titles appear in the letter sent by the Conservator and acting director of MNAA, Manuel de Macedo, to the Director of MNAC, Carlos Reis, dated 18th of October of 1912[165]:

- *"O Cardeal D. Henrique recebendo a notícia da Batalha de Alcacer-Quibir"*
- *"O cardeal D. Henrique recebendo a notícia da morte de el-rei D. Sebastião"*

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[165] Photographic copy provided by Dr. Ângela Ferraz. The letter is available in the archive of MNAC as mentioned in her PhD Thesis (Ferraz 2017a, 162). The first page has the following information on the top left side "MUSEU NACIONAL DE ARTE ANTIGA, L.° I, N.° 229" and on the top left side is the red written number "41". The second page shows the pencil written date "8-out. 912" on the top left and on the top right side the red number "42".

B.2.2 Photographs and Mappings

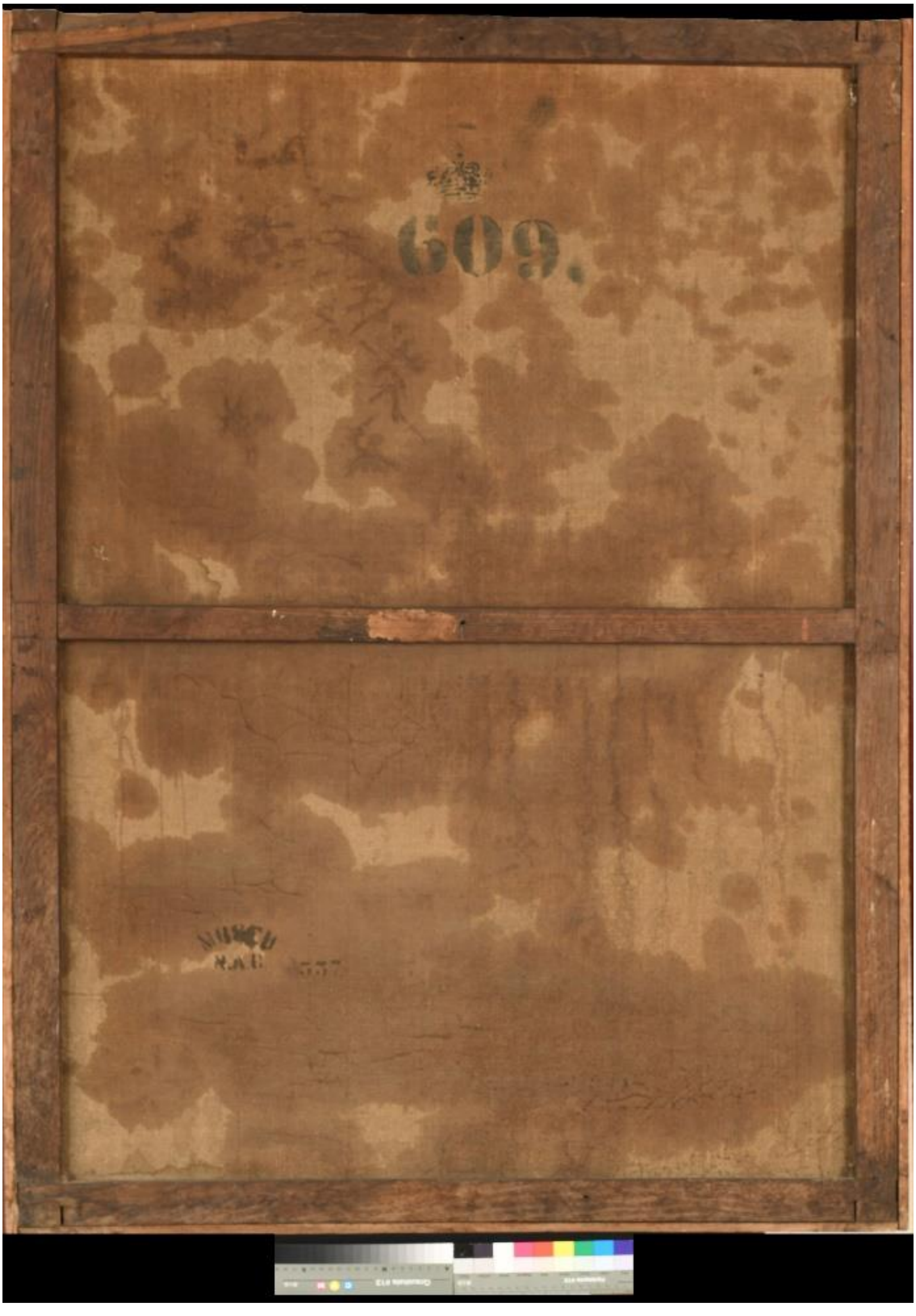

Figure B.6: Overall normal light back.

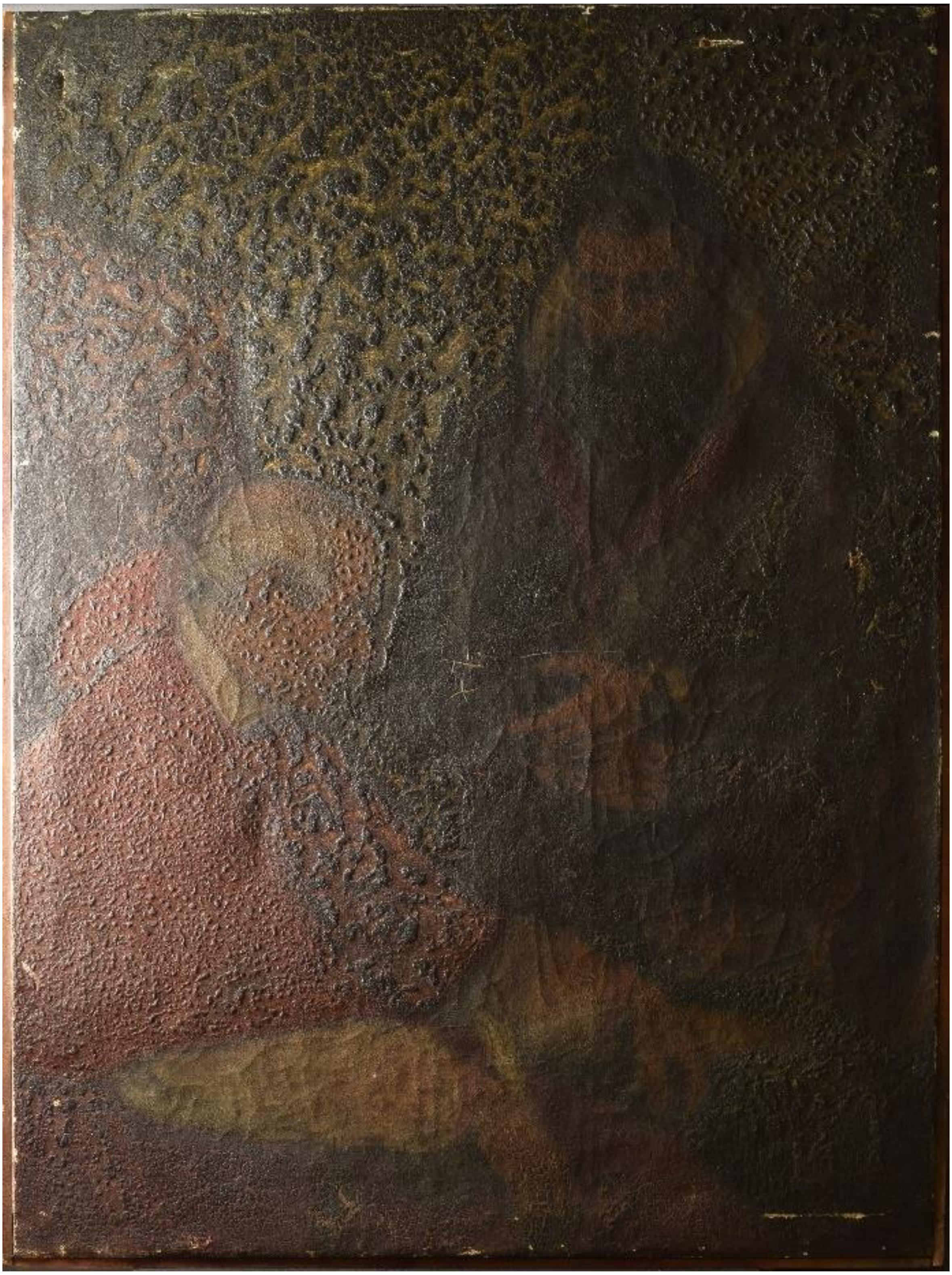

Figure B.7: Overall raking light front, light from the left side.

Figure B.8: Overall raking light front, light from the right side.

Figure B.9: Overall Ultraviolet light front.

Figure B.10: Overall Infrared photography front.

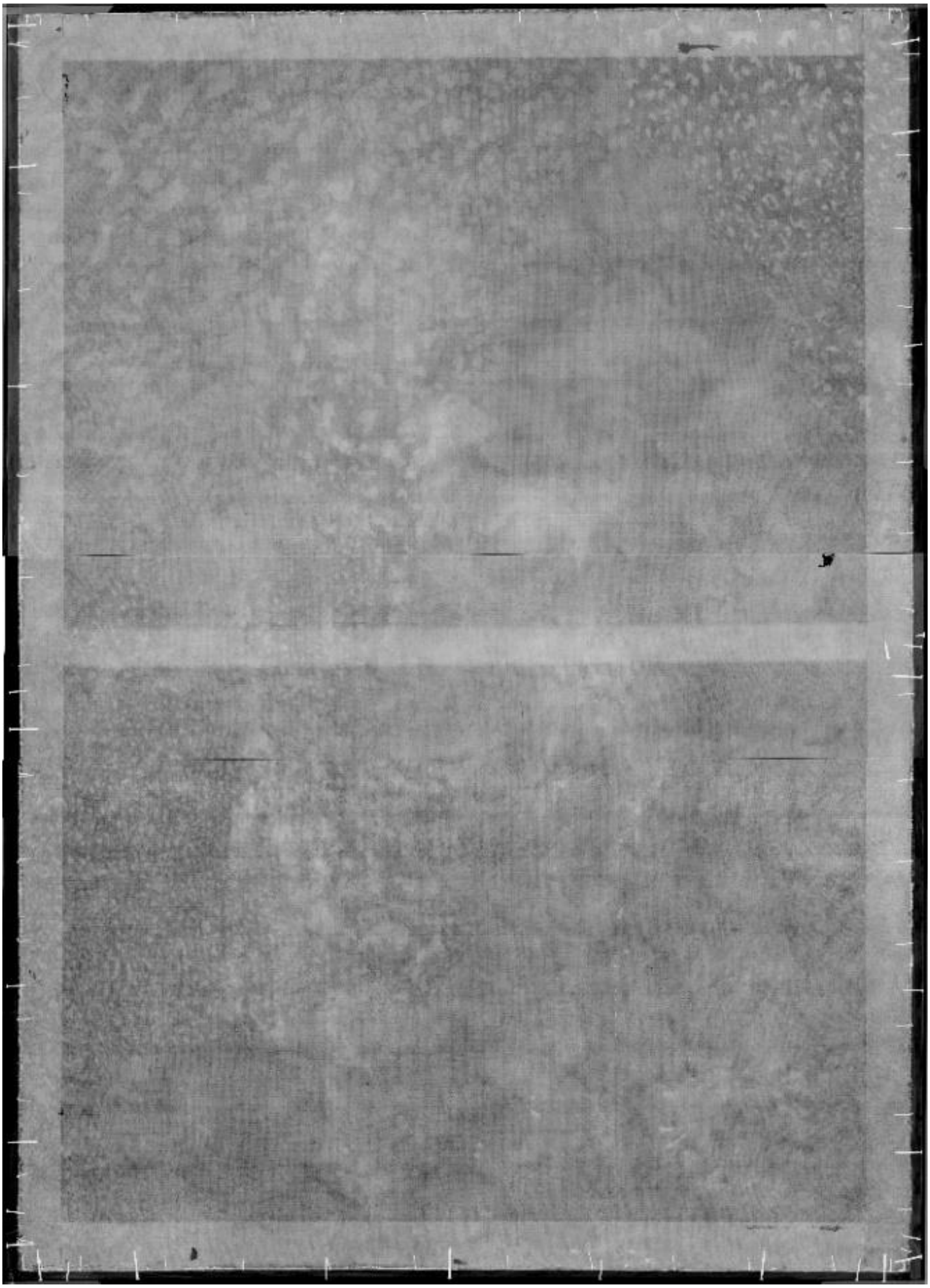

Figure B.11: X-radiography, conditions: 75kV, 50mA and 150ms.

Figure B.12: Mapped in light grey are areas affected by alligatoring. The selection was made on the flat areas (not the paint islands), because these visually noticeable areas reflect the extreme movement of the paint layers.

Figure B.13: Damage Mapping.

B.3 Painting's Condition

Auxiliary Support - Stretcher

The stretcher appears to be hard wood, possibly oak, with a "Double Fork Mortise with one key" corner construction. Each member of the auxiliary support has approximately 5 x 2,2 cm (width x depth) with a horizontal cross bar of 4 x 1,6 cm (width x depth). While the cross bar is chamfered, the other bars seem to be bevelled (with a thickness of 2,2 cm on the inside and 3 cm on the out-side) preventing direct contact with the canvas. Four out of the six wooden keys are present, the two missing keys are from the top left corner and from the right side of the horizontal cross bar.

Overall the stretcher is in fair condition with no significant breaks or splits to the wood and the corners and the keys are secure in position. The stretcher has a slight convex warp in all four bars. There are signs of previous insect infestation and the wood of the stretcher is significantly dusty.

On the left, right and bottom margin there are strips of wood 2.5 x 1 x 1 cm nailed to the margins (possibly applied to protect the otherwise exposed tacking margin, or representing an expansion to fit a previous frame). The X-radiography (Figure B.) shows that the left and right strip have 10 nails holding the strip to the paintings margin, those nails are divided into 5 larger ones and 5 smaller ones. The bottom strip has 5 larger nails and 4 smaller ones, a total of 9 nails holding the strip to the painting. Written by hand on the right strip nailed to the stretcher is "Museu do Chiado - Antigo M.N.A.C.".

Support - Fabric

In terms of fabric condition the fibres are brittle and the tension is somewhat slack with significant movement of the canvas. When lying flat a soft depression is noticeable across the painting and more significant on the lower part. The tears and damages are mapped in Figure B.13.

Ground and Paint layers

The adhesion to the support is very good as well as the cohesion between the ground layers with no active flaking, the most vulnerable areas are the ones resulting from apparent physical damages such as the tears, where impact has caused some losses to the ground layers, and areas of abrasion around the margins (see Damage Mapping, Figure B.13). These damages and abrasions appear to have occurred after 1950, since they are not visible in the published black and white photograph of the painting (Figure 2.8).

The paint layers appear to have a good cohesion and adhesion with no active flaking. There is no evidence of blooming, a small area of blanching on the bottom left side appears to be related to the abrasions along the margin of the image and the paint losses are located in areas of tears and abrasions (mostly around the margins) (see Damage Mapping, Figure B.13).

B.4 Equipment and experimental conditions

Photographs

Except for the IR photography, the photographic documentation was performed with a DSLR NIKON D500. For macro photography a Sigma Macro 70mm F2.8 EX DG lens was used. Tungsten lamps were used, at different angles, for normal and raking illumination and a Philips TLD 36W/08 for UV illumination.

Both the grey scale and the colour chart used were from B.I.G. photo equipment (B.I.G. Stufengraukeil und Farbkarte # 13-18 cm, Art. - Nr. 486020; B.I.G. GmbH. 92637 Weiden - Germany).

Infra-red (IR) photography

IR photography was carried out using a Sony digital camera, model DSC-F828 cyber-shot, on "night shot mode", with a Infrared (R72) Hoya filter. The painting was being iluminated with two tungsten lamps at a 45º degree angle from the paintings surface.

Dino-Lite

Detail images with higher magnification were taken with two Dino-Lite digital microscopes. A microscope eye-piece camera, Dino Eye-AM-423X model, from AnMo Electronics Corporation. Made in Taiwan. P/N: 17B0100; and a Dino-Lite digital microscope, AM7915MZTL model.

Both were mounted on supports to help with focus and positioning.

X-radiograph

X-radiographs were taken using a ArtXRay from NTB electronische Geraete GmbH digital system. This system is composed of a X-ray generator Y.MBS/160-F01, with a directional beam with a focal spot size of 1,9mm, a 40-160kV voltage, 0,2-5,0mA current and a maximum X-ray power of 480W; a manipulator of 4µm/step and 5000steps/revolution resolution; and a camera with 10-160kV radiation sensitive range, 0,083mm pixel size, and 12pixel/mm resolution.

For the X-radiograph taken, the following conditions were used: 75kV, 50mA and 150ms. The digital images were acquired and processed with iX-Pect software.

C

Appendix to Chapter 3

ANALYTICAL CHARACTERIZATION

C.1 Equipment and experimental conditions

Optical Microscope (at DCR/NOVA)

The optical microscope is an Axioplan 2ie Zeiss microscope equipped with a transmitted and incident halogen light illuminator (tungsten light source, HAL 100); incident UV radiation (mercury light source, HBO 100 illuminator); and a digital Nikon camera DXM1200F, with Nikon ACT-1 application program software, for microphotographs. Samples were analysed with 10x ocular lenses and 5x/10x/20x/50x objective Epiplan lenses (giving total optical magnification of 50x, 100x, 200x, and 500x). For the incident and transmitted light (normal light) the samples were analysed under cross polars – polariser and analyser filters; and for UV radiation the Zeiss filter set 2 [BP300-400, FT 395, LP 420] and filter set 9 [BP 450-490, FT510, LP515] were used. The scales for all objectives were calibrated within the Nikon ACT-1 software.

µ-FTIR (Micro Fourier Transform Infrared Spectroscopy) (at DCR/NOVA)

Infrared spectra acquired using a Nicolet Nexus spectrophotometer coupled to a Continumm microscope (15x objective) with a MCT-A detector cooled by liquid nitrogen. The spectra were collected in transmission mode, between 4000 and 650 cm^{-1}, in 50-100 µm areas, resolution setting 4 cm^{-1} and 128 or 256 scans, using a Thermo diamond anvil compression cell. When necessary, the system was purged with nitrogen prior to the data acquisition.

Analysis with µ-FTIR were kindly performed by Vanessa Otero, at DCR/NOVA.

FTIR-ATR (at LAMS)

FTIR spectra were recorded at room temperature with a Cary 630 Agilent spectrometer using the ATR accessory. Results are reported as an accumulation of 32 scans, with a spectral resolution of 4 cm^{-1}.

Analysis were carried out by the author, thanks to instructions from Laurence De Viguerie.

ATR-FTIR Microscopy (at UVA)

The ATR-FTIR analysis analyses were performed at the University of Amsterdam (UVA), using a Perkin Elmer Spectrum 100 FTIR spectrometer combined with a Spectrum Spotlight 400 FTIR microscope equipped with a 16x1 pixel linear mercury cadmium telluride (MCT) array detector. A Perkin Elmer ATR imaging accessory consisting of a germanium crystal was used for ATR imaging. The spectral resolution was 8 cm−1. The map size was 200 × 200 μm^2 and the spatial resolution 1.5µm/pixel. Maps were analysed using the PyMCA ROI imaging package.

Briefly, chemical maps were obtained by the integration the FTIR intensity over different regions of interest (ROI). Then, FTIR average spectra were calculated from the different locations by selecting pixels (brush tool) in the most intense parts of the ROI maps.

ATR-FTIR analyses were carried out at University of Amsterdam, thanks to Dr. Marine Cotte, with the support of Victor Gonzalez, Katrien Keune, and Joen Hermans.

The FTIR spectra (obtained with the three instruments mentioned above), are shown as acquired, without corrections or any further manipulations, except for the removal of the CO_2 absorption at *ca.* 2300–2400 cm^{-1}.

µ-RAMAN (at MONARIS)

Raman spectra were recorded with a Bruker Senterra spectrometer, using an infrared diode laser for the 785 nm excitation wavelength. The laser was focused on the sample by a microscope, using a x50 or a x100 long working distance objective lens with a specific coating for the infrared excitation. The laser power was less than 5/10mW (approximately) on the sample and the time of acquisition was 4 x 60 seconds to obtain a better signal/noise ratio. The grating used had 1200 lines/mm, giving a spectral resolution of about 3-5 cm^{-1}. The Raman signal was detected using an air-cooled CCD detector. All spectra were acquired with “Concave Rubberband Correction”.

Access and instructions for the author to use the equipment were kindly given by Céline Paris and Ludovic Bellot-Gurlet, at MONARIS – *de la Molécule aux Nano-objets: Réactivité, Interactions et Spectroscopies* – UMR 8233, Univ. Pierre et Marie Curie, Paris.

FT-Raman (at MONARIS)

FT-Raman analyses were performed using a near-infrared excitation at 1064 nm provided by an Nd-YAG laser diode available on a Bruker RFS 100/S spectrometer based on a Michelson-type interferometer and equipped with a liquid nitrogen-cooled germanium detector. The commercial references were analyzed using a microscopic interface equipped with a 40x objective, allowing a spot size of 30 µm approximately. The samples from the painting and material references were analyzed using a 100x objective which led to an approximate 15-µm spot size. The laser power was adjusted depending on the sample. Reference materials and the painting samples were placed on a silver mirror to improve the collected Raman signal intensity. Spectra were recorded between 3500 and 50 cm^{-1} with a 4 cm^{-1} resolution, and with 1000 to 1500 scans to optimize the signal-to-noise ratio.

Analyses with FT-Raman were kindly performed by Céline Paris, at MONARIS – *de la Molécule aux Nano-objets: Réactivité, Interactions et Spectroscopies* – UMR 8233, Univ. Pierre et Marie Curie, Paris.

SEM-EDX (at IMPC FR2482)

For the Scanning Electron Microscopy/energy-dispersive X-Ray spectroscopy, imaging and microanalysis were performed on a Hitachi SU-70 FEGSEM (Schottky emission gun), fitted out with an X-Max 50mm^2 Oxford EDX spectrometer. The Oxford spectrometer software used was first INCA and later AZTEC after an update.

Prior to analyses all samples were carbon coated (an estimated 40 nm) to ensure the presence of a conductive layer on top and to consequently enable or improve the imaging of the samples which are otherwise insulating. Even with the thin film of carbon, during spectrum acquisition, damage at the surface of some samples was still observed in the form of small dots across the area analysed. This damage is likely caused by resistive loss as electrons from the primary beam penetrate inside the material. This resistive loss results in heating of the sample which has a significant organic composition and consequently may deform or even break chemical bonds until destruction. For this reason, in some samples, acquisition of the spectra had to be done in a very short time to minimize this drawback, this unfortunately results in spectra with poor signal to noise ratio, which makes detection of trace elements more difficult.

The analyses were kindly performed by David Montero. Access to the Semfeg & EDX instrumentation was facilitated by the Institut des Matériaux de Paris Centre (IMPC FR2482) and was funded by UPMC, CNRS and by the C'Nano projects of the Région Ile-de-France.

TOF-SIMS Imaging (at LAMS)

The instrument used to perform the analyses is the TOF-SIMS IV (IONTOF GmbH, Germany) in the Laboratory of Molecular and Structural Archaeology (LAMS, CNRS – Sorbonne University, Paris, France). The data were acquired using SurfaceLab 6.7 software (IONTOF GmbH, Germany) and processed with SurfaceLab 7.0.

The primary ion source used for analysis is a liquid metal ion gun delivering a bismuth cluster pulsed ion beam (25 keV energy Bi3+ ions) hitting the surface with an incidence angle of 45°, with a low energy electron flood gun neutralizing the surface between each analysis scan. The time-of-flight analyzer is equipped with delayed extraction of secondary ions, which permits the combination of a high spatial resolution with a mass resolution of a few thousand, thanks to the so-called "burst alignment with delayed extraction" (BA+DE) focusing mode in which the beam diameter is reduced down to 400 nm. This was described by Vanbellingen et al. (2015) The primary ion current is however low, of 0.08 pA (at a frequency of 10 kHz), requiring longer acquisition time.

The mass spectrometer is also equipped with an argon Gas Cluster Ion Beam (GCIB), which allows a gentle sputtering of the surface without damaging the underlying layers. Thus, before the analysis, a 1000 µm side square around the analyzed areas was cleaned with a dose of 1.1015 ions/cm^2 using argon clusters of 2000 atoms with a total energy of 10 keV. This way, the potentially contaminated surface (by exogenous lipids or silicones (in particular, polydimethylsiloxane (PDMS)) was sputtered onto at least twice the size of the analyzed area.

For the analyses, ion images were acquired on areas of 400 µm × 400 µm, separated in 1024 × 1024 pixels so the pixel size equaled 390 nm, around the primary ion beam size. The Bi3+ primary dose was 5.1012 ions/cm^2. Between each analysis scans a soft sputtering using GCIB was performed, using a dose of 1.1014 ions/cm^2 again on an area of 1000 µm × 1000 µm. This dual beam analysis combines depth profiling and high-resolution imaging. This setup is adapted to observe small inorganic particles with sufficient secondary ion yield to retrieve mass spectra with adequate intensity, although it must be considered that it can lead to a selective loss of the organic signature in organic-inorganic mixtures. Therefore, several modalities were then used to collect the maximum of chemical information. That is, small regions were analysed using conditions adapted to the detection of organic materials, or dual beam imaging was used to access better-contrasted images of inorganic features such as pigments particles.

The analyses and data processing were kindly performed by Caroline Bouvier during her PhD at LAMS – *Laboratoire d'Archéologie Moléculaire et Structurale* – UMR 8220, Univ. Pierre et Marie Curie, Paris.

Py-TMAH-GC/MS (at RCE)

On-line: thermally assisted methylation. After adding 3 µl of tetramethylammonium hydroxide (TMAH) in methanol (5%) with tridecanoic acid (FA-C13) as internal standard (the concentration of FA-C13 is 16ug/ml), the sample is homogenized and then placed in a stainless steel cup (Frontier LabDisposable Eco-Cup SF).

Pyrolysis transesterification gas chromatography/mass spectrometry (Py-TMAH-GC/MS). The pyrolysis unit used was a Frontier Lab 3030D pyrolyser mounted on a Thermo Scientific Trace 1310 GC / ISQ mass spectrometer combination. The analytical column was directly coupled to the pyrolyser via a home-made split device. A SLB5 ms (Supelco) column was used (length 20 m, int. diameter 0.18 mm, film thickness 0.18 µm). Helium was used as carrier with a programmed pressured flow of 0.7–1.2 ml/min and split ratio of 1:30. The pyrolysis temperature was 480 °C. The temperature program was the following: 35 °C (1.5 min), heating at 60 °C /min to 100 °C, heating at 14 °C/min to 250 °C, heating at 6 °C/min to 315 °C (2 min). The column was directly coupled to the ion source of the mass spectrometer. The temperature of the interface and the ion source was 270 °C and 220 °C, respectively. Mass spectra were recorded from 29 until 600 amu with a speed of 7 scans per second. Xcalibur 2.1, AMDIS 2.73 and GCMSsolution (version 4.45) software were used for collecting and processing of the data.

Py-TMAH-GC/MS analyses were carried out by Henk van Keulen at RCE - Cultural Heritage Agency of the Netherlands, with the help of Dr. Klaas Jan van den Berg.

C.2 Analytical Protocols

- **Cross-section Preparation (at DCR/NOVA)**

Each sample was removed with a scalpel, blade nº11, while using the stereomicroscope and for most samples contains the complete stratigraphy of that paint area.

