The Study of Lead White Oil Paints
A molecular approach to the whites of Amadeo de Souza-Cardoso

MARTA GONÇALVES FÉLIX DE OLIVEIRA CAMPOS

Dissertação apresentada na faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa para obtenção de grau de Mestre em Conservação e Restauro

Orientador:
Prof. Doutora Maria João Melo

Co-orientadores:
Prof. Doutora Leslie Carlyle
Prof. Doutora Márcia Vilarígues

Monte de Caparica
2010
Agradecimentos

Gostaria de deixar os meus sinceros agradecimentos à Professora Doutora Maria João Melo, à Professora Doutora Márcia Vilarigues e à Professora Doutora Leslie Carlyle pela orientação, incentivo e dedicação durante todo o trabalho desenvolvido.

Ao Professor Doutor Carlos Sá e ao Doutor Rui Rocha do Centro de Materiais da Universidade do Porto (CEMUP) agradeço o apoio, profissionalismo e esclarecimentos em análises de Microscopia Eletrónica de Varredura (SEM), e ao Professor Doutor João Lopes do Laboratório de Química Analítica e Físico-Química da Faculdade de Farmácia da Universidade do Porto (FF-UP) agradeço o acompanhamento constante na realização e compreensão de Análises de Componentes Principais (PCA).

Muito agradeço aos meus colegas de laboratório, de trabalho e de mestrado, Dr." Vanessa Otero, Dr." Ana Isabel Pereira, Eng." Catarina Miguel, Dr." Sara Babo, Dr." Joana Pedroso, Dr." Joana Lia Ferreira, Dr." Cristina Montagner, Dr." Ana Margarida Silva, Dr. Diogo Sanches, Dr. Pedro Alves e Dr." Mathilda Larsson pelo acompanhamento, ajuda, dicas preciosas e discussões esclarecedoras.

À minha família agradeço todo o incentivo, apoio incondicional e guarida sempre que foi necessária em deslocações.

Aos meus amigos deixo um profundo agradecimento por todo o apoio, em especial à Ana Pedro pelo incentivo incansável e eterna paciência em aturar-me ao longo deste processo.

A todos vós, o meu sincero obrigada.
Ao meu pai.
Sumário

A dissertação apresenta um estudo de tintas a óleo com pigmento branco de chumbo com uma abordagem multi-analítica para a caracterização dos seus componentes e como estes se relacionam com a sua degradação para conseguir a sua identificação em amostras reais.

Estudos anteriores das obras de Amadeo de Souza-Cardoso revelavam o avançado estado de degradação observado nas suas tintas de branco de chumbo. Com base nas mais recentes investigações na caracterização de matrizes lipídicas de aglutinantes pictóricos foram reproduzidas tintas a óleo com pigmento branco de chumbo de acordo com receitas históricas do século XIX. Estas reconstruções foram depois utilizadas como referências para seguir o envelhecimento da matriz do óleo, através de Micro-Espectroscopia de Infravermelhos (µ-FITR), e para a caracterização do pigmento de acordo com as consequências que o processo de manufactura tem nas suas propriedades morfológicas, através de Microscopia Eletrónica de Varredura Ambiental (ESEM).

Os dados obtidos através de FTIR foram posteriormente processados através de uma abordagem quimiométrica com Análise de Componentes Principais (PCA) para desenvolver uma nova metodologia de diferenciação do tipo de óleo utilizado, focando os mais importantes óleos secativos – linho e papoila.

Uma constante preocupação na conservação de quadros a óleo é a alteração cromática que ocorre ao longo dos tempos, que se pode dever a diversos factores. Como estudo colorimétrico complementar, e usando as reconstruções de tintas a óleo mencionadas, seguiu-se a influência da exposição ou ausência de luz, elucidando o que poderá ser feito para reverter estes efeitos sem qualquer acção directa na superfície da tinta.
Abstract

The present dissertation focuses on the study of lead white oil paints, relying on a multi-analytical approach to characterize their components, how they relate to its degradation and to assess the issue of identification of such components in real paint samples.

Having one of the most critically acclaimed Portuguese painters as a starting point, previous studies of Amadeo de Souza-Cardoso works stressed the advanced degradation observed in his lead white oil paints. Based on state of the art research in the characterization of Ipidic binding media, sets of lead white oil paints were manufactured according to 19th century recipes, aiming for historical accuracy. These reconstructions were then used as reference samples to follow up the aging of the oil matrix, using micro-Fourier transformed infrared spectroscopy (μ-FTIR), and to characterize the pigment based on the consequences that its manufacturing processes have had on its properties and morphology, by environmental scanning electron microscopy (ESEM).

A chemometric approach to the FTIR results, using principal component analysis (PCA), is applied to look further into the spectral data and reach new grounds in the differentiation of the type of oil in the paint, focussing on the most important drying oils - linseed and poppy seed.

A constant concern in oil paintings is the colour changes they undergo through age, which may be due to many factors. As a side study, and using the oil paint reconstructions made, a colourimetric follow up of the influence of light and darkness offers an insight to what can be done to