Acrylic Resin

Due to concerns about the potential contamination of the samples with polyester embedding resin (pers. Comm. Vanessa Otero, from samples taken to the synchrotron) an acrylic resin[166] was selected for the first set of samples (S1 to S13). To use this acrylic resin, samples are mounted on the base of a cylindrical teflon mould with a detachable bottom. The main

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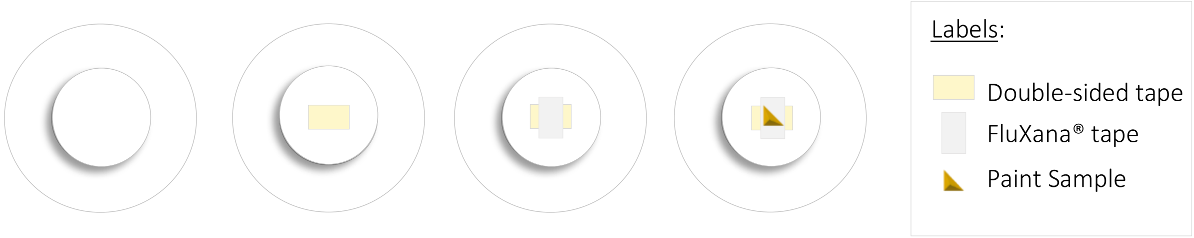
[166] Technovit® 2000 LC resin, a light curing, one component, highly transparent embedding resin based on methacrylate, and then polymerized with a blue-light in a Technotray POWER unit. (http://kulzer-technik.de/en_kt/kt/maerkte/metallographie/produktbereiche/verbrauchsmaterialien_einbetten_1/technovit_2000lc.aspx)

disadvantage of this sytem is that it uses a “fixing paste” to hold the sample in place prior to the introduction of the acrylic resin. The fixing paste contains barium (analysis by Isabel Pombo Cardoso) which can interfer with subsequent analyses. A different method for holding the sample was developd by Isabel Pombo Cardoso and Vanessa Otero (see Scheme C.1). Double-sided adhesive tape is adhered to the surface of the detachable teflon bottom then FluXana® TF-500 tape used for XRF analysis is adhered to the double-sided adhesive tape. The paint sample is then placed (stratigraphy facing upwards) on top of the FluXana® TF-500 tape which holds the sample in place during the introduction of the acrylic resin.

The advantage of the FluXana® TF-500 tape, according to the supplier, is the fact that it is sulfur and halogen free, therefore having minimal interference with the sample.



Scheme C.1: Sequence of steps to adhere the sample on the base of the embedding mould.

The acrylic embedding resin is Technovit® 2000 LC liquid, a light curing, one component, highly transparent embedding resin based on methacrylate. It is cured in 20 mintues by polymerization using visible blue light in a Technotray Unit [Kulzer Technik]. After curing the top of the embedded sample is coated with a few drops of Technovit® 2000 LC "covering varnish" [Kulzer Technik] which hardens the top of the embedding resin mould while simultaneously holding a tracing paper label identifying the sample in place.

Once removed from the embedding moulds the cured resin surface was polished to reveal the sample in cross-section. Polishing was achieved with a set of Micromesh abrasive sheets (micron graded silicon carbide crystals from grade 600 up to 8000) without any lubricant.

Polyester Resin

The second set of samples (S14 to S27) were embedded in a polyester resin since there were several problems with the acrylic resin such as poor penetration (resulting in holes after polishing), shrinking during curing, and a large surface area due to the moulds used, which did not allow polishing with a MOPAS XS-polisher[167]. This last reason was particularly important given the need for an extremely clean and flat sample surface for analyses with imaging techniques.

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[167] https://www.jaap-enterprise.com/products/

The embedding resin selected was a polyester resin: MR Dinis Resina Poliester Cristal[168]. Small rectangular silicone moulds were filled half way with the resin and left to set for approximately 30 min, then the paint samples were placed on top with the stratigraphy paralel to the base of the moulds. Then the moulds were filled all the way up, leaving to set for 24h.

The small blocks of cured resin containing the samples were then removed from the moulds and polished with a set of Micromesh abrasive sheets (micron graded silicon carbide crystals from grade 600 up to 8000) without any lubricant, using a MOPAS XS-polisher. A special thanks is due to Jaap Boon for making one of his MOPAS XS polishers available to the DCR/NOVA.

- **SYPRO™ Ruby (at DCR/NOVA)**

SYPRO™ Ruby is an organometallic ruthenium chelate stain for the detection of proteinacious materials. A protocol developd by Stefan Schäfer (Schäfer 2013) was followed with some modifications as described in the following. The procedure for fixing the proteins within the cross-section was performed with a vapor phase application of a 37% formaldehyde solution[169] during 48h at room temperature in an enclosed glass beaker. A longer period of time (48h) was chosen since the protocol gives 24h as the minimum time without heating, and no volume for the beaker is discussed in the protocol. The samples were removed from the formaldehyde atmosphere and left to dry for a day in a laboratory fume-hood.

Procedure for each cross-section:

- The cross-section was photographed in the OM with the fluorescence filter set 9 (BP 450-490, FT510, LP515) at different magnifications;
- Application of the Sypro Ruby staining solution[170] in a dark room, with a single drop from a glass pipette, without touching the surface and monitoring the drop (it should not drip);
- After 3 minutes the excess solution was removed by absorption into a tissue paper held to one side without touching the surface of the cross-section, followed by 5 minutes of drying (the dye needs to be completely dry for the fluorescence/luminescence to remain photostable);
- The cross-section was photographed again in the OM with the fluorescence filter set 9 (BP 450-490, FT510, LP515) at the same set of magnifications for comparison with the initial images.

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[168] Polyester Resin “Resina Poliester Pré/Acel. Cristal” with a catalyst at 5%. Distributed by MR Dinis dos Santos, Lda., 2840-754 Aldeia de Paio Pires – Seixal, Portugal. https://www.dinissantos.com/resinas?lightbox=i01xrt

[169] Formaldehyde solution min. 37% free from acid stabilized with about 10% methanol and calcium carbonate for histology. Sigma-Aldrich, ref: 1.03999.1000.

[170] SYPRO™ Ruby protein blot stain. invitrogen by Thermo Fisher Scientific, ref: S11791.

C.3 Mapping and Descriptions: Cross-sections

Figure C.1: Mapping of cross-sections S1 to S27, marked in green.

Table C.1: Sampling details of cross-sections S1 to S27.

	Sample Reference	Colour Area	Location Measurements		Location Description	Sampling notes
			Top/Bottom*	Left*/Right* Side		
🟥	S1	Bright Red	B. 57.1cm	L.S. 6.1cm	Cardinal, "Cloak", Small paint loss.	During sampling the sample broke along the upper white ground‡. Both pieces - one with the red paint layer and part of the upper white ground and the one with part of the upper white ground, the green paint layer and the lower ground - were collected and assembled together in the embedding resin.
🟫	S2	Dark Red, blanched	B. 07cm	L.S. 2.6cm	Cardinal, Bottom right side. Area of paint losses	Easy access to the full stratigraphy. Very complete sample, from the blanched red to the canvas all being mounted in the embedding resin. In adition a second sample was taken from the "lower" ground, the layer in contact with the canvas. This sample was stored on a glass slide to be used in further analysis.
🟧	S3	Flesh Tone	B. 63cm	L.S. 31.5cm	Cardinal, Face. Area of paint loss.	Mechanical cracks converging close to a top layer of paint loss allowed the removal of a triangular sample. The paint was extremely brittle and separated from the upper white ground layer. The two pieces were repositioned to be as close as possible during mounting in the embedding resin.
🟧	S4	Flesh Tone	B. 51.9cm	R.S. 38.5cm	Jorge Serrão, right hand	Very brittle surface, sample removed from along a mechanical crack. The sample broke but all the pieces were collected, and two of them were mounted together, giving the full stratigraphy of that area. The remnants were kept on a glass slide to be used in other analytical techniques.
🟨	S5	White	B. 20.3cm	L.S. 38.9cm	Cardinal, right sleeve. Area of paint loss	Sampled from an area of paint loss. Extremely brittle and flaking paint. Removal of a complete sample and some extra broken pieces around. The sample is complete but broke in the middle during mounting. The remaining samples are stored on a glass slide.
⬛	S6	Black	B. 4.6cm	R.S. 17.8cm	Table? Background, Tear bottom right side.	Around the tear the paint was flaking which facilitated the removal of a complete sample. Small pieces of the lower ground were kept on a glass slide.

🟫	S7	Brown	T. 60.3cm	R.S. 8.9cm	Jorge Serrão, left arm. Area of paint loss.	Flaking paint around a large tear with associated paint losses, removal of a complete sample. This area provided useful for samples of the ground.
⬛	S8	Black	T. 7.5cm	L.S. 5.5cm	Background, Tear top left side	Flaking paint around the tear, S8 is part of an “island” thicker/darker paint sample, correlates to S9.
⬛	S9		T. 8.9cm	L.S. 5.3cm	"	Flaking paint around the tear, S9 is part of the “flat” thinner/lighter paint sample, correlates to S8.
⬛	S10	Black	T. 4.8cm	R.S. 22cm	Background, Tear (above the Jorge Serrão head)	Sample with both areas, “flat” and “island”. Because it was removed from an intermediate area, it has both profiles – flat area and thick island.
🟫	S11	Brown	T. ~61.5cm	R.S. ~10.5cm	Tear left side (Jorge Serrão jacket)	Flaking paint around the tear, S11 is part of an “island” thicker/darker paint sample, correlates to S12.
🟫	S12	Brown	T. -61cm	R.S. ~9.5cm	"	Flaking paint around the tear, S12 is part of the “flat” thinner/lighter paint sample, correlates to S11.
🟥	S13	Red Bead	B. ~65.5cm	L.S. ~6.4cm	Cardinal, “red bead on an island”.	On top of the bright red islands in the “Hood of the Cloak” , there are several “beads”. This is one of those.
🟥	S14	Dark Red, blanched	B. 17.4 cm	L.S. 4.1 cm	Cardinal pants, Island.	Area of paint loss, in some areas to the lower ground, but mainly to the upper white ground. This is an island area and has an interesting “pulled” lower triangular shaped flat area, which has a higher gloss. There is also what appears to be some “blanched area” above the paint island.
🟨	S15	White	B. 18.9 cm	L.S. 27.4 cm	Cardinal, right sleeve. Flat area, wrinkled paint.	Even though the surface appears to be in “good condition” under the stereomicroscope is possible to see that it is cracked and wrinkled on a micro scale. Mechanical cracks converging allowed the removal of the sample. Extremely brittle paint behaved as previously: separating by the upper white ground layer, leaving only a

🟨						small amount of the lower ground. Interesting striations on the paint surface (with the appearance of a bat wing). Appears to have the black pigmented layer bellow the paint layer.
🟧	S16	Flesh Tone	B. 14.3 cm	R.S. 44.8 cm	Cardinal's hand. Flat area, wrinkled paint.	Even though the surface appears to be in “good condition” under the stereomicroscope is possible to see that it is cracked and wrinkled on a micro scale. Extremely brittle paint behaved as previously separating by the upper white ground layer, no lower ground present in the sample.
🟥	S17	Bright Red	B. 60.5 cm	L.S. 11.5 cm	Cardinal's cape, Island.	Sampled from a mechanical crack going through an island. Very elongated sample and extremely brittle paint which separated from the upper white ground layer, leaving only a small amount of the greenish paint layer and the lower ground. The paint surface is “bumpy” and seems to have beads on it.
🟧	S18	Flesh Tone	B. 69.5 cm	L.S. 24.5 cm	Cardinal’s face. Island.	Sampled from a mechanical crack going through an island. Large sample, extremely brittle paint layer that separated along the upper ground layer during sampling. The paint surface is showing pronounced ridges in the form of “waves”.
🟫	S19	Brown	T. 27.4 cm	L.S. 36.8 cm	Background, Island.	Sampled from the edges of a crack going through an island. Both profiles – flat area and thick island - were sampled. Very big sample and extremely brittle paint layer that separated along the upper ground layer during sampling. The paint surface is showing striations, and bumpy areas, and possibly part of the “exudate” area.
🟧	S20	Flesh Tone	T. 25.5 cm	R.S. 36.2 cm	Jorge Serrão’s face	Even though the surface appears to be in “good condition” under the stereomicroscope is possible to see that it is cracked and wrinkled on a micro scale. Mechanical cracks converging allowed the removal of the sample. Went all the way to the canvas leaving a visible hole which extended into the interstices of the threads. Complete sample with all layers, except on the elongated part, that only goes to the upper ground layer. Interesting striations on the paint surface (looks like grid marks). Appears to have the black pigmented layer bellow the paint layer.
🟩	S21	Greyish White	T. 30 cm	R.S. 21.3 cm	Jorge Serrão’s collar Shadow. Flat area.	Even though the surface appears to be in “good condition” under the stereomicroscope is possible to see that it is cracked and wrinkled on a micro scale. Mechanical cracks converging allowed the removal of the sample. Went all the way to the canvas leaving a visible hole which extended into the interstices of the threads. Complete sample with all layers (even a fibre).
⬜	S22	White	T. 38 cm	R.S. 20.5 cm	Jorge Serrão 's collar Highlight. Flat area.	Even though the surface appears to be in “good condition” under the stereomicroscope is possible to see that it is cracked and wrinkled on a micro scale. Mechanical cracks

🟨						converging allowed the removal of the sample. Extremely brittle paint, broke into two samples, one smaller with very little paint layer, but lower ground. And a bigger one with complete paint layer but only upper ground layer, which is the one in the embedding resin.
🟫	S23	Brown	T. 28.4 cm	R.S. 0.9 cm	Background. “Frame area” “good condition”, but wrinkled paint.	Even though the surface appears to be in “good condition” under the stereomicroscope is possible to see that it is cracked and “unwell” on a micro scale. Cracks converging allowed removal of the sample, with complete stratigraphy.
🟫	S24	Brown	T. 28.4 cm	R.S. 4.1 cm	Background. “Frame area” “bad condition”. Island.	Sampled from the edges of a crack going through an island. Extremely brittle paint layer that separated, leaving only the top paint layer (very thin in one end of the sample) and on the other end a partial upper ground layer. The paint surface is showing beads.
🟦	S25	Greenish	B. 59.1 cm	R.S. 29.7 cm	Jorge Serrão "sword". Flat area.	Even though the surface appears to be in “good condition” under the stereomicroscope is possible to see that it is cracked and wrinkled on a micro scale. Mechanical cracks converging allowed the removal of the sample. Went all the way to the canvas leaving a visible hole which extended into the interstices of the threads. Complete sample with all layers.
🟧	S26	Flesh Tone	B. 60.3 cm	R.S. 33.8 cm	Jorge Serrão left hand. Flat area.	Even though the surface appears to be in “good condition” under the stereomicroscope is possible to see that it is cracked and wrinkled on a micro scale. Mechanical cracks converging allowed the removal of the sample. Brittle paint layer, separated by the upper ground layer. Appears to have the black pigmented layer bellow the paint layer.
🟥	S27	Dark Red	B. 41.2 cm	L.S. 36 cm	Cardinal’s inside cape, Island.	Sampled from the edges of a crack going through an island. Very big sample and extremely brittle paint layer that separated, leaving only a partial upper ground layer in the middle of the sample. This is an Island area and has an interesting “pulled” lower triangular shaped flat area, which has higher gloss. The paint surface is showing striations, and bumpy areas. During embedding it broke at an existing crack, and was placed as close as possible to the original position. This must be kept in mind when observing the broken ground layer in the cross-section.

*All measurements were made to the edge of the painting. NOT the edge of the side and bottom wood strips.

[‡] As described in section 3.2.1.2, there are two ground layers: an upper ground layer and a lower ground layer, which are separated by a series of paint layers (from a previous painting).

C.4 Cross-sections by colour

Table C.2: Cross-sections from areas of red paint.

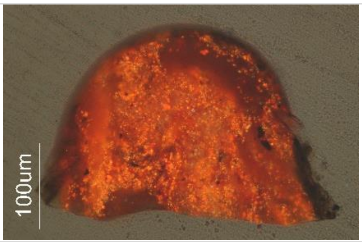
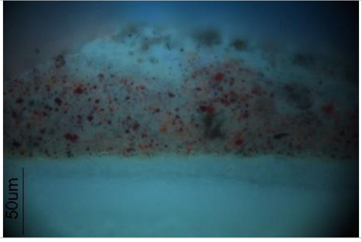
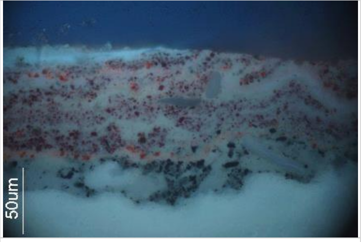
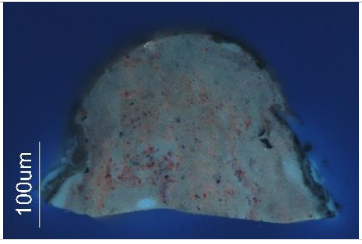
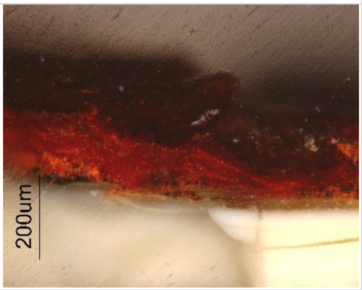
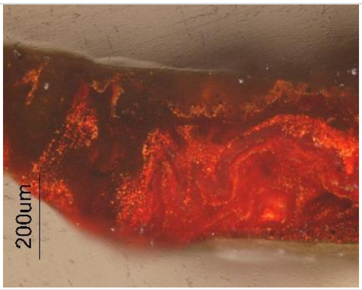
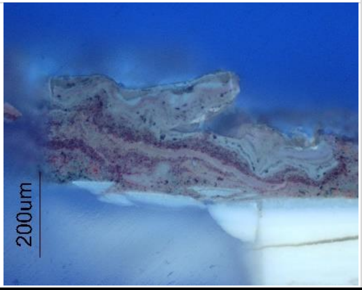
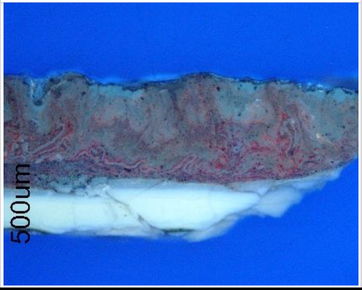
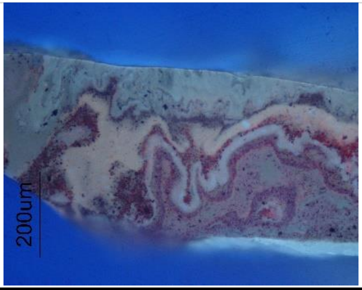
Red paint		
S1	**S2**	**S13**
		
		
S14	**S17**	**S27**
		
		

Table C.3: Cross-sections from areas of brown paint.

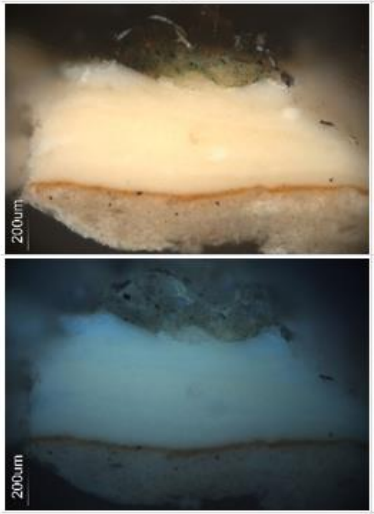
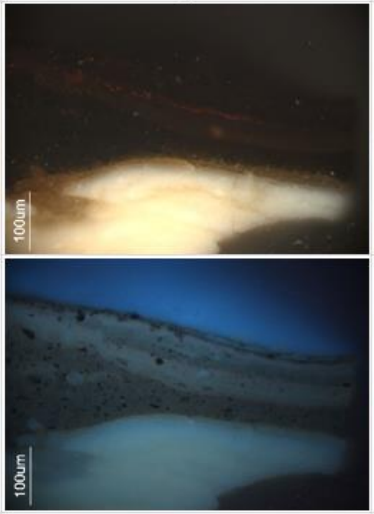
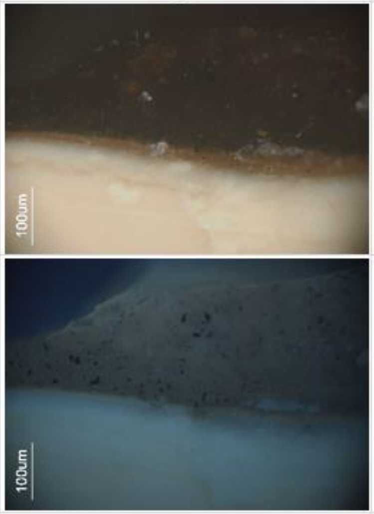
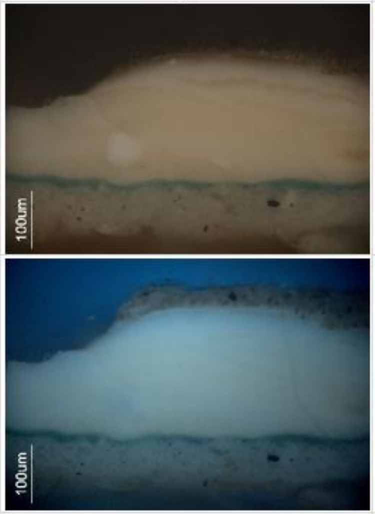
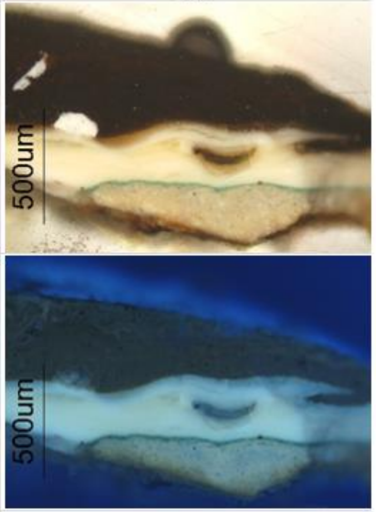
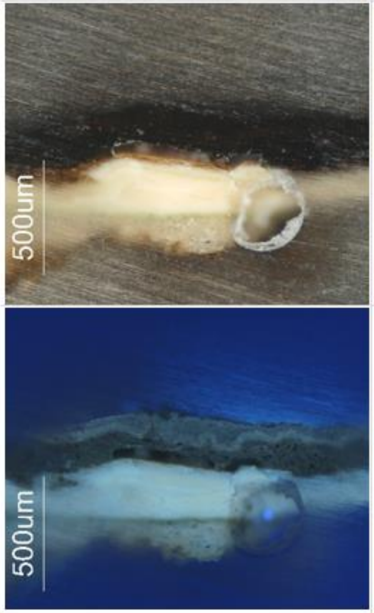
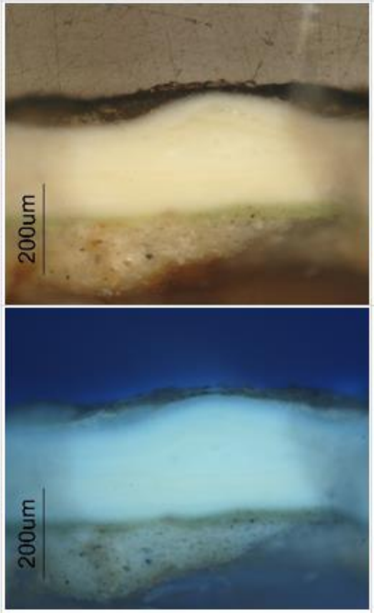
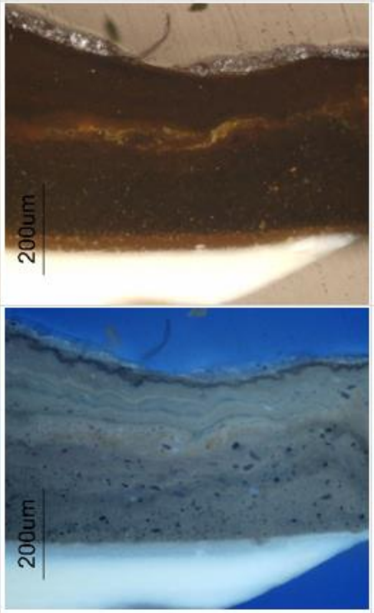
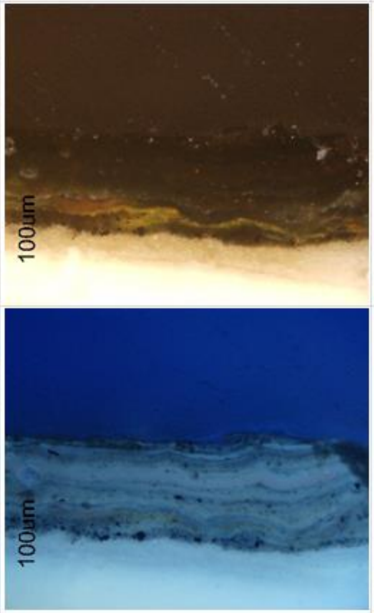
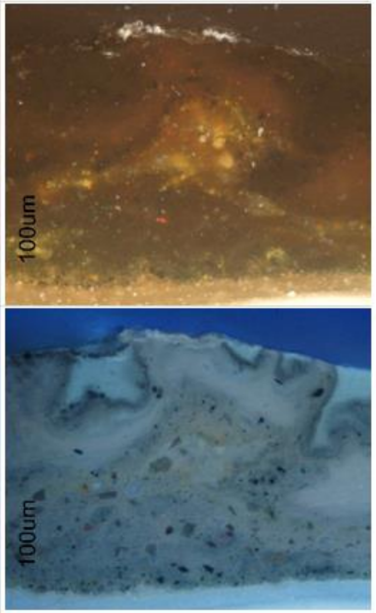
Brown/Black paint				
S6	**S7**	**S8**	**S9**	**S10**
				
S11	**S12**	**S19**	**S23**	**S24**
				

Table C.4: Cross-sections from areas of flesh paint.

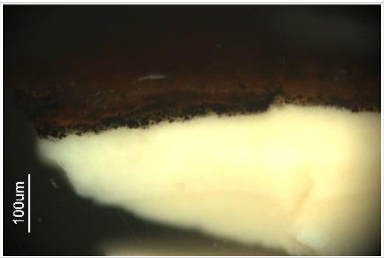
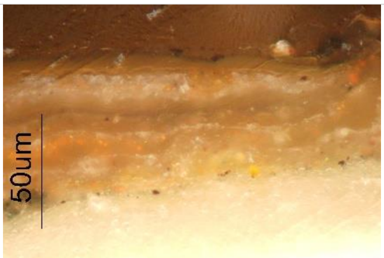
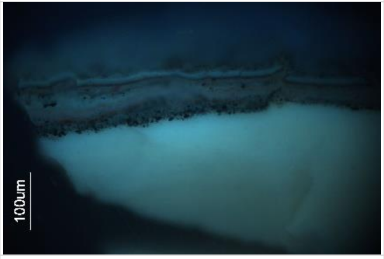
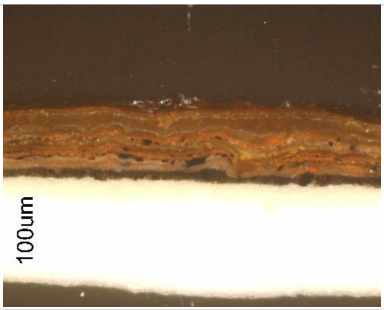
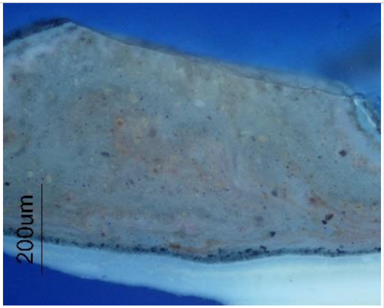
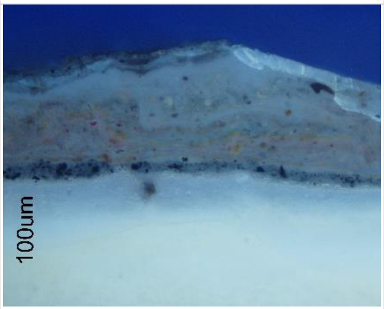
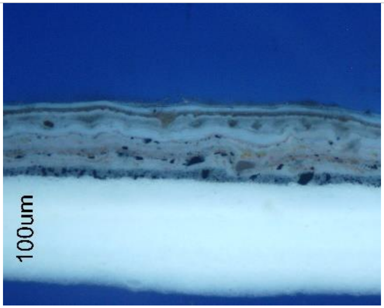
Flesh Tones		
S3	**S4**	**S16**
		
		
S18	**S20**	**S26**
		
		

Table C.5: Cross-sections from whitish paint areas.

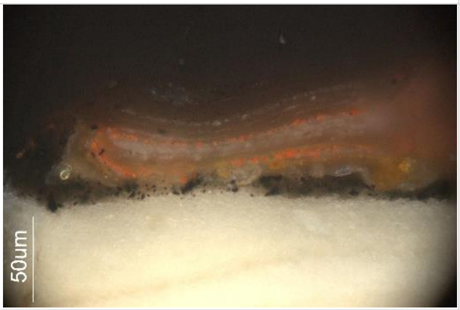
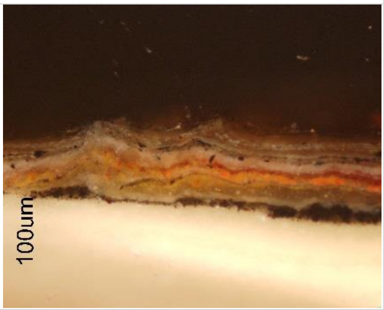
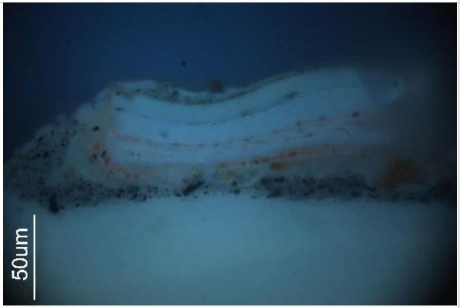
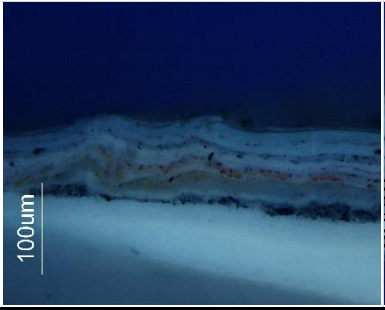
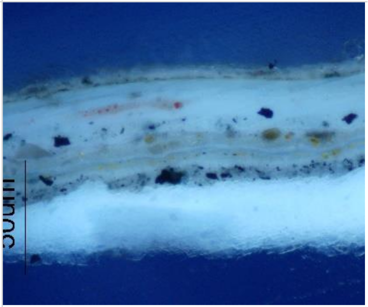
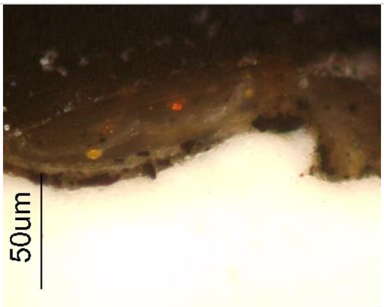
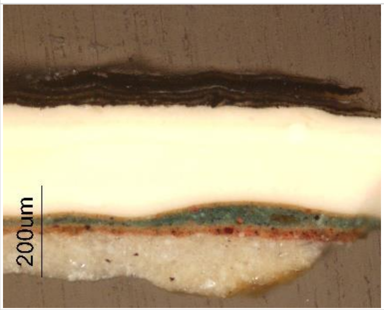
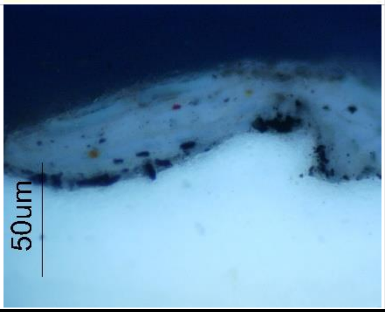
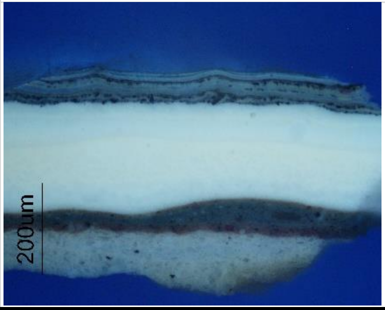
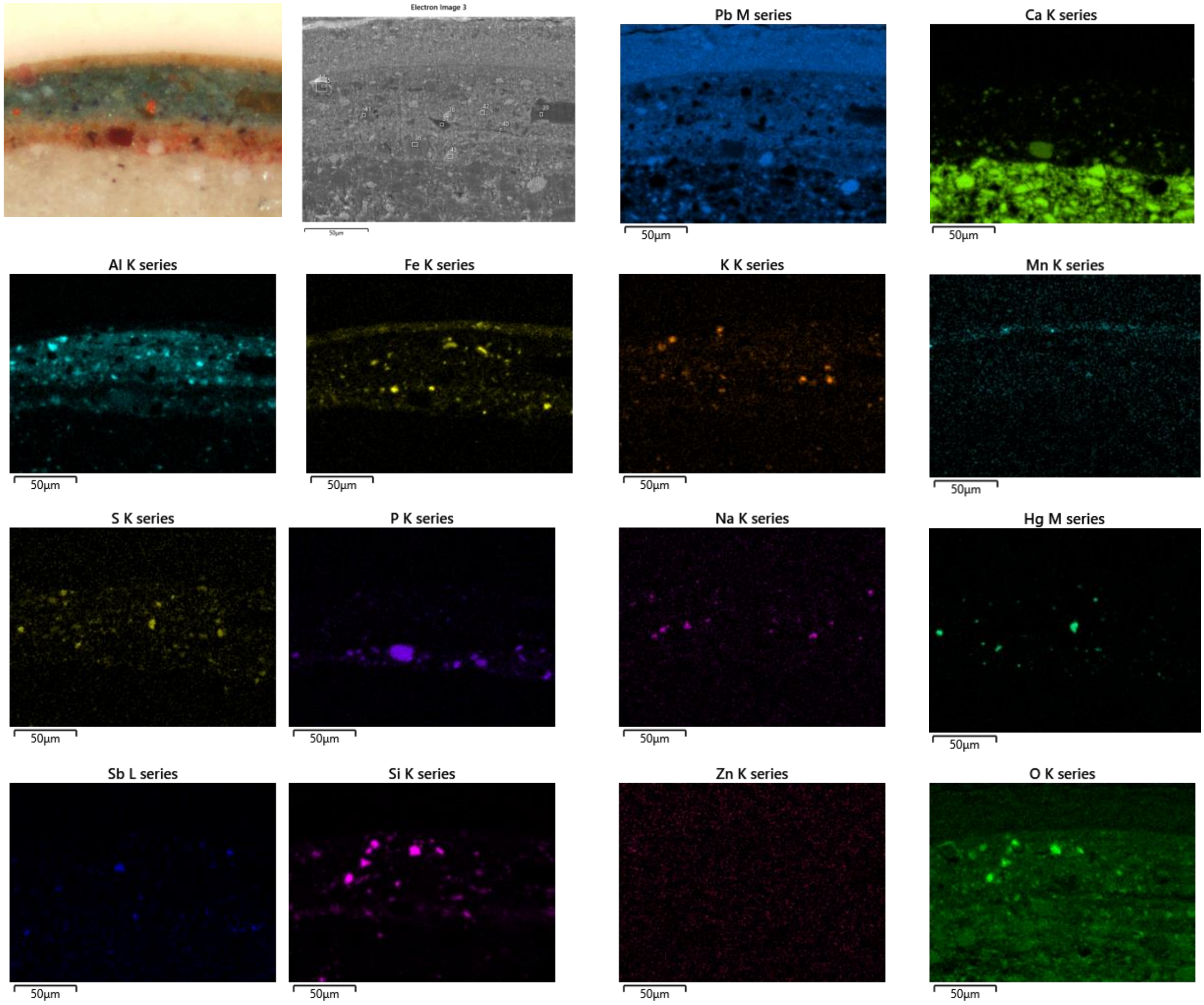
Whitish paint		
S5	**S15**	**S22**
		
		

Table C.6: Cross-sections from other colours - greyish white and greenish paint.

Greyish white and Greenish paint	
S21	**S25**
	
	

C.5 EDX Mapping of S25, paint layers between the ground layers (assumed previous painting)

Table C.7: EDX elemental mapping of the paint layers between the ground layers (delimited by the map of Ca and Pb) of sample S25.



C.6 ATR-FTIR Microscopy of brown paint sample S7

Sample S7 taken from Jorge Serrão left arm, brown paint (paint island), presents the average stratigraphy of the brown paint: top paint layer showing more than one layer in UV light; translucent layer bellow which is more pronounced in this sample due to a “pocket”; lead white ground and then one paint layer and a calcium carbonate ground layer likely from the previous painting.

Three distinct areas were analysed by ATR FTIR Microscopy, maps i,ii,iii (yellow, orange and red respectively). These areas, visible in Figure C.2, were analysed with the following conditions: Resolution of 8cm^{-1}, 1 scan per second, Speed 2.2 cm/s, Map 200x200 and 1.5µm pixel (11 minutes per map).

To relate the chemical maps to the cross-section stratigraphy, OM images in UV light are shown. Only the results of map i are presented below, since it captures the main three layers of interest: the brown paint layer, the translucent layer and the upper ground layer.

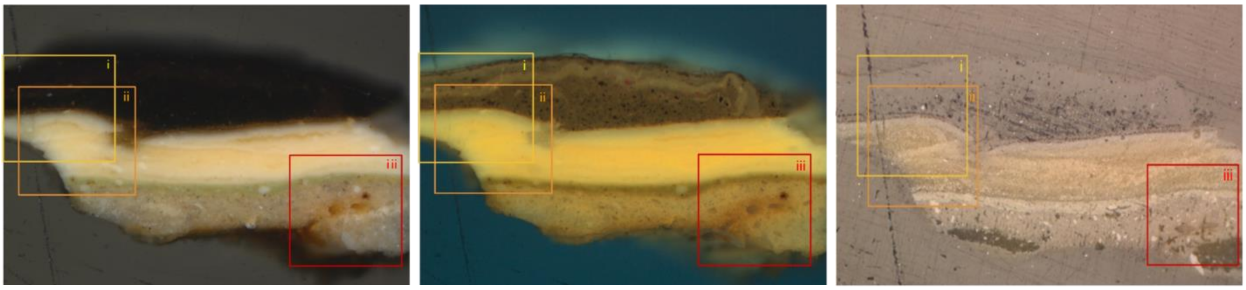


Figure C.2: Optical microscopy photographs of S7 under cross-polarized light (left), under UV light (middle) and under bright field (right). Marked in yellow, orange and red are the areas analysed by ATR-FTIR microscopy, namely maps i, ii and iii, respectively.

Map i

The three chemical maps (Figure C. **a, b, c**) that best represent the three layers present in the area of **map i** (Figure C.) were obtained by the integration of different bands of interest (grey rectangles Figure C.4 **a, b, c**).

FTIR spectra was acquired from the different locations by selecting the red areas of each chemical map, therefore spectrum **1** corresponds to chemical map **a**, spectrum **2** to chemical map **b** and spectrum **3** to chemical map **c** (Figure C.4).

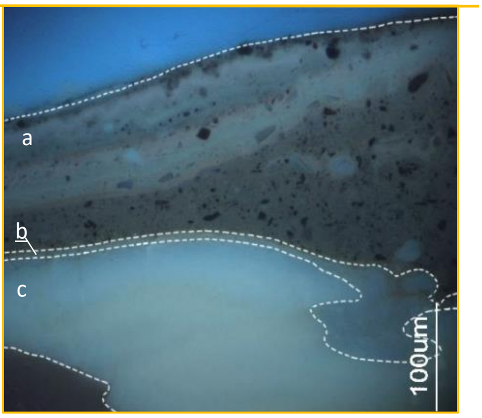


Figure C.3: Detail of S7 under UV light. Area of map i, with white outline of layers a, b and c.

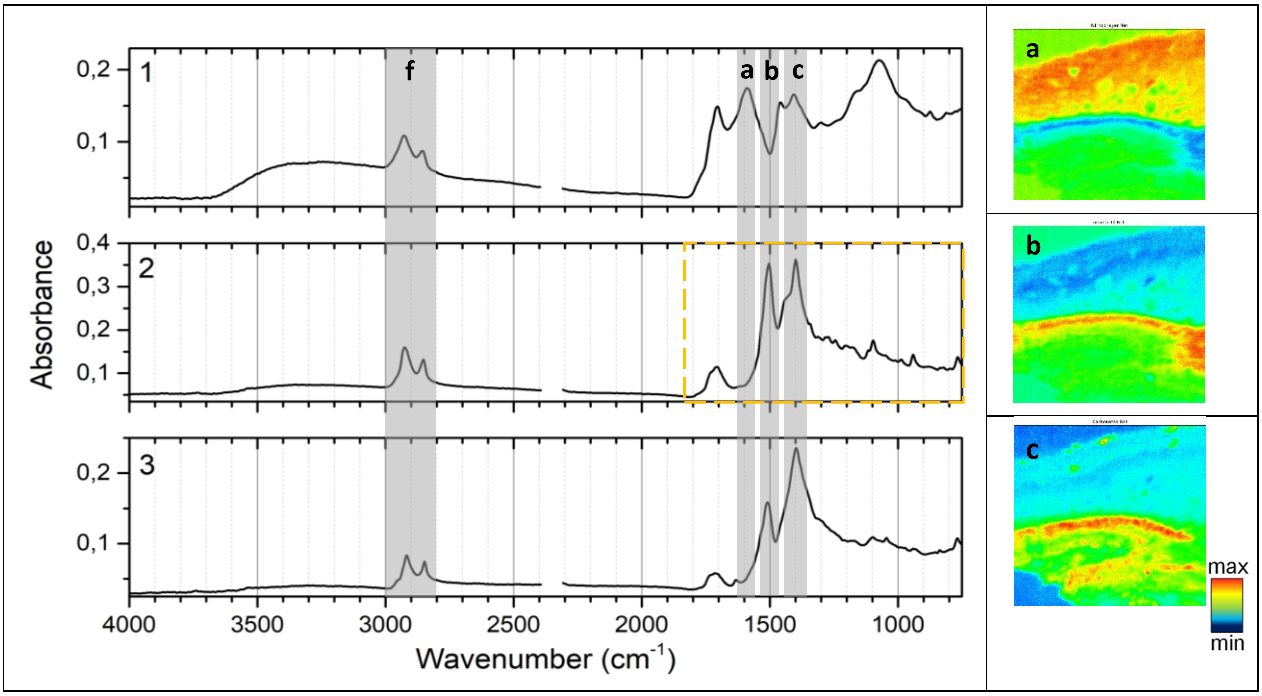


Figure C.4: Analysis by ATR-FTIR microscopy of S7 (brown paint sample). Average spectra **1, 2** and **3** were calculated from the maximum values (in red) of the chemical maps **a, b** and **c**, respectively. Chemical maps **a** of the top layer (intensity from 1663 to 1501 cm^{-1}), **b** of the "translucent" layer (intensity from 1557 to 1478 cm^{-1}) and **c** of the upper ground layer (intensity from 1468 to 1332 cm^{-1}).

The chemical map **a**, represents the integration of the band centred at 1587 cm^{-1}, and encompasses the brown paint layer from sample S7 (Figure C.5).

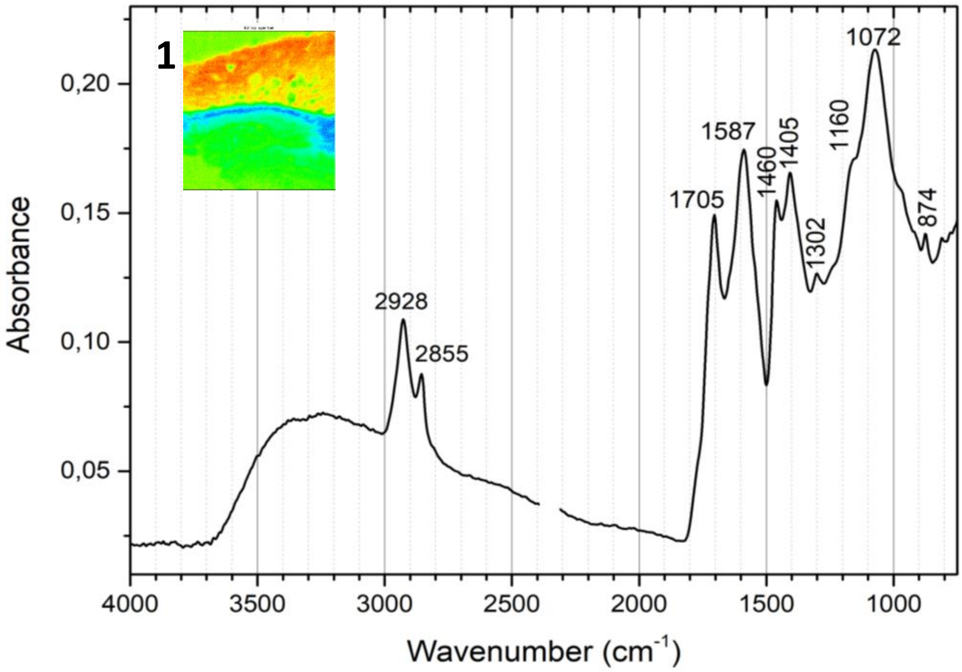


Figure C.5: Spectrum **1**, acquired from the maximum values (in red) of the chemical map **a** (intensity from 1663 to 1501 cm^{-1}).

Further distinction of this brown paint layer in S7 was obtained with a ROI between 1397 and 1506 cm^{-1} (chemical map a+) where two layers are highlighted which match the fluorescent layers visible under UV light (Figure C.6 **a1, a2**) likely due to the presence of lake pigments~~.~~ No difference was visible when making a new multichannel analysis (MCA) from the red area of chemical map **a+**.

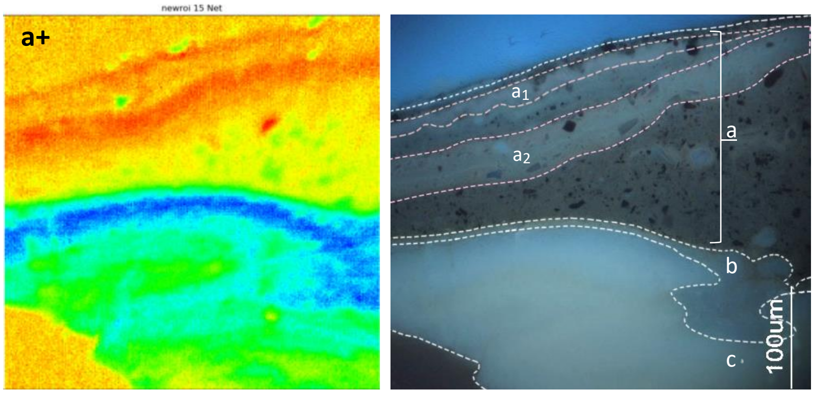


Figure C.6: Left image: Chemical map **a+** of the top layer with highlighted features/layers (intensity from 1506 to 1397 cm^{-1}). Right image: Detail S7 under UV light, in the area of map **i**, with white outline of layers **a, a1, a2,** **b** and **c**.

Two extra chemical maps ($\mathbf{a_{p1}}$, $\mathbf{a_{p2}}$) and respective spectra (**1.1, 1.2**) were obtained for the identifiable particles in the top layer of S7 (Figures C.7 and C.8).

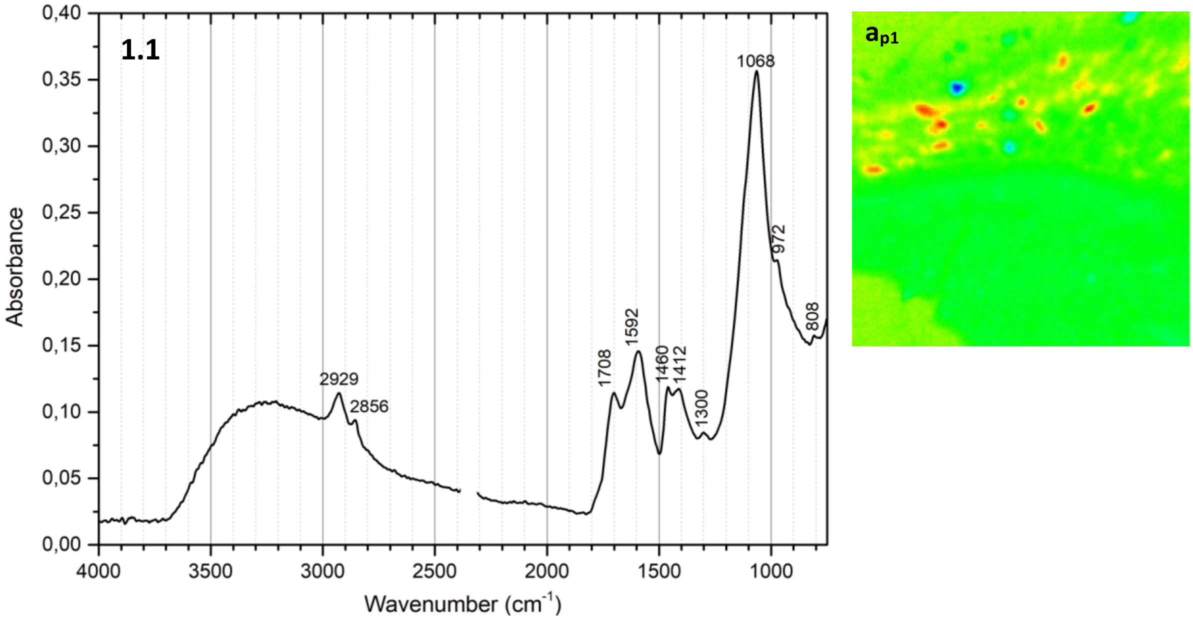


Figure C.7: Spectrum **1.1**, acquired from the maximum values of the chemical map $\mathbf{a_{p1}}$ (intensity from 861 to 1263 cm^{-1}).

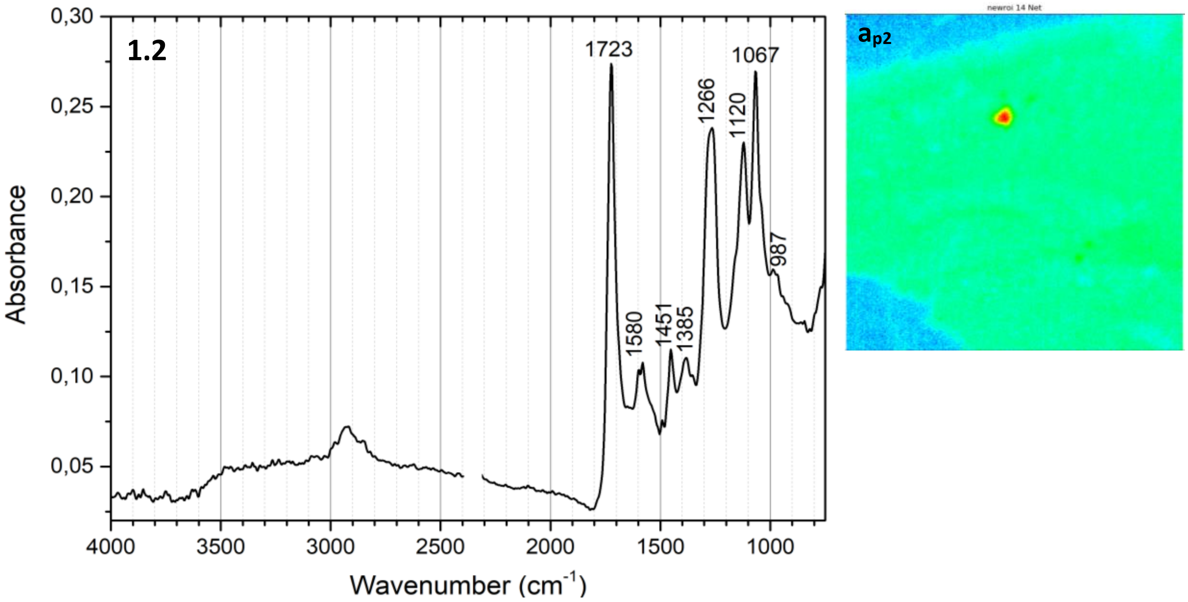
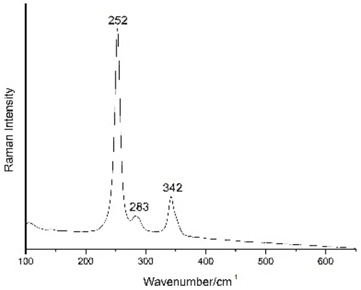
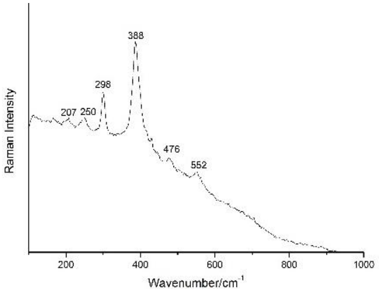
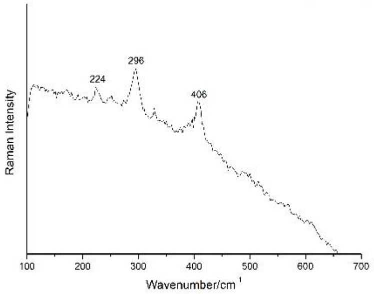
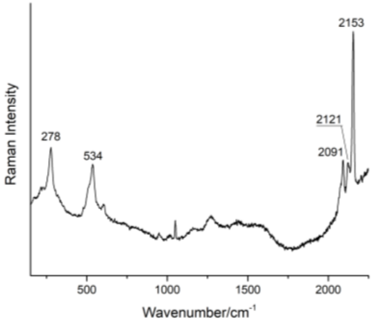
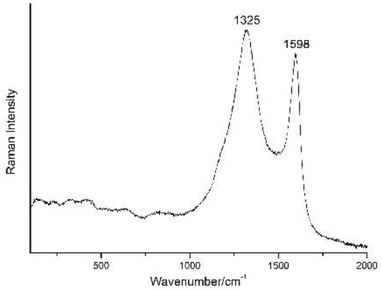
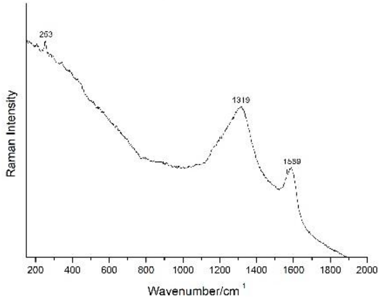


Figure C.8: Spectrum **1.2**, acquired from the maximum values (in red) of the chemical map **a$_{p2}$** (intensity from 1231 to 1321 cm^{-1}).

Kirby et al. identifies the peaks at 1580, 1451 and 1383 cm^{-1} as being characteristic for Sn-containing and Al-containing carmine pigments (Kirby, Spring, and Higgitt 2007). Bands tentatively assigned to an aluminate compound from the pigment’s substrate are the ones at 1120 and 987 cm^{-1} (Kirby, Spring, and Higgitt 2005).

C.7 Pigments and cross-section characterisation results with μ-EDXRF, SEM-EDX and μ-Raman

Spectrum Thumbnail	μ-Raman		SEM-EDX	Interpreted Pigment	In Cross-sections:
	Wavenumber (cm^{-1})*	Assignment**			
	252vs, 283w 342m	δ (S-Hg-S) ν (Hg-S)	Hg, S	Vermilion HgS	S1, S2, S5, S13
	207vw, 250w 298m, 388s 476w 552w	- δ_s (Fe-O) δ_{as} (Fe-O) ν_{as} (Fe-O)	Fe	Goethite α-FeOOH	S4, S8, S10 (middle paint layer), S11 paint layer
	224w, 296vs, 406m	- δ_s (Fe-O)	Fe	Hematite α-Fe_2O_3	S4, S8

	278m 534m 2091s, 2121w, 2153vs	δ (C-Fe-C) δ (Fe-C≡N) ν (C≡N)	Fe	Prussian Blue* $Fe_4[Fe(CN)_6]_3$	S8, S10, S11
 	1325vs (br) 1598vs (br)	*sp*^{3} (C-C) *sp*^{2} (C-C)	C, (P)" "only in some particles	Carbon Black C	S2, S5, S11
-	-	-	Pb, Sb	Naples yellow. Lead antimonate $Pb_2Sb_2O_7$	S24
-	-	-	Co, Al	Cobalt Blue $CoO.Al_2O_3$	S10, S11, S19, S23, S24, S26, S25
-	-	-	Al, S, ◊	Likely Lake Pigments: Red and possibly yellow/brown	All samples

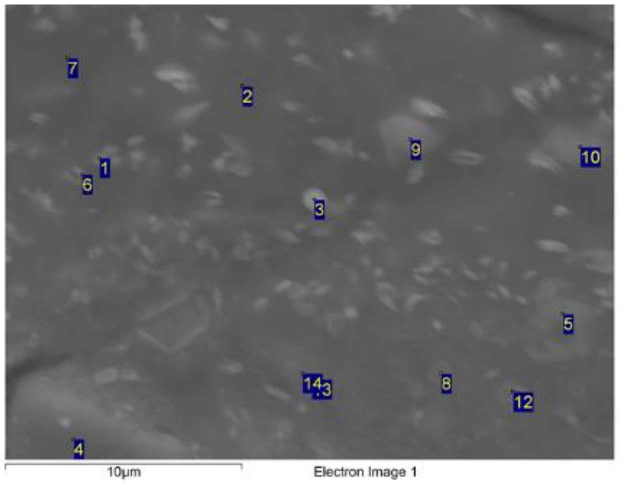
*Also identified with μ-FTIR

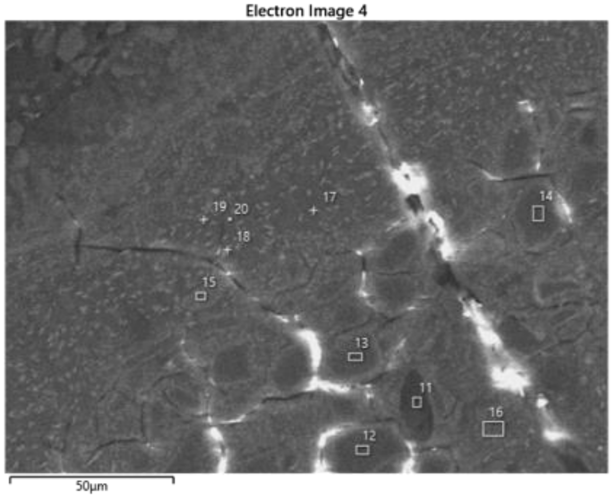
◊ The composition of the trace elements varies according to the particles. See Table in C.8.2 for more SEM-EDX results.

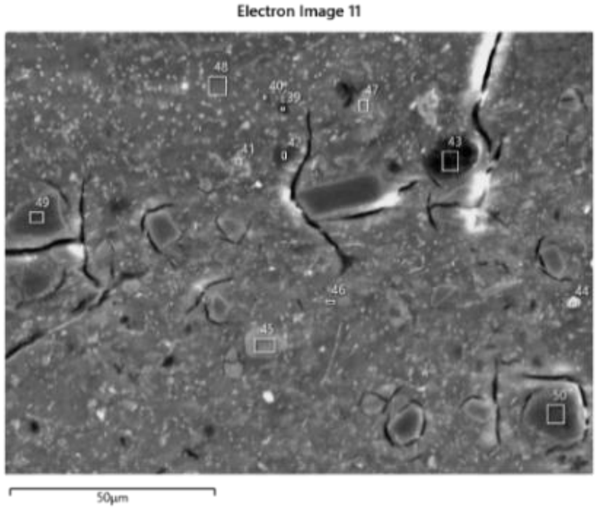
C.8 Analytical results with SEM-EDX: point analyses and EDX mappings (Raw data)

C.8.1 - Lead Drier

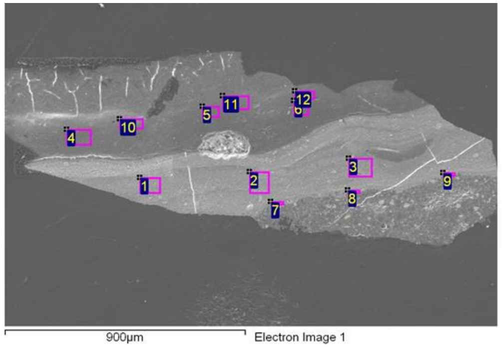
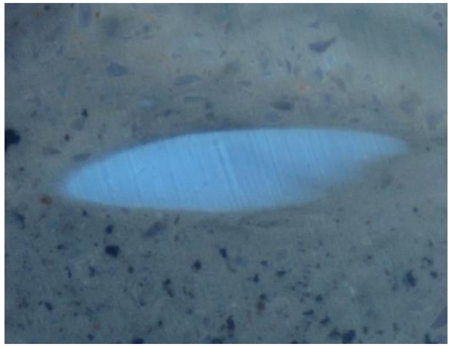
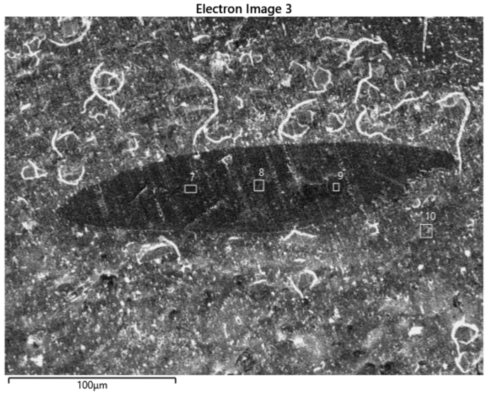
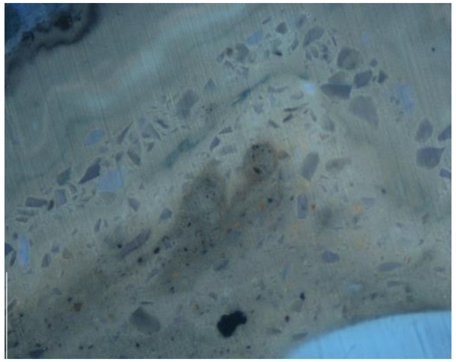
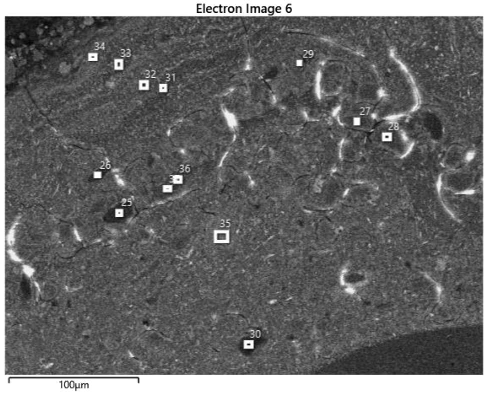
The significant and overall presence of lead in the paint samples was confirmed through SEM analysis, not only as lead white pigment in the ground layers but also in all paint layers visible in the SE images as small dots of opaque material which could not be resolved as pigment particles. This could indicate its use as a siccative compound in the drying oil.

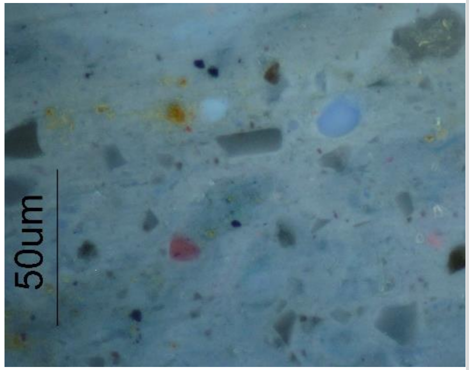
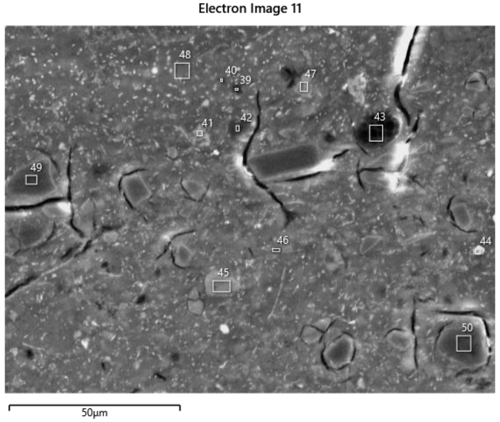
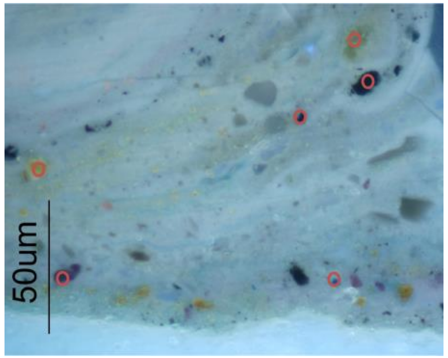
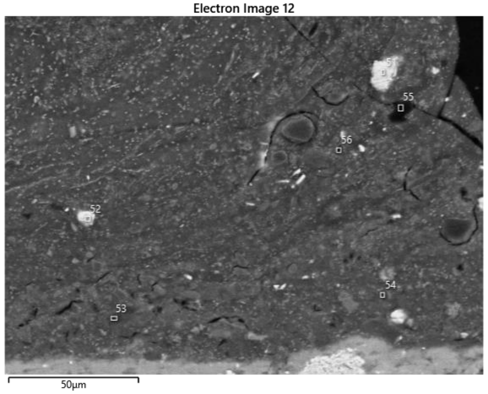


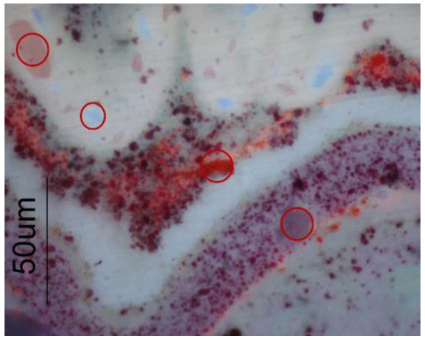
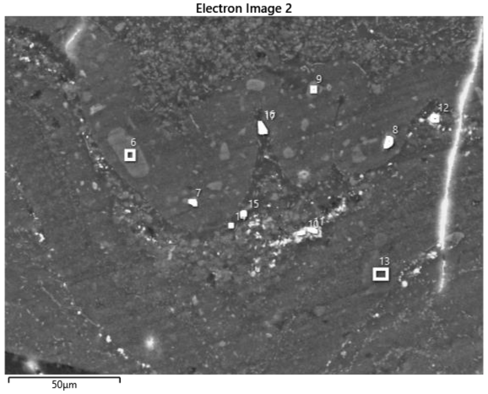
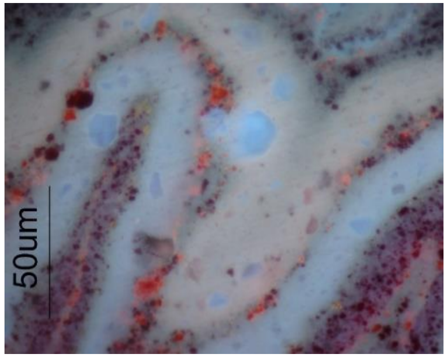
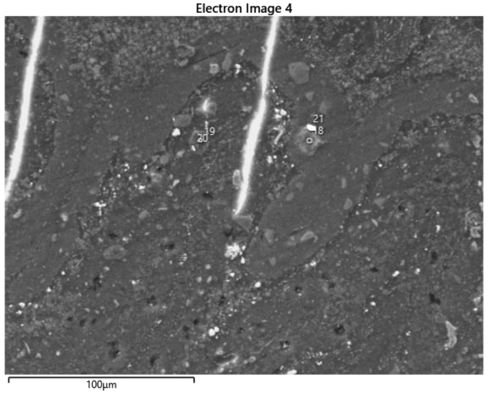
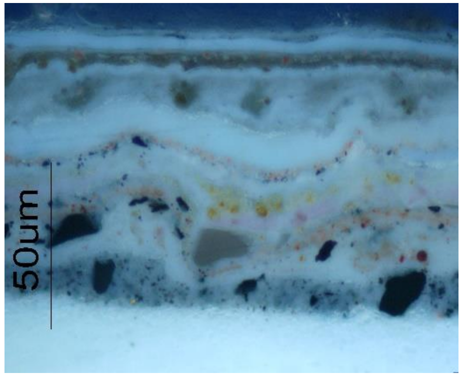
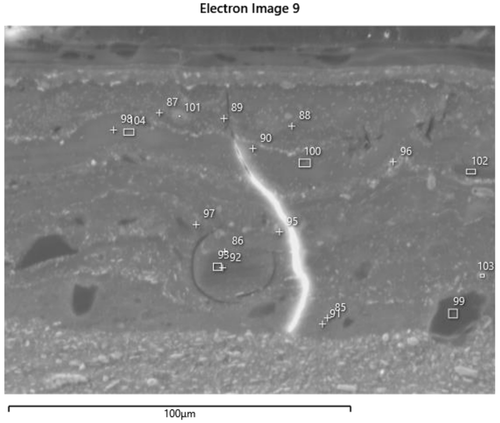


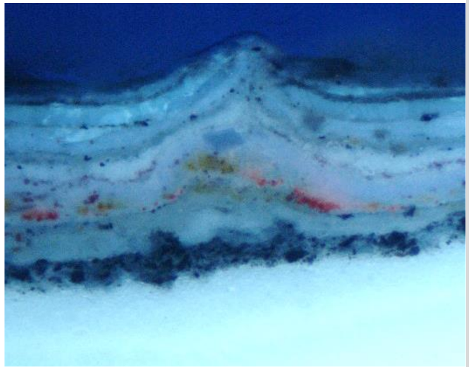
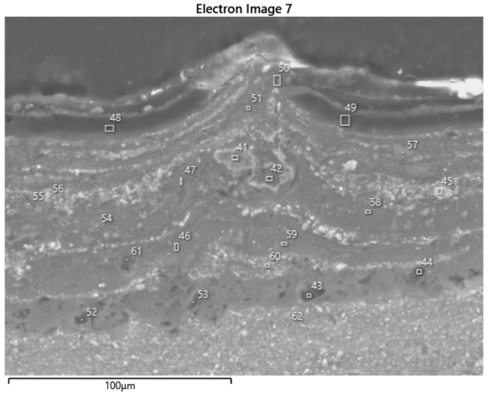


C.8.2 - SEM-EDX point analyses in cross-sections from different colour areas. The points of analyse are marked in the SEM-EDX image and the elementes detected are divided by layers of the painting.

Cross-sections	UV (OM)	SEM-EDX	Elements detected
S10 (Brown paint layer)	-		Paint layers: 4, 5, 6, 10, 11: Al, Pb, Si, Co, (Na), (Fe), (Zn) 12: Al, Pb, Co, Si, Zn, Na, Fe, K, Ca Upper Ground layer: 1, 2, 3: **Pb,** (Cl) Paint layer (between the ground layers): 7, 8, 9: Pb, Al, Fe, Si, (Na)*, (K), (Ca) *only on 7 **For Elemental Mappings see page 297.**
S19 (Brown paint layer			Large fluorescent particle (OM) 7, 8, 9: C, O, N, S, (Pb), (Al) Paint layer: 10: C, O, Al, Pb, S, (Si)
S19 (Brown paint layer			Blue fluorescent particles (OM) 25, 26: C, O, (Pb), (Al), (K) Purplish fluorescent particles (OM) 27, 28, 29: O, C, Al, S, (Si), (K) Black particle 30: C, O, (K), (Ca) Fluorescent top paint layers (OM) 31, 32, 33: C, O, Pb, Al, (K), (Ca) 34: C, O, N, Pb, (Al), (Ca), (K), (Fe), (Na), (Si), (Mg) Paint layer 35: C, O, Pb, Al, (K), (Fe), (Ca) Blue/green fluorescent layer (OM) 36, 37: C, O, Al, Pb, K, (N?), (Na), (Si), (Ca)

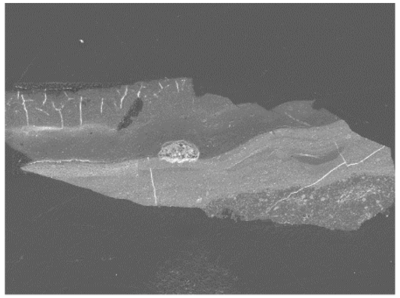
S24 **(Brown paint layer**			Particles dark blue in UV and surrounding paint (OM) 39: C, O, Ca, (Al), (Mg), (Pb), (Co), (Cl), (K) 40: C, O, (Pb), (Al), (K), (Ca), (Fe) 46: C, O, Pb, (Al), (Si), (Fe), (Ca), (K), (P), (Co) Yellow particle (OM) 41: O, C, Fe, (Si), (Pb), (Al), (S), (K), (Ca) White fluorescent particles (OM) 42: C, O, Pb, (Al), (K) Blue fluorescent particles (OM) 43: C, O, Pb, (Al), (K), (Na) Particle (White?) 44: C, O, Pb, (Al) Pink fluorescent particle 45: C, O, Al, S, Pb, (Si), (K) Brown fluorescent particle? 47: C, O, Al, S, Pb, K, (Na) Fluorescent top paint layer 48: C, O, Pb, (Al), (K), (Ca) Grey fluorescent particles 49, 50: O, C, Al, S, (K), (Si), (Pb), (P)
S24 **(Brown paint layer**			Yellow particles (OM) 51, 52: C, O, Pb, Sb Purple fluorescent particle (OM) 53: C, O, Pb, Al Black particle 55: C, O, (Pb), (Si), (Al), (Ca) Black particle with surrounding paint 56: C, O, Pb, Al, Si, (Fe), (Co) Paint layer 54: C, O, Pb, Al, Fe **For Elemental Mappings see page 301.**

S27 (Red paint layer)			Pink fluorescent particle (OM) 6: C, O, Al, S, Pb, (Si), (K) Blue fluorescent particles (OM) 7, 8, 9: C, O, Al, S, Pb, K*, (Si), (Ca) * vestigial in 7 and 9. Red particles (OM) 10, 11, 12: C, O, S, Hg Purplish fluorescent particle (OM) 13: O, C, Al, S, K, (Cu), (Mg), (As) Greenish fluorescent paint layer (OM) 14, 15, 16, 17: C, O, Pb, Al, (Ca), (K), (S), (Zn)
S27 (Red paint layer)			Blue fluorescent particles (OM) 18, 19, 20, 21: C, O, Al, S, K, Pb, (Si), (P*), (Zn**) *only in 18 and 19; **only in 18. Purple fluorescent particle (OM) 27: C, O, Pb, (Al), (Ca), (K), (Zn) Red fluorescent particle (OM) 28: C, S, Hg, O, (As) Pink (?) fluorescent particle (OM) 29: O, C, Si, Al, Na, K, (Fe), (Ca), (Cl), (Mg), (Ti), (Mn) Pink fluorescent particle (OM) 30: C, O, Al, S, Pb, (Si), (K) **For Elemental Mappings see page 303.**
S26 (Flesh tones)			Paint layer with black particles (OM) 85, 91: O, Si, Al, K, Na, Pb, (Ca), (Fe), (Zn) 97: O, Si, (Pb), (Al), (Fe), (Zn) Black particle: 99: C, O, Pb, (Ca), (K), (Zn) Grey fluorescent particles 86, 92, 93: O, Al, S, Na, Cl*, (Si), (Pb), (K), (P**), (Ca), (P), (K***), (Zn) | *only on 88 **only on 87 *** except on 87. Blue/grey fluorescent paint layer (OM) 87, 88, 89: O, Al, Pb, Co, Si, (Fe), (Zn) Blue fluorescent paint layer (OM) 90, 100: O, Pb, Al, Cl*, Na*, (Si), (K*), (Ca), (Zn) *only on 100 98, 104: O, Pb, Al, (Zn), (Fe) Orange particles (OM) 95, 101: O, Fe, As*, Si, Pb, Al, (Cl), (Co*), (Mn*), (Zn) *only on 101

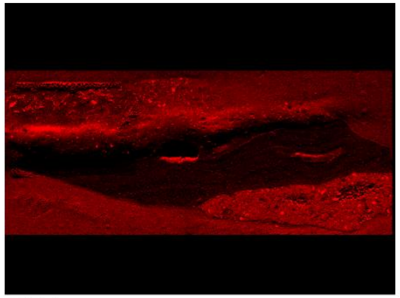
			Red particle (OM) 96: O, S, Hg, Al, Pb, K, (Fe) Blue fluorescent particle (OM) 102: O, Pb, Cl, S, Ca, Al, (Mg), (Si), (K), (Zn), (Fe) Dark red fluorescent particle (OM) 103: O, Fe, Si, Pb, (Al), (Zn)
S15 **(White paint layer)**			Blue fluorescent particle and transparent particle (OM) 41, 42: O, K, S, Al, Na, Pb, (Si) Black particles 43, 44, 52, 53: C, O, Al*, Pb, Ca, Si, (K*), (Zn) | *only in 43 White particles (OM) 45, 56, 60, 62: O, Pb Greyish flourescent paint layer (OM) 46, 59: O, Pb, Si, Al, Fe, Na, Sb*, (Zn) *only in 46 61: Pb, Si, Al, Fe, (Zn) Grey fluorescent particle (OM) 57: O, Si, Ca, Al, Pb, P, S, Fe, Mg, (K), (Na), (Zn)? Light purple flourescent paint layer (OM) 47, 58: O, Al, Pb, S, K, Na*, (Cl*), (Si), (Ca), (Zn) *only on 47 Blue fluorescent layer (OM) 48, 49: O, Na, Pb, K, Si*, Ca, (Zn*)?, (Cl**), (Fe**) *only on 48 **only on 49 Fluorescent paint layer (OM) 50: O, Pb, Ca, Al, K, Na, Cl, Si, (Mg), (S), (Fe) 51: O, Pb, Al, Cl, Si, Ca, Na, K, (Co), (Fe), (Zn)? Purple fluorescent particles (OM) 54, 55: O, Pb, Al, Ca*, K*, (Zn), (Fe*) | *only on 54 **For Elemental Mappings see page 304.**

C.8.3 - SEM-EDX elemental mappings of cross-sections from different colour areas.

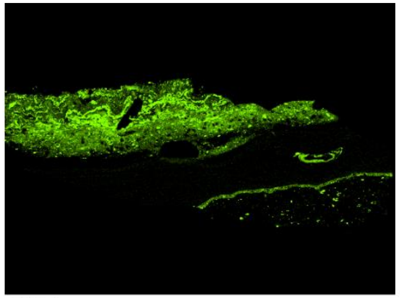
- **S10 - brown paint layer**



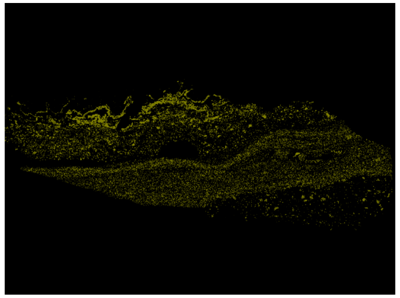
900µm Electron Image 1



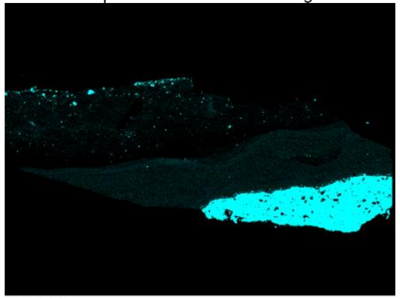
O Ka1



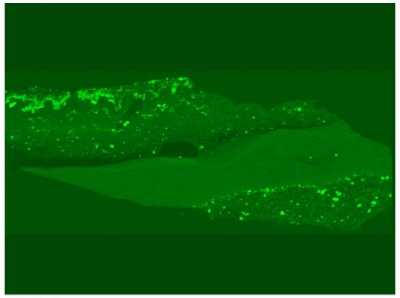
Al Ka1



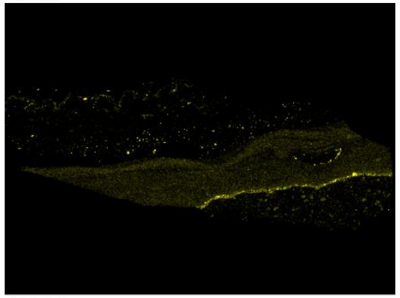
Co Ka1



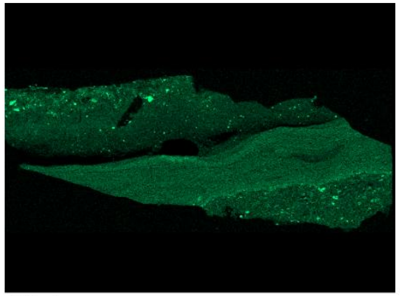
Ca Ka1



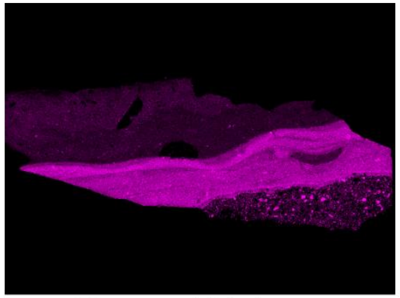
Si Ka1



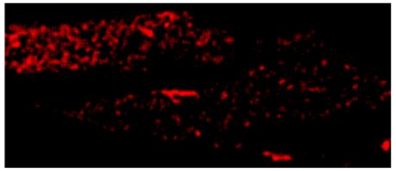
Fe Ka1



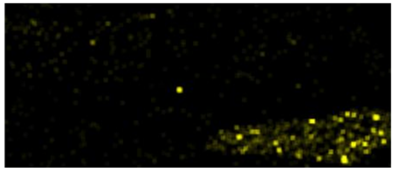
K Ka1



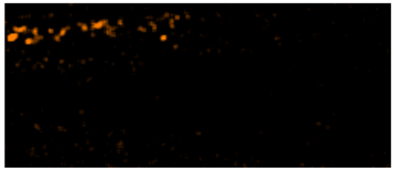
900µm Pb La1



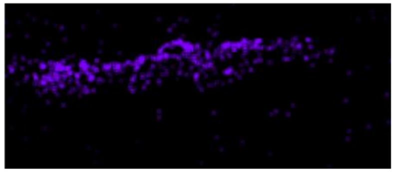
500µm **Cl K series**



500µm **Mg K series**

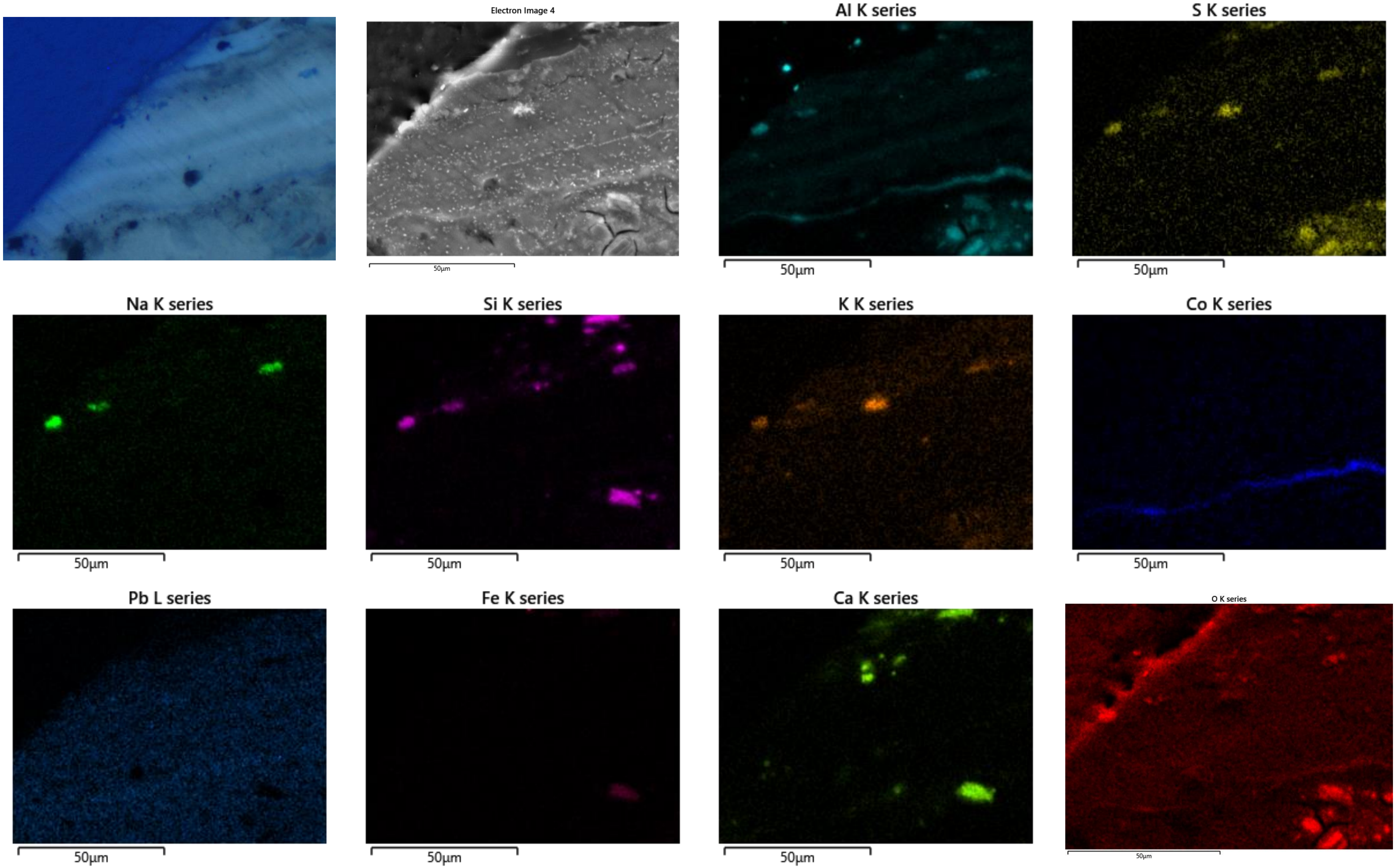


500µm **Na K series**

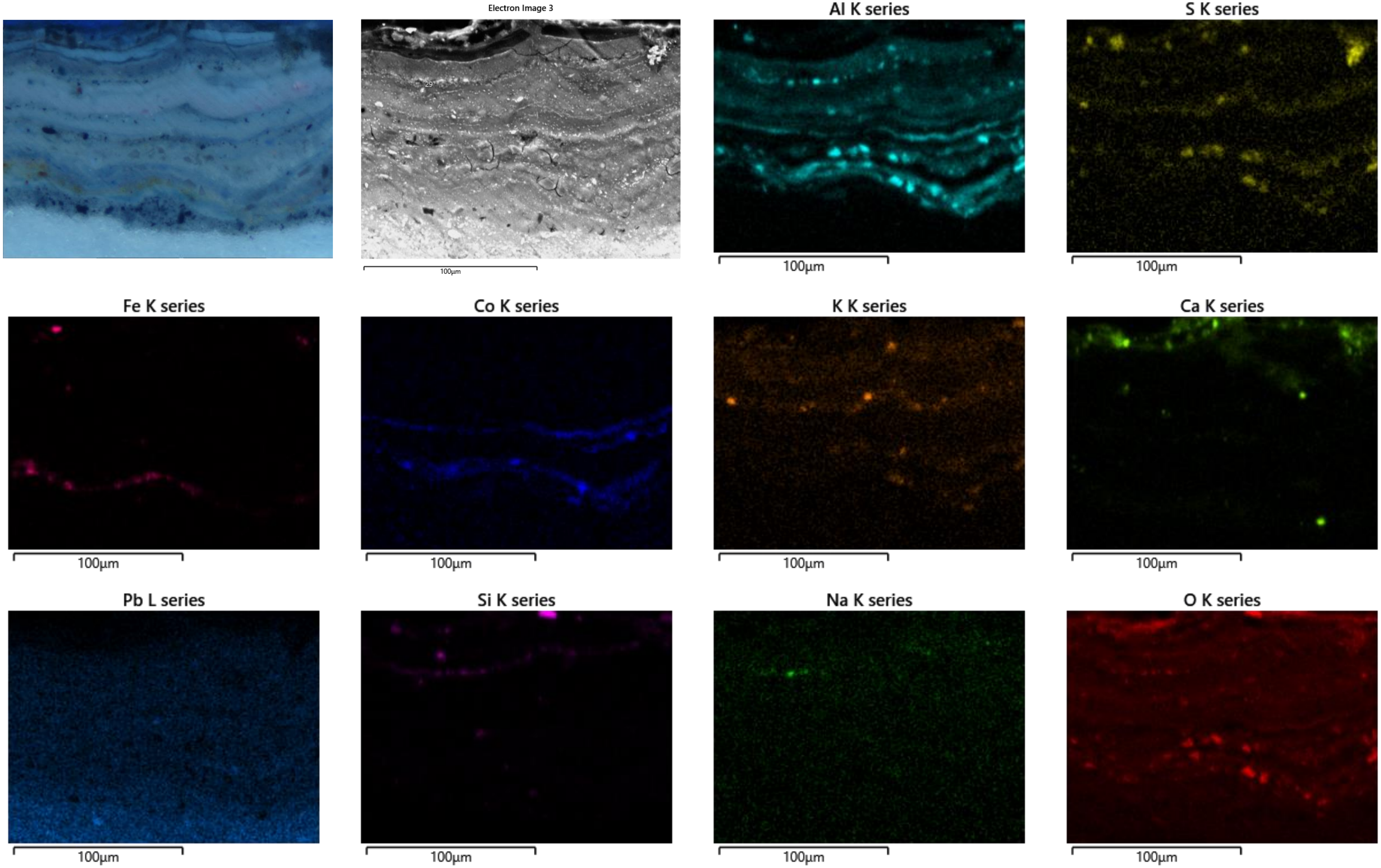


500µm **Zn K series**

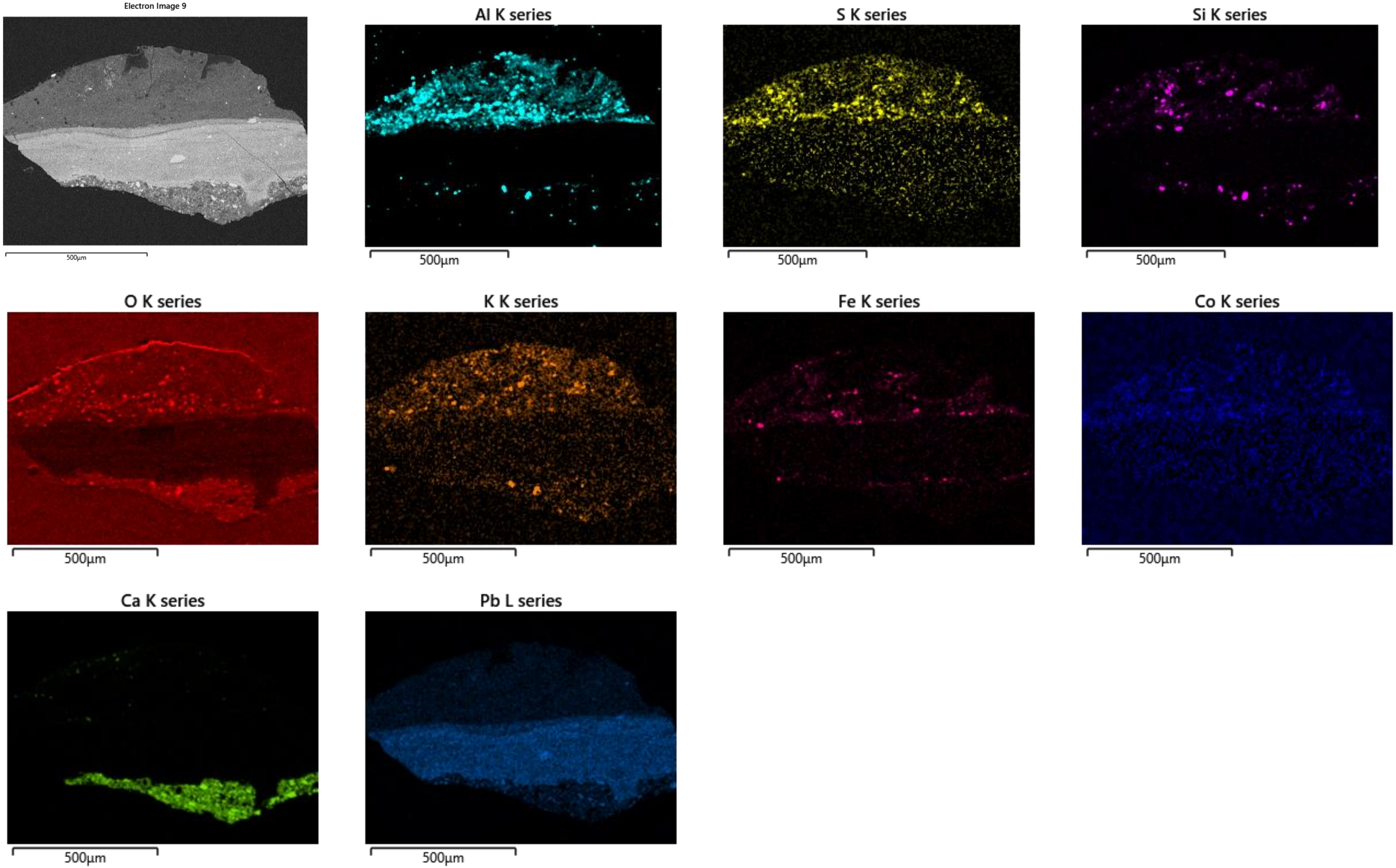
- **S23 - brown paint layer**



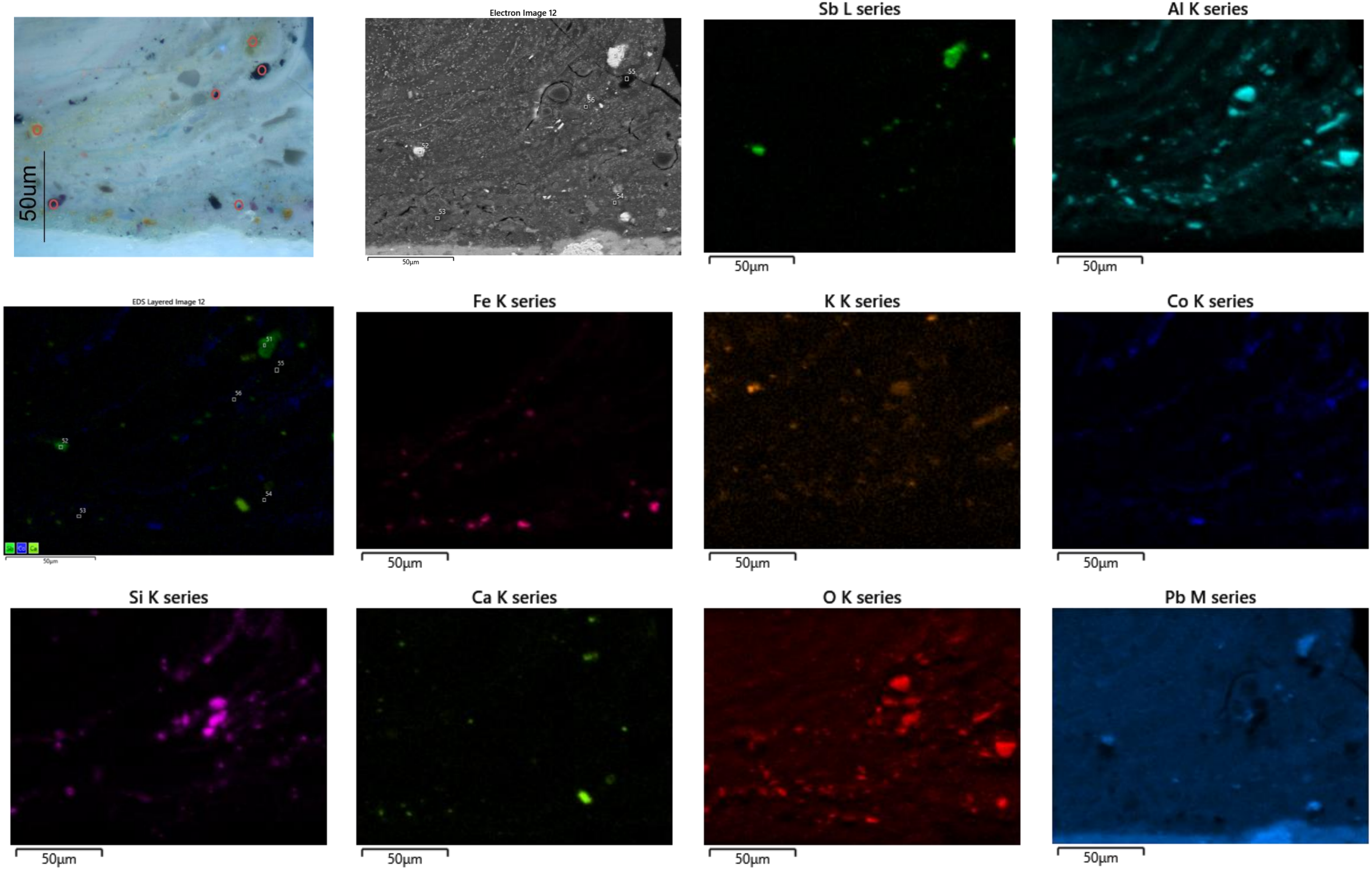
- **S23 - brown paint layer**



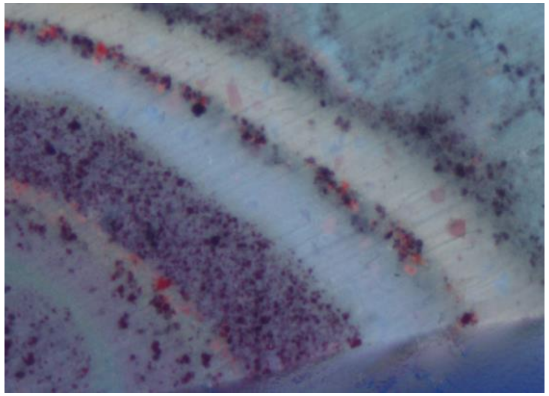
- **S24 - brown paint layer**



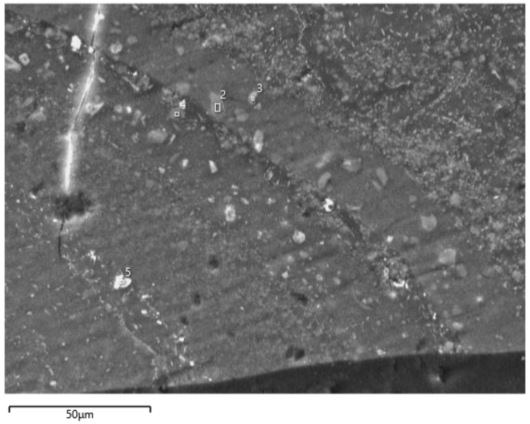
- **S24 - brown paint layer (detail)**



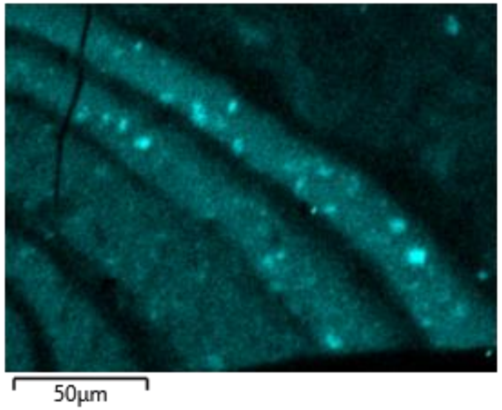
- **S27 - red paint layer (detail)**



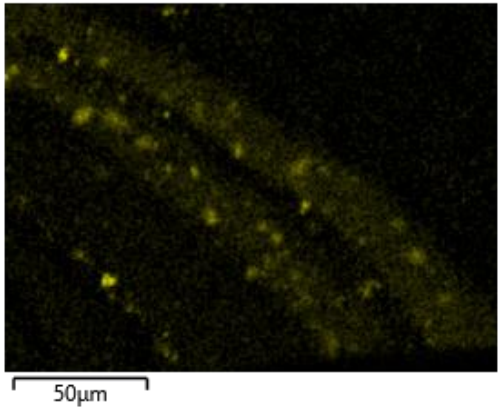
Electron Image 1



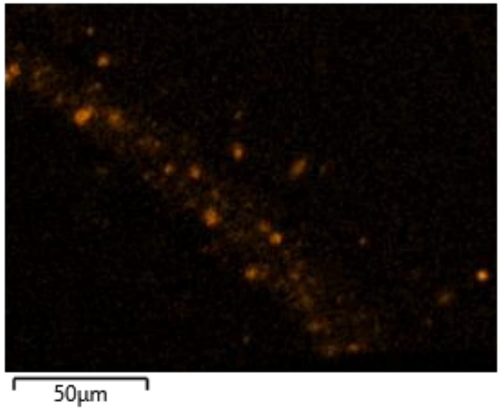
Al K series



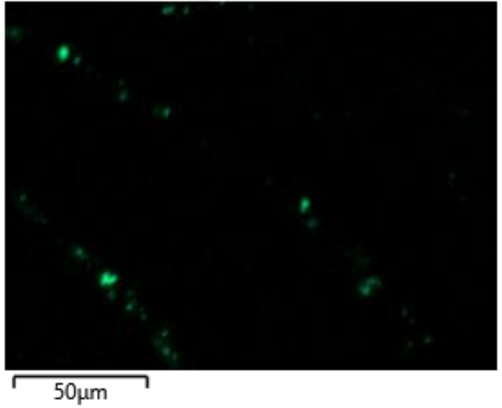
S K series



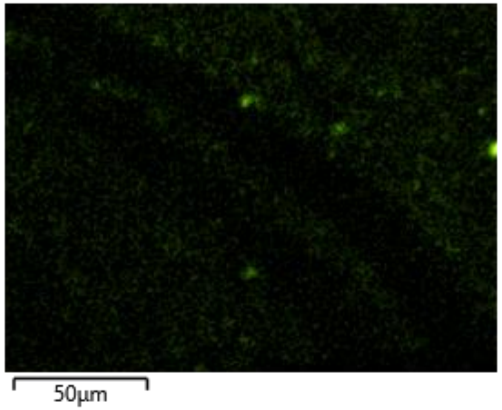
K K series



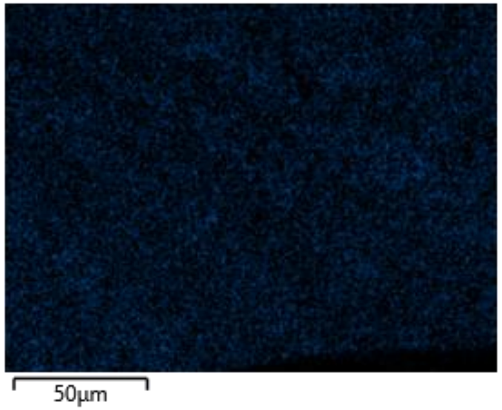
Hg M series



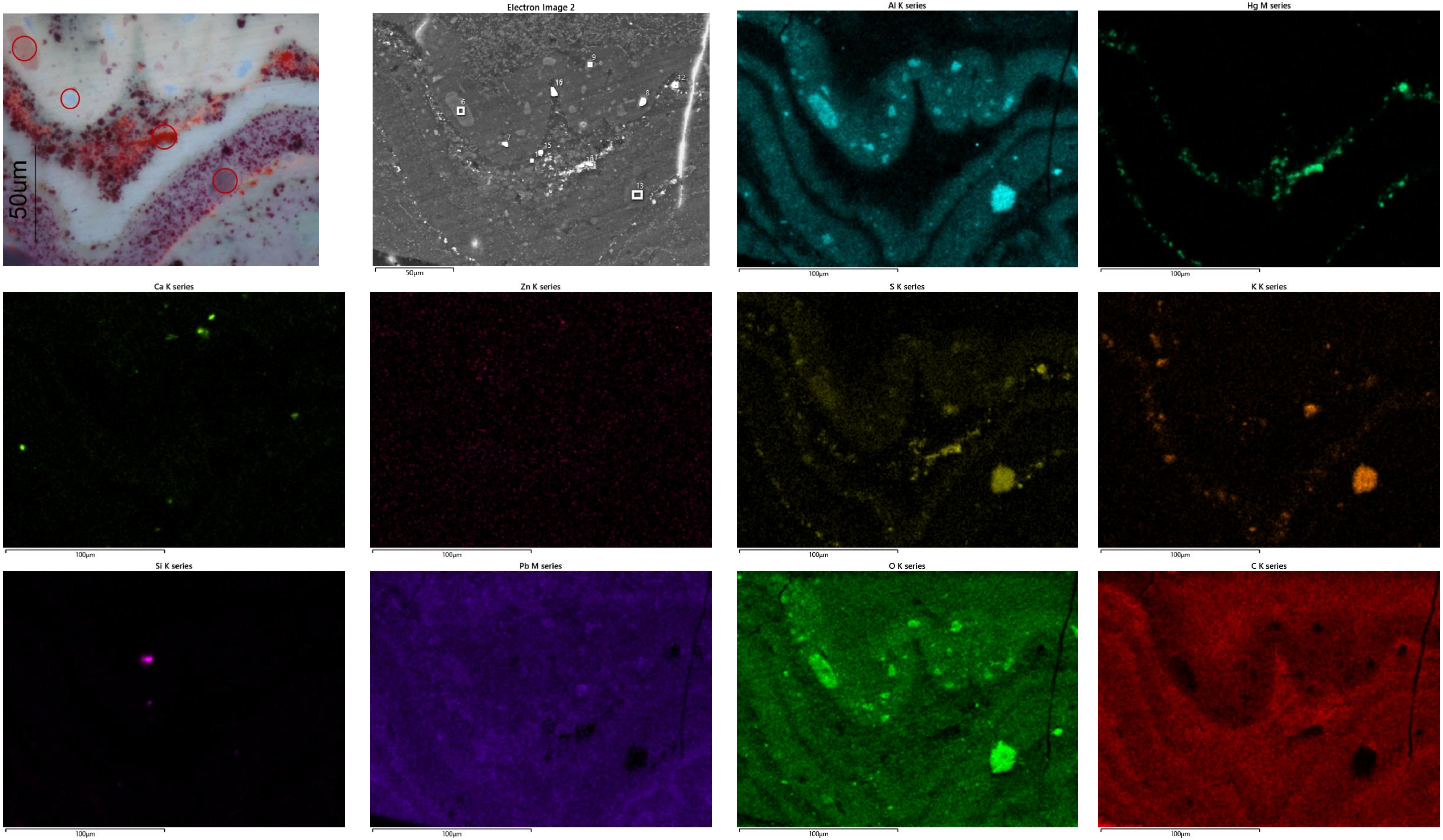
Ca K series



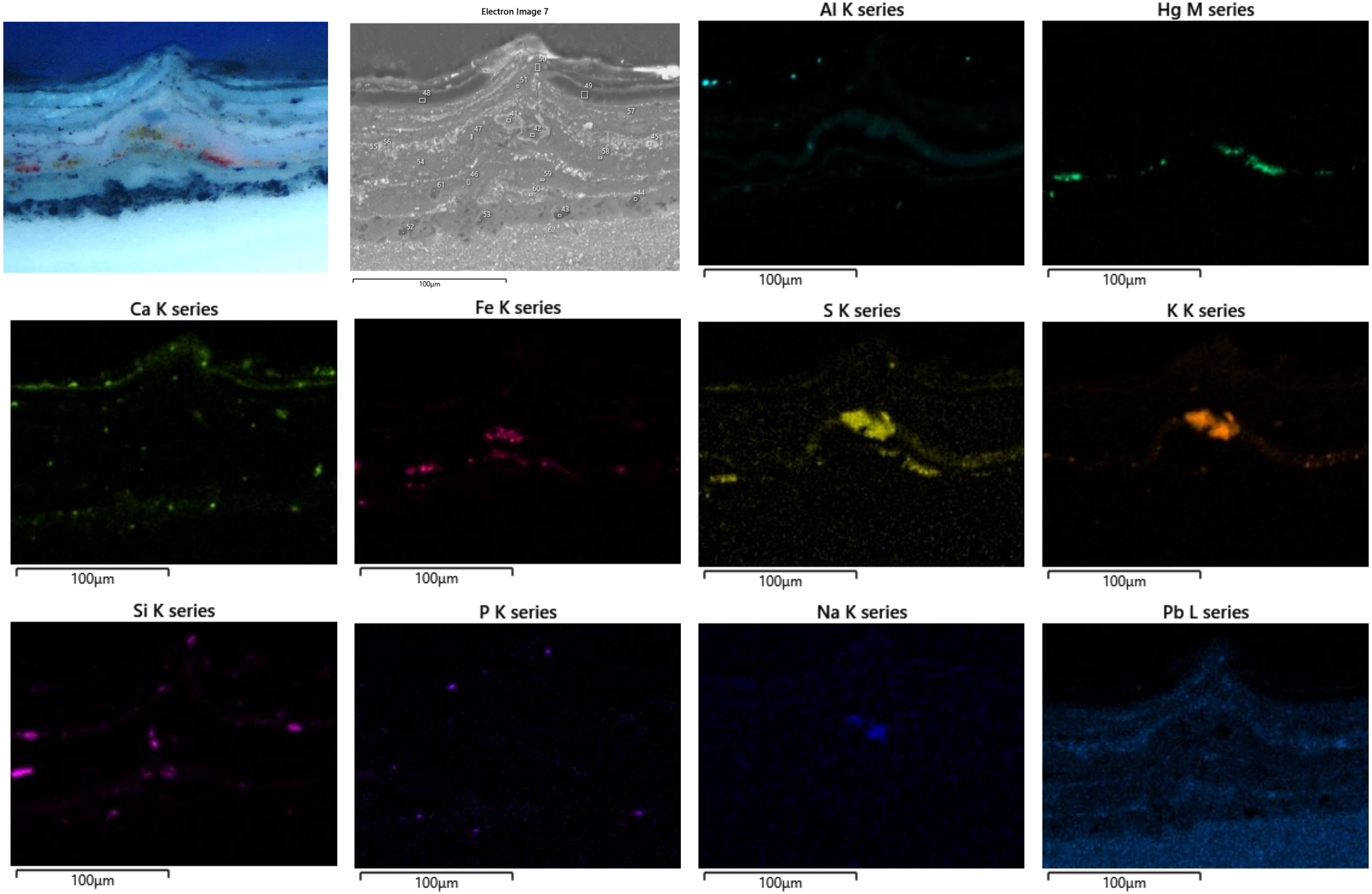
Pb L series



- **S27 - red paint layer (detail)**



- **S15 White paint layer (detail)**



C.9 Py-TMAH-GC/MS micro-samples and results

Table C.8: Identification of the samples codes, colour or paint layer and sampling location.

Sample Code	Colour/Paint Layer	Location*, **
Py1	Brown paint	T. 18.25 cm; L.S. 46 cm
Py2	Brown bead & glossy exudate	Same area as Py1
Py3	Brown soft exudate	T. 3.5 cm; R.S. 11.7 cm
Py4	Red soft & glossy exudate	B. 38 cm; R.S. 7.9 cm
Py5	Red paint (island)	Same area as Py4
Py6	"Translucent layer"	T. 60.3 cm; R.S. 8.9 cm
Py7	Ground Layer	T. 18 cm; L.S. 31.5 cm

* T. = Top; B. = Bottom; L.S. = Left Side; R.S. = Right Side.

** All measurements were made to the edge of the painting, not the edge of the side and bottom bars.

Table C.9: Presence (✓) or absence (-) of the identified Fatty Acids, Diacids and Glycerol derivatives in the samples.

RT (min)	Label	Compound	M.W.	Samples						
				Py1	Py2	Py3	Py4	Py5	Py6	Py7
1.47	C3F	Propanoic acid, methyl ester	88	✓	✓	✓	✓	✓	✓	✓
2.10	C4F	Butanoic acid, methyl ester	102	✓	✓	✓	✓	✓	✓	✓
2.68	C5F	Pentanoic acid, methyl ester	116	✓	✓	✓	✓	✓	✓	✓
2.97	1,3mx gly	1,3-dimethoxy-2-propanol	120	✓	✓	✓	✓	✓	✓	✓
3.05	1,2,3 mx gly	1,2,3-trimethoxy-propane	134	✓	✓	✓	✓	✓	✓	✓
3.11	2,3 mx gly	2,3-dimethoxy-1-propanol	120	✓	✓	✓	✓	✓	✓	✓
3.14	C6:1F	5-Hexenoic acid, methyl ester	128	✓	✓	✓	✓	✓	-	-
3.21	C6F	Hexanoic acid, methyl ester	130	✓	✓	✓	✓	✓	✓	✓
3.71	C7:1F	6-Heptenoic acid, methyl ester	142	✓	✓	✓	✓	✓	✓	✓
3.75	C7F	Heptanoic acid, methyl ester	144	✓	✓	✓	✓	✓	✓	✓
3.80	C4DF	Butanedioic acid, dimethyl ester	146	✓	✓	✓	✓	✓	✓	✓
4.40	C8F	Octanoic acid, methyl ester	158	✓	✓	✓	✓	✓	✓	✓
4.48	C5DF	Pentanedioic acid, dimethyl ester	160	✓	✓	✓	✓	✓	✓	✓
5.08	C9:1F	8-Nonenoic acid, methyl ester	170	✓	✓	✓	✓	✓	-	✓
5.15	C9F	Nonanoic acid, methyl ester	172	✓	✓	✓	✓	✓	✓	✓
5.28	C6DF	Hexanedioic acid, dimethyl ester	174	✓	✓	✓	✓	✓	✓	✓
5.96	C10F	Decanoic acid, methyl ester	186	✓	✓	✓	✓	✓	✓	✓
6.13	C7DF	Heptanedioic acid, dimethyl ester	188	✓	✓	✓	✓	✓	✓	✓
6.18	8-Mx-C8F	8-methoxy-octanoic acid, methyl ester	188	✓	✓	✓	✓	✓	✓	✓
6.60	8-OH-C8F	8-hydroxy-octanoic acid, methyl ester	174	✓	✓	-	✓	✓	-	✓

6.81	C11F	Undecanoic acid, methyl ester	200	✓	✓	-	-	-	-	✓
7.00	C8DF	Octanedioic acid, dimethyl ester	202	✓	✓	✓	✓	✓	✓	✓
7.66	C12F	Dodecanoic acid, methyl ester	214	✓	✓	-	✓	✓	✓	✓
7.89	C9DF	Nonanedioic acid, dimethyl ester	216	✓	✓	✓	✓	✓	✓	✓
8.48	IS/C13F	Tridecanoic acid, methyl ester	228	✓	✓	✓	✓	✓	✓	✓
8.67	C10DF	Decanedioic acid, dimethyl ester	230	✓	✓	✓	✓	✓	✓	✓
9.27	C14F	Tetradecanoic acid, methyl ester	242	✓	✓	✓	✓	✓	✓	✓
9.45	C11DF	Undecanedioic acid, dimethyl ester	244	✓	✓	✓	✓	✓	✓	✓
9.60	2-Mx-C10DF	2-methoxy-decanedioic acid, dimethyl ester	260	✓	✓	✓	✓	✓	✓	✓
10.05	C15F	Pentadecanoic acid, methyl ester	256	✓	✓	✓	✓	✓	✓	✓
10.21	C12DF	Dodecanedioic acid, dimethyl ester	258	✓	✓	✓	✓	✓	✓	✓
10.34	2-Mx-C11DF	2-methoxy-undecanedioic acid, dimethyl ester	274	✓	✓	-	✓	✓	✓	✓
10.76	P/C16F	Hexadecanoic acid, methyl ester	270	✓	✓	✓	✓	✓	✓	✓
10.93	C13DF	Tridecanedioic acid, dimethyl ester	272	✓	✓	✓	✓	✓	✓	✓
11.46	C17F	Heptadecanoic acid, methyl ester	284	✓	✓	✓	✓	✓	✓	✓
11.95	C18:2	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	294	-	-	-	-	-	-	-
11.96	C18:1	9-Octadecenoic acid, methyl ester (Z)-	296	✓	✓	✓	✓	✓	✓	✓
12.13	S/C18F	Octadecanoic acid, methyl ester	298	✓	✓	✓	✓	✓	✓	✓
12.29	C16DF	Hexadecanedioic acid, dimethyl ester	314	✓	✓	-	✓	-	-	-
13.10	9,10-epoxy-C18F	9,10-epoxy-octadecanoic acid, methyl ester	312	✓	✓	✓	✓	✓	✓	✓
13.38	C20F	Eicosanoic acid, methyl ester	326	✓	✓	✓	✓	✓	✓	✓
13.50	9,10-diMx-C18F	9,10-dimethoxy-octadecanoic acid, methyl ester	358	✓	✓	✓	✓	✓	✓	✓
13.90	9,10-diOH-C18F	9,10-dihydroxy-octadecanoic acid, methyl ester	330	✓	✓	✓	✓	✓	✓	✓
14.68	C22F	Docosanoic acid, methyl ester	354	✓	✓	✓	✓	✓	✓	✓
15.41	C23F	Tricosanoic acid, methyl ester	368	-	✓	✓	-	✓	✓	-
16.19	C24F	Tetracosanoic acid, methyl ester	382	✓	✓	✓	✓	✓	✓	✓
17.00	C25F	Pentacosanoic acid, methyl ester	396	-	✓	-	-	-	-	✓
17.85	C26F	Hexacosanoic acid, methyl ester	410	✓	✓	✓	-	✓	✓	✓
18.48	C27F	Heptacosanoic acid, methyl ester	424	-	-	-	-	-	-	-

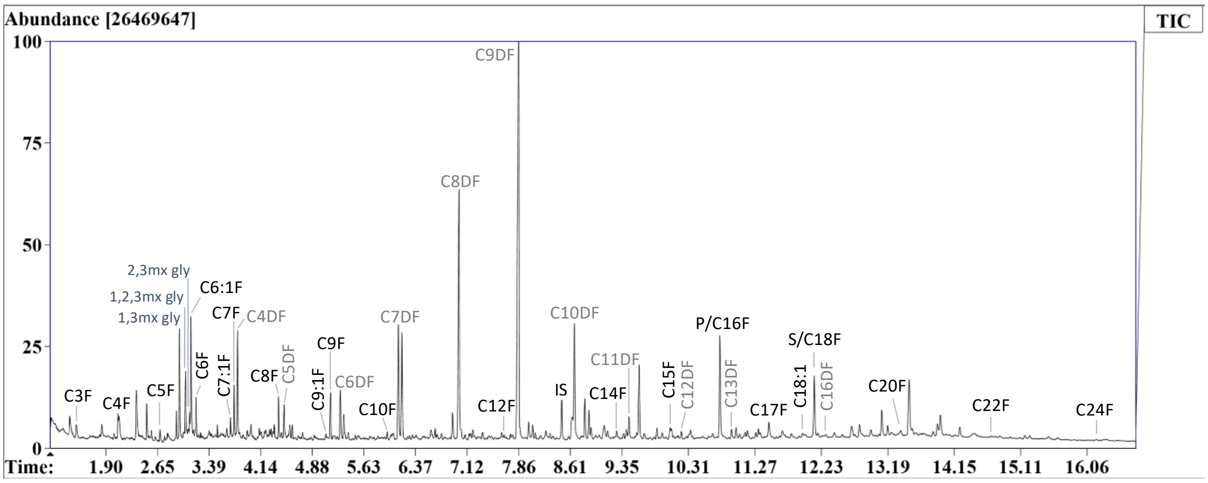


Figure C.9: Total ion chromatogram of Py4 (red paint, shinny exudate), sample derivatized with TMAH. "F" stands for fatty acids while "DF" for diacids, and "mx gly" identifies the glycerol derivatives

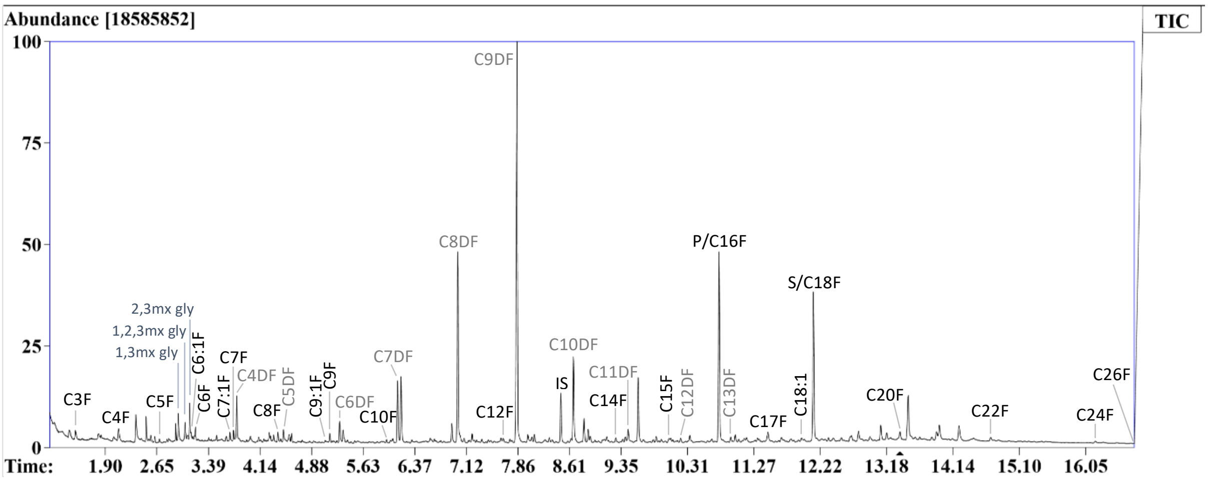


Figure C.10: Total ion chromatogram of Py5 (red paint), sample derivatized with TMAH. "F" stands for fatty acids while "DF" for diacids, and "mx gly" identifies the glycerol derivatives.

D

Appendix to Chapter 4

W&N's production records for *Bitumen* oil paint

Table D.1: W&N's production records for Bitumen, from 1834 to 1846, summary of ingredients and quantities.

Code	Date		Name	Asphaltum	Bitumen	Drying Oil	Linseed Oil	Boiled Oil	Japan Gold Size	Baker's Black Japan	Sugar of Lead	Burnt Copperas	Litharge	Red Lead	Venice Turpentine	Turps	Venice Turpentine	Gum Mastic	Double Mastic Varnish	Baker's Carriage Varnish	Shell Lac	Dragon's Blood	White Wax	Beeswax	Megilp
				*lbs	lbs	pt	pt	pt	pt	gall	oz	oz	oz	oz	oz	pt	oz	oz	pt	pt	oz	oz	oz	oz	
HSP034	1834	13/oct	French Bitumen	1,88		5lbs		1							5		5	6			20	3			
V1P368	1844	18/jul	Bitumen	4		3			1			2				4							8		
V1P306	1844	Dez	Bitumen Exp^t A	1			0,5		0,19			0,5				0,75							2		
V1P307	1844		Bitumen Exp^t B	1		0,25			1							0,75			0,25				2		
V1P305	1844		Bitumen C	1		1,5						1				0,5			1,25			0,5			
V1P303	1844	30/dez	Bitumen D	1	2,2	0,5			1			1				0,75			1,5			1			
V1P290	1845	22/jan	Bitumen E	1		1,5				1										1		2			✓
V1P286	1845	Fev	Bitumen F	2		1,5				1,5									1,5			2			✓
V1P256	1845	01/jul	Alteration of Bitumen		25 pt	3																		8	
V1P237	1845	27/oct	Alteration of Bitumen		39	4,5																		16	
V1P199	1846	02/mar	Bitumen	2		3				1,5									3			4		16	
V1P195	1846	3/apr	Small Batch Bitumen	0,5			1		0,5		0,5		1,5	1,5								4	3		
V1P194	1846	26/apr	Small Batch Bitumen	0,5			1,5				0,5		1	1								8			

* lbs = Pounds; pt = Pints; gall = gallon; oz = ounces

Table D.2: W&N’s production records for Bitumen, from 1850 to 1858, summary of ingredients and batch quantities.

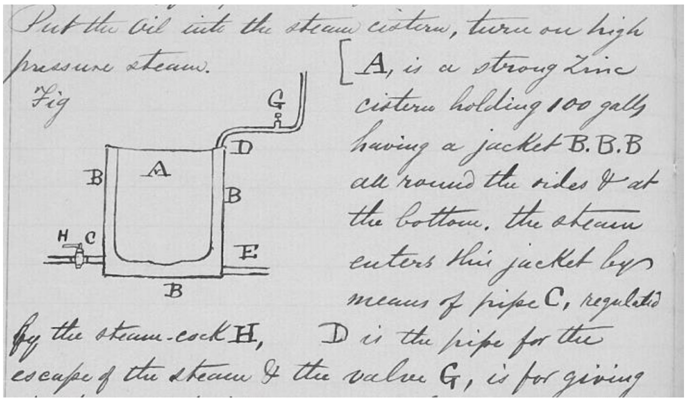
				Asphaltum	Drying Oil	Double Mastic Varnish	Sugar of Lead	Purple Lake	Turpentine (Turps)	R's Old Stout Asphaltum	Megilp
Code	**Date**		**Name**	Pounds	Gallons	Gallons	Pounds	Pounds	Pint	Gallons	
V1P074	1850	24/apr	Bitumen for Tubes (x6)	24	6	4,5	3	1,1	6		✓
				4	**1**	**0,75**	**0,5**	**0,2**	**1**		
V1P052	1851	11/mar	Bitumen	**4**	**1**	**1**	**2**	**0,3**	**1**		
V2P261	1853	August	Bitumen for Tubes	32	8	8	12	1,5	8		✓
X6P139	1853	14/nov	Bitumen	32	8	8	16	3	1		
V2P354	1855	27/mar	Bitumen [for tubes]	32	8	8	12	2,8	8		
V2P403	1855	27/oct	Bitumen	32	8	8	12	3	8		✓?
V2P465	1857		[Bitumen] 1st Batch	**4**	**1**	**0,75**	**1**	**0,4**	**1,25**		
P1P277A*	1857	March	Bitumen for Oil Tubes	32	9	8	6	3	0,25	6	✓
X7P086	1857	March	Bitumen for Oil Tubes (x8)	32	9	8	6	3		6	✓
				4	**1,13**	**1**	**1**	**0,6**	**1**	**0,75**	
V2P493	1858	24/aug	Bitumen	**4**	**1,25**	**1**	**0,5**	**0,5**	**1**		✓
V2P498A*	1858	25/sept	Bitumen	48	15	9	6	6	12		✓
P2P115A	1858	Sept	Bitumen (x12)	48	15	9	6	6	12		✓
				4	**1,25**	**0,75**	**0,5**	**0,5**	**1**		

* Records repeated

W&N’s products used in their *Bitumen* formulation

D.1 Strong Drying Oil

In W&N's archive, of 128 references to “drying oil” between 1844 and 1926, only 16 records specify “Strong Drying Oil” (1844 to 1859). After 1845 records are consistent in calling for both red lead (lead tetroxide) and litharge (lead (II) oxide), see Table D.3. In the last detailed record for *Strong Drying Oil* (1854, X6P285), equal parts of powdered red lead and litharge were mixed together dry, then added to the “Best Raw Linseed Oil” previously heated to 200°F (93°C) in a steam apparatus (Figure D.1). Heat was maintained and the mixture stirred continuously (for “10 hours” P1P327A). Large amounts were made at once: 50 lbs (22.7 kg) of the combined driers were added to 50 gallons (227 L) of linseed oil. The next day the final product was drawn off with the sediments left behind: “the bright oil was [a] very limpid, beautiful rich amber tint, not very dark for strong drying oil…” (X6P285).



Put the Oil into the steam cistern, turn on high
pressure steam. [A, is a strong Zinc
cistern holding 100 galls
having a jacket B.B.B
all round the sides & at
the bottom, the steam
enters this jacket by
means of pipe C, regulated
by the steam-cock H, D is the pipe for the
escape of the steam & the valve G, is for giving

Figure D.1: Illustration of a “Steam Cistern” from W&N record P2P124A.

Table D.3: Ingredients in W&N's *Strong Drying Oil*. (The record highlighted in blue was used in the reconstruction, see Chapter 5).

				Oil	**Linseed Oil**	**Litharge**	**Red Lead**	**White Lead**	**Lead**
Code	**Date**		**Name**	Gallons	Gallons	Pounds	Pounds	Pounds	Pounds
03P015	MS: 1844		Strong Drying Oil (for shop use)	10				5	
V1P366	1844	12/July	Strong Drying Oil for Shop		4			2	
V1P240	1845	27/Sept	Strong Drying Oil		10	1		5	
V1P244	1845	30/July	Strong Drying Oil (shop)	10*		*		5	
V1P262	1845	19/March	Strong Drying Oil		0.75 (3 Qts)		0.047 (¾ oz)		
V1P269	1845	21/March	Strong Drying Oil Experiment		0.75 (3 Qts)				0.094 (1½ oz) [i]
V1P270	1845	18/March	Experiment Strong Drying Oil		0.75 (3 Qts)		0.094 (1½ oz)		
V2P181	1853	3/Jan	Strong Drying Oil for R P	**					
V2P224	1853	25/May	Drying Oil (very strong & glossy)		40	10	20		
P2P136A	1853	22/Sept	Strong Drying Oil		40	15	30		
P1P327A	MS: 1846-58		Strong Drying Oil		50	25	25		
X6P285	1854	7/Feb	A Strong Drying Oil		50	25	25		
V2P440	1856	Aug	Strong Drying Oil	N&H - recipe and quantities not specified ***					
V2P476	1857	24/Dec	Strong Drying Oil						
V2P527	1859	14/July	Strong Drying Oil						

* The oil used had been boiled with Litharge, to obtain a "rich pale colour"

[i] "calcinated Dry Lead"

** Two sorts of Pale Drying Oil are used: "a considerable portion of the [Dk] Pale Dg Oil done June 17/52 - & a smaller portion of a paler kind of oil done Augt 16/52".

*** W&N purchased Strong Drying Oil from Nobles & Hoare from 1854-1859 which they used in their *Bitumen* formulation.

D.2 Burnt Sugar of Lead

The majority of records for *Bitumen* from the 1850s call for *Burnt Sugar of Lead* ground in oil (Table D.4). The 19 records found for “Sugar of Lead”[171] consist mainly of notes about grinding it in poppy oil, linseed or a combination both, with only 3 specifically mentioning “Burnt Sugar of Lead”.

The earliest reference states that 42 lbs (19 kg) of sugar of lead “in the rough state” when burned, yields 29 lbs (13 kg) (V1P300). Burning takes about “6 or 7 hours” and involves “skimming frequently”. This implies that “burning” is carried out, at least in part, to purify the raw material. Record P2P432A (1866), the only one with detailed instructions, states that 574 lbs (260 kg) of “raw white

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[171] W&N sold "Sugar of Lead" which appeared in their list of oil tube paints in their catalogues throughout the 19th century (Carlyle 2001, 534).

Sugar of Lead" was heated for a day in pots placed in a sand bath (to avoid catching fire). At the end it "ought to look opalescent & not opaque, the latter denoting that too much acid (acetic) has been expelled."[172] Furthermore "when dry [it] assumes the appearance of some white native Spar".[173]

The *Burnt Sugar of Lead* was ground in oil prior to being added to the *Bitumen* (Table D.4) with 8 out of 11 records specifying linseed oil (poppy oil "…caused the Bitumen not to dry so well" V2P150). Grinding on the roller mill ranged from 8 to 11 hours (X7P081, X7P086).

Table D.4: Amounts and descriptions of *Sugar of Lead* in W&N's *Bitumen* (1850-1858).

Code	Date		Name	Name & Amount	Description (quoted from the records)
V1P074	1850	24/Apr	Bitumen for Tubes	½^{lbs} Sugar Lead	finely ground dried Sugar Lead
V1P052	1851	11/Mar	Bitumen	2^{lbs} B^{t} Sug Lead	Gro^{d}. B^{t} [Burnt] Sugar Lead in L. Oil
V2P150	1852	3/Aug	Bitumen	Sugar Lead	The Sugar Lead was gro^{d} in Linseed Oil, some which has been gro^{d} in Poppy caused the Bitumen not to dry so well.
V2P261	1853	August	Bitumen for Tubes	12^{lbs} "Burnt Sugar Lead"	Perfectly dry "Burnt Sugar Lead". Ground fine in Linseed oil – this I estimate will produce 16^{lbs} of ground material. Any Sugar Lead slightly discoloured in burning (if not burnt to oxide) will do for this purpose.
X6P139	1853	14/Nov	Bitumen	16^{lbs} Bt Sugar Lead	Ground.
V2P354	1855	27/Mar	Bitumen	12^{lbs} Burnt Sugar of Lead	Dry Burnt Sugar of Lead. Gro^{d} in L Oil (when gro^{d} 17$^{\#}$ 5^{oz}).
V2P403	1855	27/Oct	Bitumen	12^{lbs} Burnt Sugar Lead	Dry Burnt Sugar of Lead. Gro^{d} by Edlin in L Oil & weighed when gro^{d} 17¼ ^{lbs} – (ground rather thin).
V2P465	1857		Bitumen 1st Batch	12^{lbs} Burnt Sugar Lead	Given to Church with instructions to grind it fine in Linseed Oil rather thinner than usual, put in jar till wanted.
X7P086	1857	March	Bitumen for Oil Tubes	6$^{\#}$ dry (Dried Sugar Lead)	Dry. Same as we grind for Tubes – only that if there be any darker than usual, it will answer for this purpose. It is to be gro'd in all Linseed Oil & rather thin took 2¾ ^{Pints} & the produce was 8$^{\#}$ ½^{oz} this is enough for 8 makings (Mill 8 hours).
V2P493	1858	24/Aug	Bitumen	½^{lbs} Sugar Lead	Ground (see p 465).
P2P115A	1858	Sept	Bitumen	½^{lbs} Sugar Lead (burnt kind)	gro^{d} Sugar Lead, the burnt kind gro^{d} in Linseed oil finely, rather thin.

D.3 Double Mastic Varnish

W&N sold both "Mastic Varnish" (or "Single Mastic Varnish") and "Double Mastic Varnish" throughout the 19th century. After 1850 these products were listed as "Mastic Varnish for Varnishing Pictures" or "Picture Mastic Varnish" and "Mastic Varnish Double Strength for Making Megilp" (Carlyle 2001, 355). There are 37 records between 1851 and 1881: 19 for *Mastic Varnish* and 18 for *Double Mastic Varnish* (Table D.5). In the early records the primary difference was the proportion of mastic resin present,

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[172] From this description W&N's *Burnt Sugar of Lead* was likely a lead acetate trihydrate which had been cleaned of dirt and debris through melting.

[173] It is important to note that in their archive W&N defines "Spar" consistently as magnesium carbonate ($MgCO_3.xH_2O$) (Otero 2018, 62).

however records from 1853–1882 show that W&N's "*Picture Mastic Varnish*" contained dammar resin[174] and in one instance a lesser quality mastic varnish.[175]

The majority of *Double Mastic Varnish* records (13 of 18), show two ingredients only: "Gum Mastic" (mastic resin) and "Turps" (turpentine). However, 5 records include the addition of previously prepared mastic varnish referred to variously as "thin mastic" and "double mastic" (Table D.5).

Different resin suppliers were recorded including the date of purchase.[176] In some productions resin from more than one supplier was used. The quality of the resin was defined variously as "Good", "Clean", "Bold", "Fair", "Fine", and "Middle". No indication of further processing of the resin, such as sorting, cleaning or powdering was evident.

Table D.5: Ingredients in W&N's *Double Mastic Varnish* (ratio was calculated by weight of resin to one gallon of turpentine). (The record highlighted in blue was used in the reconstruction, see Chapter 5).

				Gum Mastic	**Turps**	**Thin Mastic**	**Double Mastic**	**Ratio**
Code	**Date**		**Name**	Pounds	Gallons	Gallons	Gallons	Pounds to 1 Gallon
V1P051	1851	26/June	Mastic Varnish (Double)	110	20			5,5
V2P173	1852	1/Oct	Double Mastic Varnish	85½	10	29		-
V2P314	1854	4/July	Double Mastic Varnish	140*	30			4,7
V2P317	1854	5/July	Fine Pale Double Mastic	109	20			5,5
V2P319	1854	20/July	Mixing off Mastic Varnishes for Double Mastic			18¼		-
V2P319A	1854		Double Mastic for Shop Sale			16¼		-
V2P323	1854	1/Dec	MX Mastic Varnish (Double) for R P Sale			18	63	-
V2P324	1854	6/Dec	Double Mastic Varnish, palish	288	48	4	1½	-
V2P414	1855	18/Dec	Double Mastic Varnish	272	45			6,0
V2P445	1856	Dec	Double Mastic Varnish	132	24			5,5
V2P447	1857	Jan	Double Mastic Varnish	142¾	26			5,5
V2P460	1857	23/May	Double Mastic Varnish	275	40			6,9
V2P484	1858	1/July	Double Mastic Varnish	156	23			6,8
P2P113A	1858	5/Nov	Double Mastic Varnish	292	45			6,5
V2P501	1858	5/Nov	Double Mastic Varnish	292	45			6,5
V2P523	1859	July	Double Mastic Varnish	193½	30			6,5
V2P532	1860	14/May	Double Mastic Varnish	288	44			6,5
PMP294	1881	11/May	Double Mastic Varnish	672	168			4,0

*Three sorts of gum mastic are used: Fair, fine and middle sorts.

Turpentine was always referred to as "Turps" with additional modifiers such as "clean & well settled"[177] and "E: Dist: Turps" [likely English Distilled Turps]. The supplier and date of purchase was not recorded.

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[174] Records from 1853 to 1882 entitled "Single Mastic Varnish" include both of W&N's products "Double Mastic Varnish" and "Crystal Varnish". Crystal Varnish, variously entitled "Crystal Map Varnish" "Bright Crystal Varnish", or "Stout Crystal Varnish" consists of dammar resin in turpentine (P2P135A). Pasco (2019) and earlier authors (e.g. Townsend et al. 1998) determined that dammar resin will not form a gel in Megilp recipes. Therefore, its presence after c.1853 in "Picture Varnish (or Single Mastic Varnish)" explains W&N's specification that it is double strength mastic varnish which is used for making Megilp.

[175] Two records include mastic varnish in turpentine being mixed with the residue left in the varnish pot (V2P450 & V2P534).

[176] For example, P2P113A specifies "Gum Mastic bot. [bought] of G. Brooks Oct 19/58 @ 12/6 [lbs]".

[177] Turpentine was reported to change in quality and strength with keeping, and it continued to produce precipitates, hence the note "well settled" (Carlyle 2001, 139–42; see also Phenix 2015).

While a standard measure of resin and turpentine was not used (Table D.5), the ratios hover closely around 5.5 lbs resin to 1 gallon turpentine (2.5 kg to 4.5 L) in the earlier records, up to 6.5 lbs to 1 gallon (3 kg to 4.5 L) later on (1858-60). One record noted that the quality of the resin could influence the viscosity of the varnish (P2P113B) which may explain the lack of a standard ratio.[178]

The resin and turpentine were put in a steam apparatus (possibly like Figure D.2) and stirred continuously while being gradually heated, reaching a top temperature from 155°F to 180°F (68.3°C to 82.2°C). In the last records (1858–1860) the highest temperature was kept between 155°F and 160°F (68 °C to 71 °C) over 7 to 8 hours of cooking.

Two production records (V2P325 & V2P523) described “cutting the gum about with a strong spatula” (V2P325) during heating and stirring. This referred to breaking up the sticky ball of resin which formed.[179]

Once the resin had dissolved the steam was turned off and the cistern covered and left overnight. The next day the varnish was strained through a sieve into a new cistern. There are numerous references to the residue or “gruff ” left at the bottom of the steam apparatus. Some records (see foonote 173) indicate that further extractions from the gruff were made with turpentine then added to W&N’s *Double Mastic Varnish*, however this appears to have been more commonly done for *Single Mastic Varnish*.

D.4 Purple Lake

There are 72 records for the manufacture of purple lake pigment with an additional 54 records simply entitled “Purple Lake” which refer to purple lake paint making, either in water colour or oil. W&N’s *Purple Lake* pigment was a complex mixture combining other previously produced lakes, and in some cases sediments or “grouts”[180] from previous lake making.[181]

Various names and descriptions were used for the purple lake in W&N's *Bitumen* formulations (Table D.6). Like their *Burnt Sugar of Lead*, the *Purple Lake* was ground in oil prior to use. A note in record V2P150 states it should be ground “rather thinner than if it has been intended for tubes”; this direction was also given for their *Burnt Sugar of Lead* ground in oil.

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[178] Author’s first-hand experience with old and new stock of mastic resin shows that the age of the mastic resin will affect the amount that dissolves in turpentine and the age of the turpentine would also be a factor.

[179] The meaning of “cutting the gum about” became clear only during the reconstruction (see Chapter 5) when the semi-melted resin formed a thick sticky ball requiring repeated separation with the stirring rod to allow access to the turpentine.

[180] “Grouts” in modern English means sediments or grounds, such as coffee grounds. This practice of combining residues from various manufacturing processes to produce other products was also found in a study of one of W&N’s artists’ ground recipes (Carlyle et al. 2008).

[181] From Tatiana Vitorino’s doctoral research into W&N’s lake pigments (Vitorino 2020).

Table D.6: *Purple Lake* in oil added to W&N's Bitumen (1850-1858).

Code	Date		Name	Name & Amount	Description (quoted from the records)
V1P074	1850	24/Apr	Bitumen for Tubes	3^{oz} deep Purple Lake	Finely ground.
V1P052	1851	11/Mar	Bitumen	4^{oz} Purple Lake	Gro^{d}.
V2P150	1852	3/Aug	Bitumen	The Purple Lake was of good rich kind	gro^{d} in Linseed Oil rather thinner than if it has been intended for Tubes therefore I had used to each $4^{\#}$ batch of asphaltum 6^{oz} of the gro^{d} Pur Lake.
V2P261	1853	August	Bitumen for Tubes	1½^{lbs} good Strong Purple Lake	ground fine in Linseed oil keeping it rather thin – this I estimate will produce upwards of 3 lbs of ground colour.
X6P139	1853	14/Nov	Bitumen	3^{lbs} Purple Lake	Ground.
V2P354	1855	27/Mar	Bitumen	2¾^{lbs} Purple Lake	Dry, making when gro^{d} in L Oil $6^{\#}$ 5^{oz} of ground colour. The whole of the Purple Lake was used it not being quite so strong as some former parcels.
V2P403	1855	27/Oct	Bitumen	3^{lbs} Purple Lake (Common, BgC)	Dry. Transp^{t} & good tint, but not quite so strong as the best. Ground rather thin by Edlin & produce when Gro^{d} in L oil 6¼ ^{lbs}. [Next time] use the strongest Purple Lake as this PL on acct of using so much slackens its drying.
V2P465	1857		Bitumen 1st Batch	1½^{lbs} Strongest Purple Lake	ground very fine in Linseed Oil, rather thinner than usual & put by in jar till wanted (Mem^{m} Common weak lake does not do well). Next time, it will be better to use a stronger kind of Purple Lake.
X7P086	1857	March	Bitumen for Oil Tubes	3^{lbs} good Purple Lake (the sort used here was that marked “Bag C Common”)	Dry. Had been in R.P. Stock & returned to K.T. was not so strong in colour as our usual kind, hence we were obliged to use more of it. This is ground in 3¼^{Pints} of Linseed Oil (ground rather thin) and produced 6^{lbs} 5^{oz} of ground colour (Mill 11 hrs). Set aside till wanted. Next time, it will be better to use a stronger kind of Purple Lake.
V2P493	1858	24/Aug	Bitumen	8^{oz} Purple Lake	Gro^{d}. (see p 465).
P2P115A	1858	Sept	Bitumen	8^{oz} Purple Lake, the strongest Pur LK	gro^{d} very fine in Linseed oil, rather thinner than usual – mem: - Common weak lake does not do well.

D.5 Megilp

A search for “Megilp” in the database found 31 records which included “Water-colour Megilp” and “Copal Megilp” with only one, P2P258A, which clearly referred to the product *Megilp* (W&N sold Megilp in tubes or pots throughout the century (Carlyle 2001, 337).[182]

Record P2P258A, from 1863, entitled “Plain Megilp” (Figure D.2) consists of a one to one mixture of “Dble Mastic Vsh” and “Pale Drying Oil”, “by measure” (volume). Information is provided giving specific quantities and the yield.[183]

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[182] “Megilp (in pots)” appears in W&N catalogues from c.1840 to and c.1868 and was listed by other British colourmen (Carlyle 2001, 337–40). The archive database does not contain information which helps to distinguish this product from the “Megilp” sold in tubes (footnote 183), however it may be related to viscosity (which is influenced by resin content, see footnote 184).

[183] When the measures are converted to SI units, each tube would contain approximately 14 ml of Megilp.

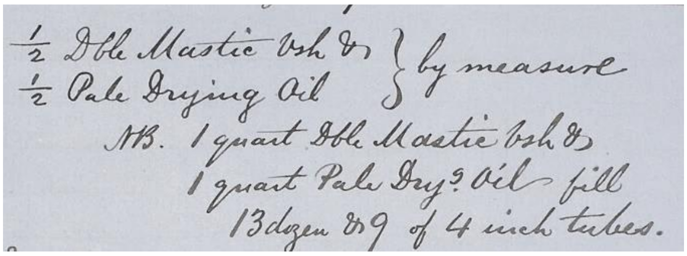
½ Dble Mastic Vsh &
½ Pale Drying Oil } by measure
NB. 1 quart Dble Mastic Vsh &
1 quart Pale Dryg Oil fill
13 dozen & 9 of 4 inch tubes.

Figure D.2: Description of "Plain Megilp" record P2P258A.

Of particular interest is the description of the difference between winter and summer formulations for this product. In winter "Strong Dryg oil" is added along with the "Pale Dryg Oil" (Figure D.3).[184]

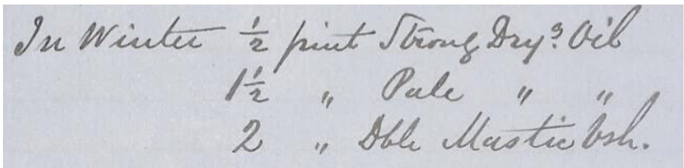
In Winter ½ pint Strong Dryg Oil
1½ " Pale " "
2 " Dble Mastic Vsh.

Figure D.3: Description of the winter formulation for "Plain Megilp" record P2P258A.

The use of a one to one proportion, to make "a good setting megilp" was also found in a record for "Scarlet Lake in Oil (for Artist's)" which called for "equal parts of "Double Mastic Varnish & of Strong Drying Oil…" (P2P054A).[185] As noted above a "Strong Megilp" was used at RP when megilp was added to the KT product (V1P0974). Since the strength or stiffness of the gel is governed by the quantity of mastic resin present[186] *Double Mastic Varnish* was essential.

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[184] The seasonal use of stronger and weaker drying oils was found in British artists' manuals on oil painting, see Carlyle (1995).

[185] *Megilp* was added to the following lakes: Scarlet (P2P045A&B and GRP005A); Crimson, and Purple (GRP005A); Extra Madder Carmine (9PP217); and as well to Emerald Green (9PP198) and Aureolin (9PP215).

[186] Recent research on the chemistry of gelled artists' Mediums determined that the primary reaction in gel formation is between the mastic resin and lead, therefore the stiffness of the gel is determined by the proportion of mastic resin present (Pasco 2019).

E

Appendix to Chapter 5

The Reconstruction

E.1 Equipment

Metal heat mantle with temperature probe

Metal heat mantle for 500 ml round flasks, heated on a magnetic hotplate stirrer, model: VMS-C4 Advanced from VWR Collection, with a temperature range of 50–500 °C and a PT1000 temperature sensor (control accuracy in the medium is ±0.5 °C).

Gas torch

Hand-held, wide flame propane torch (roofing torch) 5cm head diameter. “GALA SOL” “TÜV Product Service GS”, Made in Spain – HOM. AIG/212/82”. Propane Gas, supplied from Galp Energia, SGPS, S.A.

Infrared thermometers

Testo Infrared thermometer 826-T1 (-50° to 300 °C)
www.testo.com.
Portable IMPAC pyrometer IGA 15/5 from LumaSenseTM Technologies, Germany (250° to 1800 °C).

Drawdown bar

Stainless steel custom-made drawdown bar: width 2 cm with a fixed thickness of 0.25 µm (HART Project equipment).

Cast-iron pot

Commercially made (1960s): 8.2 cm high, 11.2 cm diameter, wall thickness 0.6 cm; capacity ~500 ml.

Glass stirring rod

Borosilicate glass stirring rod (95 cm long, circumference 4 cm). The last 2 cm was heated and flattened (1.8 cm wide, 0.3 cm thick) to a rectangle to improve stirring. Kindly produced for this project by Sr. Zé Luís (VICARTE/FCT NOVA).

HART Oil Press

Linseed oil was extracted from seeds using the HART Project stainless steel oil press designed by Ilya Cerjak, and built at the Institute for Atomic and Molecular Physics, Amsterdam (construction details in Carlyle et al. (2006)).

E.2 Substrates

Artists' board

12.7 cm x 17.7 cm, "Artists' Choice", titanium white in acrylic ground over synthetic fabric attached to cardboard. Commercially prepared product purchased in Canada 1998-99.

W&N's oil ground 1871

A reconstruction from a production record in the W&N 19th century archive database. Prepared in 2005 as a part of the HART Project. The ground was applied to washed and sized linen canvas and consisted of 3 separate layers. The bottom layer consist of chalk in a mixture of lead treated drying oil and copal-oil varnish, followed by two layers with different proportions of the chalk-oil putty and lead white pigment (detailed in Carlyle et al. 2008).

Glass slides

Laboratory grade glass slides.

Melinex®

Polyester film 100 micron thick, cut into retangles 10 x 16 cm, supplied by Preservation Equipment Ltd (https://www.preservationequipment.com/).

E.3 Materials

Asphalt

Trinidad Lake Asphalt was selected because its ingredients were characterised and it was readily available in small quantities (also because it was used in previous reconstructions of bitumen/asphaltum brown oil paint by Izat (2001). Its composition was reported as, "53–55% bitumen, 36–37% mineral matter and 9–10% water of hydration, adsorbed bitumen and volatiles" (Charles and Grimaldi 1996) and its physical properties were also well characterized by the manufacturer and others (Charles and Grimaldi 1996). The supply used for the reconstruction was fully analysed in Py-TMAH-GC/MS, Py-GCxGC/MS and µ-FTIR.

Trinidad Lake Asphalt, Trinidad Epuré, Carl Ungewitter, Trinidad Lake Asphalt, GmbH & Co. KG, 28195 Bremen, Bgm.-Smidt-Straße 56, Germany.

Linseed oil (custom extracted)

Sofie linseeds from Zeeland province in the Netherlands (purchased in 2014). Extracted 5 June 2019 by Raquel Marques using the HART Project custom-made stainless steel oil press.

Red lead

Aldrich Chemical Company red lead, lead(II,III) oxide 99%, Pb_3O_4, CAS Number 1314-41-6, F.W. 685.57. Average particle size 1–2 µm.

Litharge

Sigma-Aldrich lead(II) oxide 99+%, A.C.S. reagent, CAS Number 1317-36-8.

Sugar of lead

Fluka Chemika lead(II) acetate trihydrate >99.0%, product no. 15320, Q2539.

Mastic resin

Kremer Pigmente #60050, mastic resin from Chios, Greece, best quality.

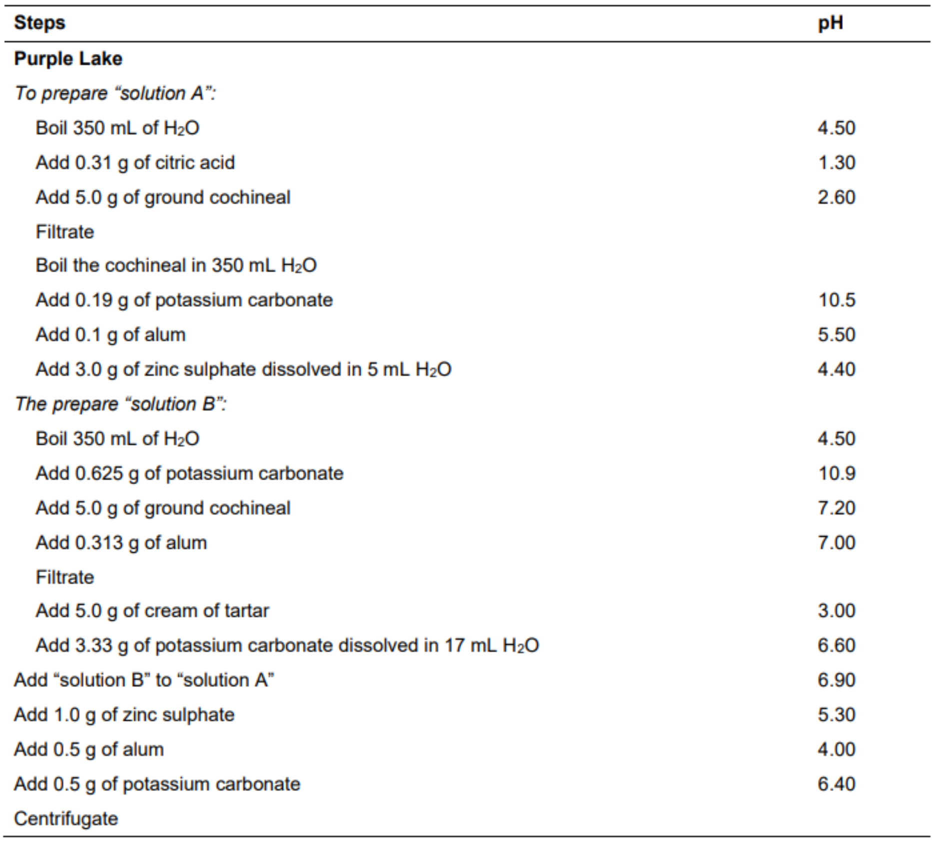
Turpentine

Kremer Pigmente #70010 Pine Turpentine, double rectified, DAB9. Chemical composition: (2-Pinen)$C_{10}H_{16}$.

Purple lake

The reconstruction of the pigment based on W&N's production record "Best Deep Purple Lake (P1P369AL03)" was made by Tatiana Vitorino on 6 June 2013 (Table E.1) (Vitorino 2020, 47, 141).

Table E.1: Steps and respective pH values during reconstruction of W&N's purple lake products. Reproduced from Vitorino (2020, 47).



Steps	pH
Purple Lake	
To prepare "solution A":	
Boil 350 mL of H_2O	4.50
Add 0.31 g of citric acid	1.30
Add 5.0 g of ground cochineal	2.60
Filtrate	
Boil the cochineal in 350 mL H_2O	
Add 0.19 g of potassium carbonate	10.5
Add 0.1 g of alum	5.50
Add 3.0 g of zinc sulphate dissolved in 5 mL H_2O	4.40
The prepare "solution B":	
Boil 350 mL of H_2O	4.50
Add 0.625 g of potassium carbonate	10.9
Add 5.0 g of ground cochineal	7.20
Add 0.313 g of alum	7.00
Filtrate	
Add 5.0 g of cream of tartar	3.00
Add 3.33 g of potassium carbonate dissolved in 17 mL H_2O	6.60
Add "solution B" to "solution A"	6.90
Add 1.0 g of zinc sulphate	5.30
Add 0.5 g of alum	4.00
Add 0.5 g of potassium carbonate	6.40
Centrifugate	

E.4 Reconstructions of W&N's products

Strong Drying Oil

W&N's production record X6P285 from 1854 for *Strong Drying Oil* was followed. A total of 250 ml of freshly extracted linseed oil was treated in a balloon flask placed in a metal heat mantle. Heating took place in a laboratory fume hood. The temperature of the oil was monitored with a glass thermometer (maximum 200 °C) held in place using clamps on a retort stand.

Powdered lead tetroxide (red lead) and lead(II) oxide (litharge) were stirred together with a glass rod in a glass container (12.5 g of each). The oil (250 ml in a 500 ml balloon flask) was gradually heated over a period of 1 hr and 30 minutes, to a temperature of 95 °C, then the powdered driers were added at once. The mixture was stirred continuously using a Teflon-coated magnetic stirrer (2 cm) during the addition of the driers and throughout subsequent heating. Heating continued for 4 hours and 10 minutes within a temperature range of 95° and 97 °C, at which point heat was turned off and the mixture left overnight covered with a watch-glass.

The next morning, driers had precipitated to the bottom of the flask. The oil was decanted to a fresh container (250 ml Schott glass) and appeared somewhat turbid with a distinctly orange colour. Precipitation of the driers continued to occur over a period of 3 months. Note that one of the W&N production records for *Strong Drying Oil* (V2P527) stated that this product will be "in fine order" after a year.

Burnt Sugar of Lead

A reconstruction of the procedure in record P2P432A from 30 May 1866 was attempted in a laboratory fume hood. However, the reconstruction of this material did not succeed in producing a viable product for use in the *Bitumen* reconstruction. Therefore, a laboratory grade lead acetate trihydrate (see sugar of lead in Materials) was used.

Lead acetate trihydrate was reduced to a powder with a ceramic muller and pestle then ground in raw linseed oil (see Materials) using a glass slab and glass muller (full protective equipment was used due to its toxicity). To reduce air exposure the 2.8 g of lead acetate ground in oil were tied into a bladder made with thin polyester film (Melinex®) and stored overnight then used the next day.

Double Mastic Varnish

W&N's production record P2P113A dated 5 November 1858 was followed. Amounts were scaled down from the production record such that 132 g resin was dissolved into 170.3 ml[187] of turpentine (a proportion by weight of resin to turpentine of 1 to 1.1).

The same equipment used to prepare *Strong Drying Oil* was employed. Mastic resin (see Materials) was used as supplied in tears with no further processing such as washing or crushing. The resin was placed in a 500 ml flask, followed by the turpentine, the mixture was continuously stirred using a Teflon coated magnetic stirrer. Heat was increased gradually taking care not to exceed the top temperature given in the recipe of 155 °F (68 °C). Temperature was measured using a glass thermometer placed in the balloon flask. It took approximately 1 hour and 15 minutes to reach 155 °F. The heat was maintained for another 2 hours and 45 minutes, until the resin was dissolved.

Initially the magnetic stirrer was sufficient to keep the resin and solvent in motion, however as heating continued the individual resin particles appeared to swell, then portions became sticky and adhered to each other. At this point it was no longer possible to achieve uniform motion with the magnetic stirrer and it was necessary to assist with manual stirring with a glass rod. After approximately 1 hour, at a temperature of 54 °C, the combination of solid and sticky resin formed a ball. It was necessary to continuously separate the ball into smaller pieces with a glass rod in order to increase

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[187] Due to a conversion error into SI units, the amount of Turpentine used was 170,3 ml when it should have been 204,6 ml. This was due to a conversion from US gallons (1 = 3,78 L) instead of Imperial gallons (1 = 4,54 L).

the surface area available for dissolution into the solvent. As noted above, W&N had referred to this procedure as "cutting the gum about with a strong spatula" (V2P325).

Heating and stirring continued until the bulk of the resin had fully dissolved (after a total of 4 hours) with only a small residue remaining. The heat was turned off , the flask was covered with a watch-glass, and left overnight (in keeping with the record's instructions to cover the cistern over-night). The next morning, the amount of residue had diminished to a very small amount which was just visible. The varnish was decanted into a fresh jar (Schott glass 250 ml) and was stored in the laboratory (not in the dark) until needed.

Purple Lake

The reconstructed *Purple Lake* pigment (see pages 319-20) was ground in raw linseed oil using a glass slab and glass muller. A total of 2.8 g was stored in in a covered glass container prior to its use the following day.

F

Appendix to Chapter 6

F.1 3D-views of the GCxGC/MS chromatograms

The reconstructed 3D-view of the bidimensional GCxGC chromatograms can be used as a quick means to estimate the relative intensities of peaks pertaining to each component of the sample during the Py-GCxGC/MS analysis. To illustrate this, comparison of the 3D-views of the TLA reference sample (Figure F.1) and of the KT-1 sample (Figure F.2) shows a marked diminution of the relative intensity of peaks associated to the complex unresolved mixture compared to the other components of the TLA (alkanes/alkenes, cyclic alkanes, groups I-V) with an intensity scale varying from the 10.10^6 to 80.10^6 range in the second dimension (Column II).

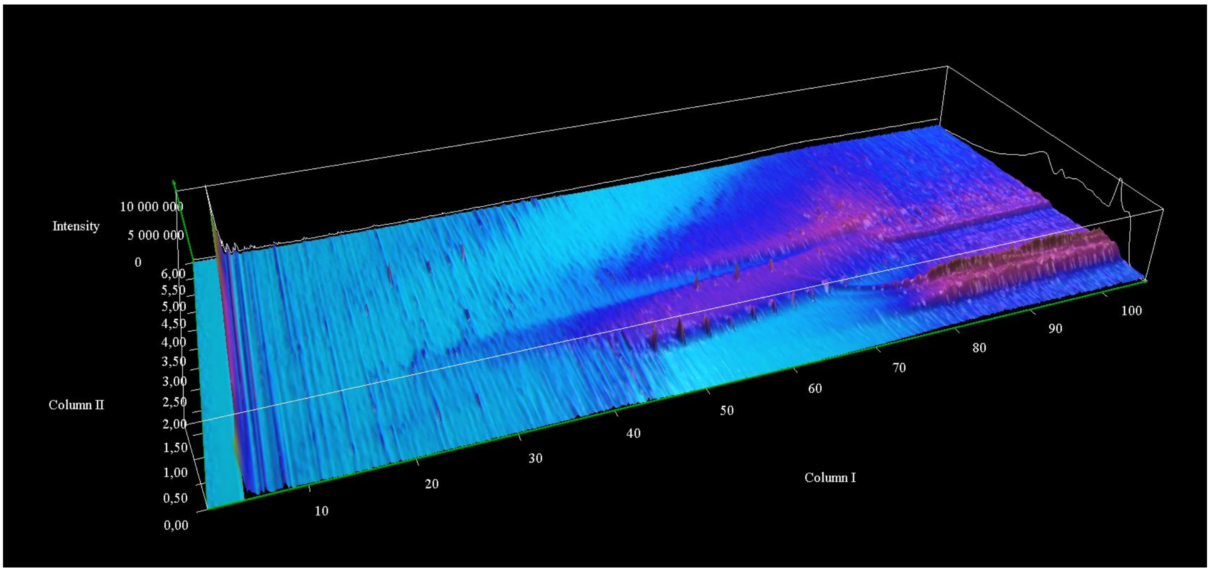


Figure F.1: 3D view of total ion chromatogram of the TLA reference sample obtained by Py-GCxGC/MS for a sample of 39 µg (see experimental part in Chapter 6 for details).

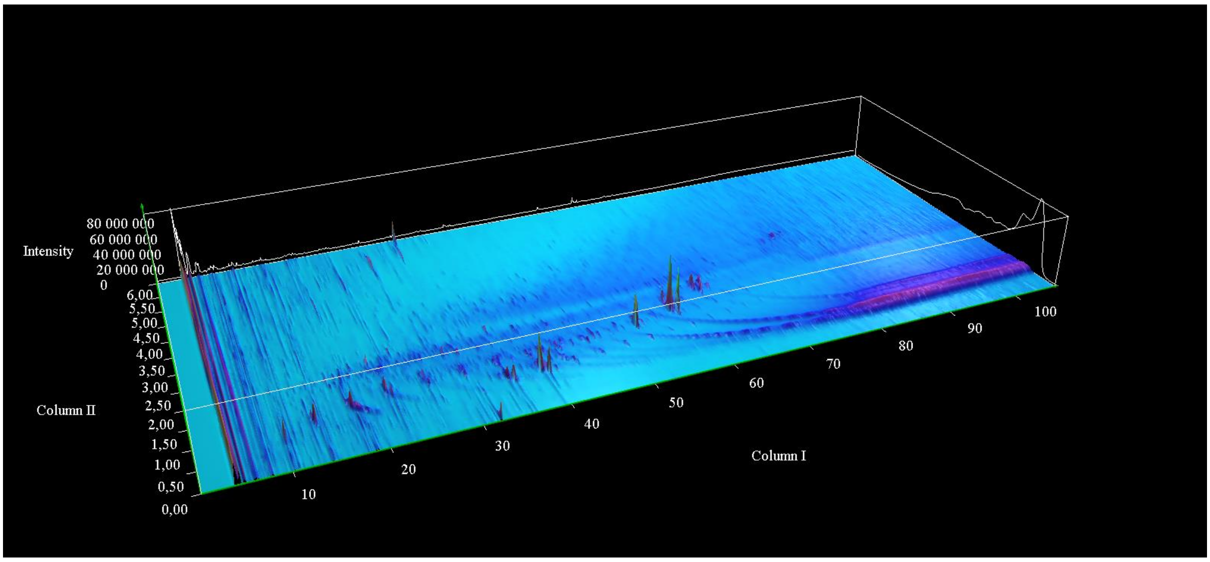
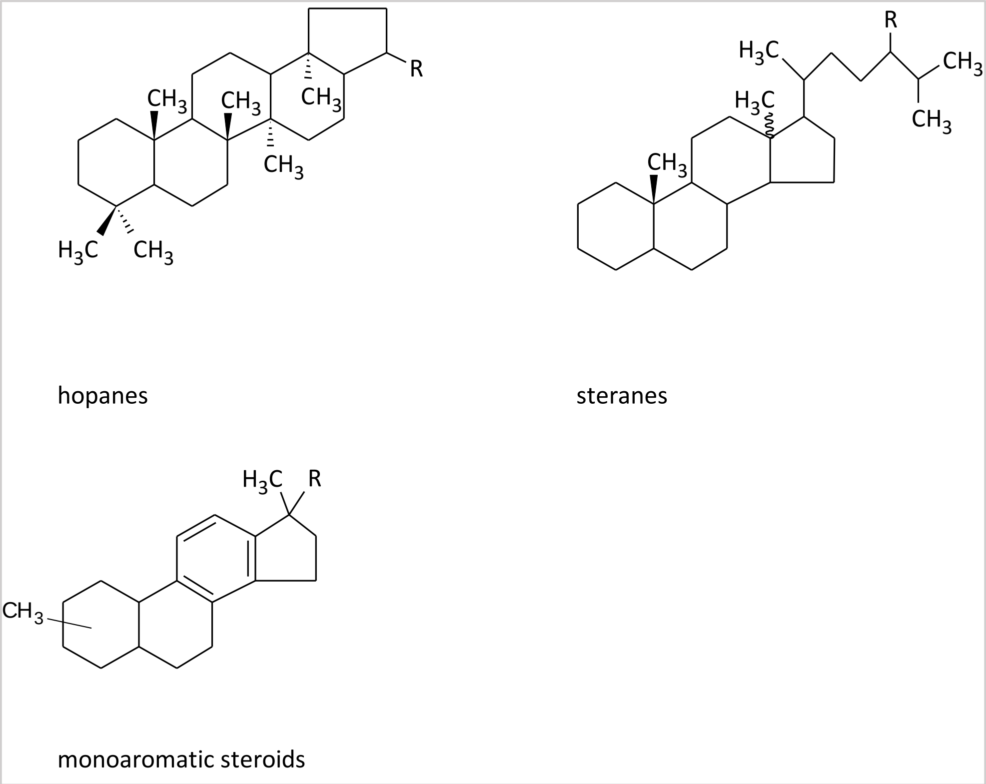


Figure F.2: 3D view of total ion chromatogram of the KT-I sample obtained by Py-GCxGC/MS for a sample of 53 µg (see experimental part in Chapter 6 for details).

F.2 General structure of expected biomarkers



hopanes

steranes

monoaromatic steroids

Figure F.3: General structures of hopanes, steranes and monoaromatic steroids made by Michel Sablier in Chemsketch.

F.3 Description of compounds identified for each sample with Py-GCxGC/MS:

Table F.1: Assignment of compounds detected by Py-GCxGC/MS in the TLA reference sample and in samples from the three steps in the reconstruction: KT-I, KT and RP, with retention time in the first and second dimension (^1t_R, ^2t_R), main fragment ions, expect molecular weights, assigned formula, most likely attribution of the products and their observed presence or absence in the resulting chromatograms.

Compounds	^1t_r (min)	^2t_r (s)	Fragment ions (in decreasing order of intensity)	MW	Formula	Assignment[a]	TLA[b]	Heated TLA[b]	KT-I[b]	KT[b]	RP[b]
Alkanes, Alkenes											
	8,1	0,1	56,43,55,41,70	126	C_9H_{18}	1-Nonene	x	x	x	x	-
	10,8	0,3	41,56,55,70,43	140	$C_{10}H_{20}$	n-1-Decene	x	x	x	x	-
	11	0,3	57,43,71,79,85	142	$C_{10}H_{22}$	n-decane	-	-	x	-	-
	14,4	0,5	41,43,56,55,70	154	$C_{11}H_{22}$	n-1-Undecene	x	x	-	x	x
	14,7	0,4	57,43,71,41,85	156	$C_{11}H_{24}$	n-Undecane	x	x	x	-	-
	18,7	0,6	41,43,55,70,56	168	$C_{12}H_{24}$	n-Dodecene	x	-	x	x	x
	19	0,55	57,43,71,41,85	170	$C_{12}H_{26}$	n-Dodecane	x	-	x	-	-
	23,2	0,7	56,55,57,69,41	182	$C_{13}H_{26}$	n-1-Tridecene	x	x	x	x	x
	23,5	0,65	57,43,71,41,85	184	$C_{13}H_{28}$	n-Tridecane	x	x	-	-	x
	27,7	0,8	55,41,70,57,56	196	$C_{14}H_{28}$	n-1-Tetradecene	x	x	x	x	x
	28	0,75	57,43,71,41,85	198	$C_{14}H_{30}$	trace tetradecane	x	x	x	-	-
	32,03	0,85	55,43,41,57,83	210	$C_{15}H_{30}$	n-1-pentadecene	-	x	-	-	x
	32,3	0,75	57,43,71,41,85	212	$C_{15}H_{32}$	Pentadecane	-	x	x	-	x
	35,7	1	55,41,67,81,82	222	$C_{16}H_{30}$	1,15-Hexadecadiene	-	-	x	-	-
	35,9	0,9	55,69,43,56,83	224	$C_{16}H_{32}$	isomer of hexadecene	-	x	x	-	-
	36,3	0,9	55,43,57,41,83	224	$C_{16}H_{32}$	n-1-Hexadecene	-	x	x	-	x
	36,5	0,85	57,43,71,85,41	226	$C_{16}H_{34}$	Hexadecane	-	x	x	-	-
	39,4	1,1	55,41,67,81,82	236	$C_{17}H_{32}$	heptadiene	-	x	x	-	-

39,7	1	55,69,41,43,83	238	$C_{17}H_{34}$	isomer of heptadecene	-	x	x	x	x
39,9	1	55,41,69,43,57	238	$C_{17}H_{34}$	8-Heptadecene	-	-	-	x	-
40,2	0,2	55,57,43,41,69	210	$C_{15}H_{30}$	n-1-pentadecene	x	-	x	x	-
40,5	0,9	57,71,43,41,85	240	$C_{17}H_{36}$	heptadecane	-	x	x	x	-
41,5	0,95	56,57,69,70,43	266	$C_{19}H_{38}$	1-hexadecene, 5 methyl	-	x	x	-	-
43,23	1,1	55,81,41,67,82	250	$C_{18}H_{34}$	isomer of octadecene	-	-	-	x	x
43,5	1,1	67,55,81,41,82	250	$C_{18}H_{34}$	isomer of octadecene	-	-	-	x	-
44	1,05	55,57,43,41,69	252	$C_{18}H_{36}$	1-n-octadecene	-	x	x	x	x
44,2	0,9	57,43,71,85,41	254	$C_{18}H_{38}$	Octadecane	x	x	x	x	-
47,5	1,05	43,57,55,97,83	266	$C_{19}H_{38}$	1-n-nonadecene	x	x	x	x	x
47,7	1	57,43,71,85,41	268	$C_{19}H_{40}$	nonadecane	x	x	x	x	-
50,9	1,15	43,55,57,83,69	280	$C_{20}H_{40}$	1-n-eicosene	x	x	x	x	x
51,1	1,05	57,71,43,85,41	282	$C_{20}H_{42}$	Eicosane	x	x	x	x	-
54,1	1,2	43,55,57,83,41	294	$C_{21}H_{42}$	n-1-Heneicosene	x	x	x	x	-
54,3	1,1	57,43,71,85,55	296	$C_{21}H_{44}$	Heneicosane	x	x	x	x	x
57,2	1,25	43,57,55,97,41	308	$C_{22}H_{44}$	1-n-docosene	x	x	x	x	-
57,3	1,15	57,71,85,55,56	310	$C_{22}H_{46}$	docosane	x	x	x	x	x
60,1	1,3	57,55,97,83,41	322	$C_{23}H_{46}$	tricosene	x	x	-	x	-
60,2	1,25	57,43,71,55,85	324	$C_{23}H_{48}$	tricosane	x	x	x	x	x
62,9	1,35	55,57,83,97,69	336	$C_{24}H_{48}$	1-n-tetracosene	x	x	-	x	-
63	1,3	57,71,55,41,85	338	$C_{24}H_{50}$	tetracosane	x	x	x	-	-
65,7	1,35	57,43,71,85,41	352	$C_{25}H_{52}$	pentacosane	x	x	x	x	x
68,3	1,4	57,71,85,44,41	366	$C_{26}H_{54}$	hexacosane	x	x	x	x	x
70,7	1,5	57,71,43,85,55	380	$C_{27}H_{56}$	heptacosane	x	x	-	x	x
73,1	1,55	57,43,71,85,55	394	$C_{28}H_{58}$	octacosane	x	x	-	-	-
75,5	1,6	57,71,43,85,55	408	$C_{29}H_{60}$	nonacosane	x	x	-	x	x
77,6	1,65	57,43,55,97,71	422	$C_{30}H_{62}$	triacontane	x	-	-	-	x
79,7	1,75	57,71,43,85,83	436	$C_{31}H_{64}$	hentriacontane	x	x	-	-	x
81,7	1,85	57,71,43,85,55	450	$C_{32}H_{66}$	dotriacontane	x	x	-	-	-

Other alkyl hydrocarbons											
	11	2,75	57,43,41,71,56	142	$C_{10}H_{22}$	substituted alkane	x	x	-	-	-
	14,4	3,4	55,41,43,56,69	154	$C_{11}H_{22}$	positional isomer undecene	x	x	x	-	-
	14,7	3,3	57,43,71,41,56	156	$C_{11}H_{24}$	substituted alkane	x	x	-	t	-
	18,6	4	41,55,43,56,69	168	$C_{12}H_{24}$	positional isomer dodecene	x	x	x	x	-
	19	3,7	57,43,71,41,85	170	$C_{12}H_{26}$	substituted alkane	x	x	-	-	-
	19,5	3,5	57,43,71,41,56	184	$C_{13}H_{28}$	Undecane, 2,6-dimethyl-	x	x	-	-	-
	23,1	4,25	55,41,43,56,69	182	$C_{13}H_{26}$	Cyclotridecane/positional isomer tridecene	x	-	x	x	x
	27,7	4,85	43,55,41,57,69	196	$C_{14}H_{28}$	Cyclotetradecane/positional isomer tetradecene	x	x	x	x	x
	27,9	4,35	57,43,71,41,85	198	$C_{14}H_{30}$	substituted alkane	x	-	-	t	-
	31,9	4,75	55,43,41,69,57	210	$C_{15}H_{30}$	cyclopentadecane/positional isomer pentadecene	x	-	x	x	x
	32,3	4,5	57,43,71,85,41	212	$C_{15}H_{32}$	substituted alkane	x	-	x	x	x
	36,1	5,4	43,41,55,57,83	224	$C_{16}H_{32}$	isomer of hexadecene	-	-	-	x	x
	40,3	5,15	57,71,43,41,85	240	$C_{17}H_{36}$	substituted alkane	x	-	-	x	x
	43,9	5,75	57,83,55,69,43	252	$C_{18}H_{36}$	isomer octadecene	x	-	-	-	-
Hopane structures											
	53,4	2,1	191,41,95,55,123	276	$C_{20}H_{36}$	NA	x	x	-	-	-
	56,1	2,15	191,95,55,109,69	290	$C_{21}H_{38}$	NA	x	x	-	-	-
	61,3	2,15	191,69,95,55,81	318	$C_{23}H_{42}$	NA	x	x	-	-	-
	62,8	2,15	191,69,95,81,55	332	$C_{24}H_{44}$	15-Isobutyl-(13αH)-isocopalane	x	x	-	-	-
	65,9	2,25	191,69,95,55,81	346	$C_{25}H_{46}$	NA	x	x	-	-	-
	68	2,25	191,95,81,69,109	360	$C_{26}H_{48}$	NA	x	x	-	-	-

	68,2	2,25	191,95,55,192,81	360	$C_{26}H_{48}$	NA	x	-	-	-	-
	68,6	2,95	191,67,81,95,109	402	$C_{29}H_{54}$	NA	x	-	-	-	-
	72,9	2,4	191,57,69,81,95	388/402	$C_{28}H_{52}$/ $C_{29}H_{54}$	NA/ norhopane	x	x	-	-	-
	73,1	2,4	191,69,43,81,95	388/412	$C_{28}H_{52}$/ $C_{30}H_{52}$	NA /norhopane	x	x	-	-	-
	76,6	3,45	191,95,67,55,81	370	$C_{27}H_{46}$	NA/norhopane	x	x	-	-	-
	77,4	3,7	191,231,161,95,69	368	$C_{27}H_{44}$	NA	x	x	-	-	-
	77,6	3,6	191,95,81,149,69	370	$C_{27}H_{46}$	hopane/17α(H)-22,29,30-trisnorhopane?	x	x	-	-	-
	80,4	3,55	191,137,177,69,81	398	$C_{29}H_{50}$	28-Nor-17β(H)-hopane/17α(H),21β(H)-30-norhopane(384)	x	x	-	-	-
	81,3	3,65	191,355,192,67,137	398	$C_{29}H_{50}$	28-Nor-17α(H)-hopane?	x	x	-	-	-
	81,8	3,55	191,95,123,192,81	412	$C_{30}H_{52}$	Gammacerane	x	x	-	-	-
	82	3,75	191,69,121,149,192	410	$C_{30}H_{50}$	A'-Neogammacer-22(29)-ene?	x	x	-	-	-
	85,3	4,9	191,69,95,192,81	412	$C_{30}H_{52}$	NA	x	x	-	-	-
Aromatic steroid structures											
	69,2	2,9	253,44,254,143,207	336?	NA	NA	x	x	-	-	-
	71,3	3	253,254,143,252,43	NA	NA	NA	x	x	-	-	-
	73	3,05	253,254,143,252,267	NA	NA	NA	x	x	-	-	-
	74,8	3,15	253,254,44,143,207	NA	NA	NA	x	x	-	-	-
	76,5	3,3	253,254,207,218,451	NA	NA	NA	x	x	-	-	-
Groups I-V markers compounds											
Group I											

	16	5,9	119,134,133,91,120	134	C10H14	Benzene, 1,2,4,5-tetramethyl-	x	x	-	-	-
	17,5	0,4	119,134,120,91,118	134	C10H14	Benzene, 1,2,3,4-tetramethyl-	x	x	-	-	-
	17,5	1,4	119,134,120,117,133	134	C10H14	Benzene, 1,2,3,4-tetramethyl-	x	x	-	-	-
	17,5	3,45	119,134,91,118,77	134	C10H14	Benzene, 1,2,4,5-tetramethyl-	x	x	-	-	-
	17,5	4,1	119,134,117,91,118	134	C10H14	Benzene, 1,2,4,5-tetramethyl-	x	x	-	-	-
	17,5	5,56	119,91,134,92,44	134	C10H14	NA	x	x	-	-	-
	17,7	1,15	130,115,129,128,63	130	C10H10	1H-Indene, 3-methyl-	x	x	x	-	-
	18,1	1,95	128,127,129,64,63	128	C10H8	Naphthalene	x	x	x	-	-
	18,2	2	105,134,133,77,119	134	C9H10O	Benzaldehyde, 4-ethyl-	-	-	x	-	-
	18,4	1,85	130,129,115,128,131	130	C10H10	2-Methylindene	x	x	x	-	-
	18,6	2,15	119,91,134,65,43	134	C9H10O	Ethanone, 1-(3-methylphenyl)-	-	-	x	-	-
	19,5	2,1	128,57,127,129,43	128	C10H8	1H-Indene, 1-methylene-	x	x	x	x	x
	19,9	1,95	121,136,91,58,135	136	C9H12O	Phenol, 2,4,5-trimethyl-	x	x	x	-	-
	21,1	2,5	119,91,148,117,105	148	C11H16	Benzene, 1-methyl-4-(1-methylpropyl)-	-	x	-	-	-
	21,8	1,35	91,104,117,105,92	160	C12H16	Benzene, 4-hexenyl-	-	-	-	-	-
	22,2	0,75	91,92,162,41,105	162	C12H18	Benzene, hexyl-	-	-	-	-	-
	22,3	2,05	119,148,91,120,147	148	NA	NA	-	-	-	-	-
Group II											
	22,5	1,9	129,144,128,130,143	144	C11H12	1H-Indene, 4,7-dimethyl-	x	x	x	x	x
	22,9	1,95	129,144,128,130,127	144	C11H12	1H-Indene, 2,3-dimethyl-	x	x	x	-	-
	23	2,1	141,142,71,115,139	142	C11H10	Benzocycloheptatriene	x	-	x	-	-
	23,9	2,1	129,144,128,127,115	144	C11H12	1H-Indene, 1,3-dimethyl-	x	x	x	-	-
	24,1	2,1	129,144,128,127,143	144	C11H12	1H-Indene, 1,1-dimethyl-	x	x	x	-	-
	24,4	2,3	142,141,115,143,39	142	C11H10	Naphthalene, 2-methyl-	x	-	x	x	x

	24,5	2,4	147,148,141,44,142	148	C9H8S	Benzo[b]thiophene, 5-methyl-	x	x	-	-	-
	25,1	2,9	142,141,115,143,58	142	C11H10	Naphthalene, 1-methyl-	x	x	x	-	-
	25,1	3,5	148,147,149,115,73	148	C9H8S	Benzo[b]thiophene, 6-methyl-	x	x	x	-	-
	25,2	2,4	142,141,115,70,143	142	C11H10	1H-Indene, 1-ethylidene-	x	x	x	x	x
	25,2	2,7	141,142,140,115,143	142	C11H10	NA	x	-	x	-	-
Group III											
	26,5	2	143,128,158,129,142	158	C12H14	1H-Indene, 1,1,3-trimethyl-	x	x	x	-	-
	27,1	2	143,128,158,142,141	158	C12H14	1H-Indene, 1,2,3-trimethyl-	x	x	x	-	-
	27,3	1,95	158,143,128,159,44	158	C12H14	Benzene, p-diisopropenyl-	x	x	x	-	-
	27,6	2	143,158,128,115,144	158	C12H14	Benzene, 1,3,5-trimethyl-2-(1,2-propadienyl)-	x	x	x	x	-
	27,63	0,7	143,128,158,129,144	158	C12H14	1,2,3-Trimethylindene	-	-	-	-	x
	28,7	2,15	143,128,158,141,142	158	C12H14	1H-Indene, 1,1,3-trimethyl-	x	x	x	x	-
	28,6	2,4	162,161,163,147,128	162	C10H10S	Benzo[b]thiophene, 3,6-dimethyl-	x	x	-	-	-
	28,6	2,85	162,161,163,147,128	162	C10H10S	Benzo[b]thiophene, 2,7-dimethyl-	x	x	-	-	x
	29,6	3,25	162,161,163,147,115	162	C10H10S	Benzo[b]thiophene, 2,5-dimethyl-	x	x	-	-	-
	29,3	2,45	156,141,155,157,115	156	C12H12	Naphthalene, 2,7-dimethyl-	x	x	x	x	-
	29,4	2,35	156,141,155,77,44	156	C12H12	Naphthalene, 1,5-dimethyl-	x	x	x	-	-
	29,9	2,45	156,141,155,157,77	156	C12H12	Naphthalene, 1,7-dimethyl-	x	x	-	-	x
	29,9	2,8	156,141,155,63,157	156	C12H12	Naphthalene, 1,6-dimethyl-	x	x	x	-	-
	30,1	2,8	156,141,155,66,157	156	C12H12	Naphthalene, 1,3-dimethyl-	x	x	x	x	-
	31,1	1,55	91,104,92,117,105	188	C14H20	Benzene, 1-octenyl-	-		x	-	-
	31,4	1,4	92,91,190,93,57	190	C14H22	Benzene, octyl-	-		x	-	-
	31,5	3,45	156,141,155,115,142	156	C12H12	Naphthalene, 1,2-dimethyl-	x		-	-	-
Group IV											
	33,6	2,35	155,170,127,84,56	170	C13H14	Naphthalene, 1,4,6-trimethyl-	x	x	x	-	-

33,6	2,95	176,161,175,177,160	176	C11H12S	Benzo[b]thiophene, 2,5,7-trimethyl-	x	x	-	-	-
33,76	2,35	155,170,154,153,171	170	C13H14	3-(2-Methyl-propenyl)-1H-indene	-	x	-	x	x
34,2	3,4	161,176,175,177,160	176	C11H12S	Benzo[b]thiophene, 2-ethyl-5-methyl-	x	x	-	-	-
34,4	2,75	170,155,169,152,154	170	C13H14	Naphthalene, 2,3,6-trimethyl-	x	x	-	x	x
34,7	2,65	170,155,169,156,154	170	C13H14	Naphthalene, 1,6,7-trimethyl-	x	x	x	x	x
34,9	3,55	176,161,175,162,177	176	C11H12S	Benzo[b]thiophene, 7-ethyl-2-methyl-	x	x	-	-	-
35	3,35	176,161,175,165,45	176	C11H12S	Benzo[b]thiophene, 2,5,7-trimethyl-	x	x	-	-	-
35,3	3,05	170,155,156,152,76	170	C13H14	3-(2-Methyl-propenyl)-1H-indene	x	x	-	-	-
35,5	2,9	170,155,156,152,154	170	C13H14	isomer of naphthalene, trimethyl-	x	x	x		x
35,7	1,45	92,91,204,93,45	204	C15H24	Benzene, nonyl-	-	-	x	x	x
36,8	3	175,190,176,174,177	190	C12H14S	Benzo[b]thiophene, 2-ethyl-5,7-dimethyl-/Benzo[b]thiophene, 2,7-diethyl-	x	x	-	-	-
37,4	2,85	161,175,44,175,162	190	C12H14S	Benzo[b]thiophene, 2,3-diethyl-	x	x	-	-	-
40,03	1,45	92,91,93,218,43	218	C16H26	Benzene, decyl-	-		-	x	x
41,1	1,15	105,106,91,232,92	232	C17H28	Benzene, (1-methyldecyl)-	-		-	x	x
42,6	1,6	119,120,91,105,232	232	C17H28	Benzene, (1,1-dimethylnonyl)-	-		x	x	x
43,9	1,6	92,105,91,106,232	232	C17H28	Benzene, undecyl-	-		x	x	x
44,1	3,6	184,185,183,152,92	184	C12H8S	Dibenzo[b,d]thiophene	x	x	-	-	-
47,7	3,55	198,197,199,198,85	198	C13H10S	Dibenzothiophene, 3-methyl-	x	x	-	-	-
48,4	3,6	198,197,199,98,45	198	C13H10S	Dibenzothiophene, 3-methyl-?	x	x	-	-	-
49,2	3,85	198,197,199,165,100	198	C13H10S	Dibenzothiophene, 4-methyl-	x	x	-	-	-

	51,8	3,55	212,211,165,105,163	212	C14H12S	2,8-Dimethyldibenzo(b,d)thiophene/2,6-Dimethyldibenzothiophene/2,7-Dimethyldibenzothiophene	x	x	-	-	-
	52,6	3,75	212,211,197,213,106	212	C14H12S	1,7-Dimethyldibenzothiophene	x	x	-	-	-
	60,6	3,9	240,225,219,234,241	240	C16H16S	Dibenzo[b,d]thiophene, 1,3,6,7-tetramethyl-	x	x	-	-	-
	68,7	5,3	248,247,249,123,124	248	C17H12S	3-Methylphenanthro[9,10-b]thiophene	x	x	-	-	-
	71,8	5,35	262,43,123,245,261	262	C18H14S	Benzo[b]naphtho[2,3-d]thiophene, 6,8-dimethyl-	x	x	-	-	-
Group V											
	45,1	3,65	178,177,89,176,179	178	C14H10	phenanthrene	-	x	x	-	-
	45,2	3,6	178,177,89,176,179	178	C14H10	phenanthrene	x	x	x	-	-
	49,4	3,6	192,191,96,193,189	192	C15H12	Phenanthrene, 3-methyl-	x	x	x	-	-
	50	3,75	192,191,189,83,94	192	C15H12	Anthracene, 1-methyl-	x	x	x	-	-
	50,1	3,7	192,191,83,193,95	192	C15H12	Phenanthrene, 4-methyl-	x	x	x	-	-
	50,2	3,75	192,191,96,95,193	192	C15H12	Anthracene, 9-methyl-	x	x	x	-	-
	53,7	3,55	206,191,205,44,89	206	C16H14	9,10-Dimethylanthracene	x	x	x	-	-
	57,1	3,65	220,205,210,202,204	220	C17H16	Phenanthrene, 2,3,5-trimethyl-	x	x	-	-	-
	57,4	3,65	220,44,221,219,189	220	C17H16	Phenanthrene, 2,3,5-trimethyl-	x	x	-	-	-
	60	4,1	220,205,104,202,101	220	C17H16	Phenanthrene, 2,3,5-trimethyl-	x	x	-	-	-
	61,1	4,75	216,215,108,213,95	216	C17H12	isomer Pyrene, methyl-	-	x	x	-	-
	61,3	4,7	216,215,95,217,43	216	C17H12	Pyrene, 1-methyl-	x	x	x	-	-
	64,2	4,6	230,44,215,43,229	230	C18H14	isomer of Pyrene, dimethyl-	x	x	-	-	-
	64,5	4,7	230,215,231,113,229	230	C18H14	Pyrene, 1,3-dimethyl-	x	x	-	-	-
	65,1	4,85	230,229,231,101,40	230	C18H14	isomer of Pyrene, dimethyl-	x	x	-	-	-
	65,4	4,85	230,231,229,201,106	230	C18H14	isomer of Pyrene, dimethyl-	x	x	-	-	-

[a] NA non assigned, [b] x present, – absent

2023

RAQUEL DE ROCHA MARQUES

ALLIGATORING: AN INVESTIGATION INTO PAINT FAILURE AND LOSS OF IMAGE INTEGRITY IN 19TH CENTURY OIL PAINTINGS

UNIVERSIDADE NOVA DE LISBOA
OMNIS CIVITAS CONTRA SE DIVISA NON STABIT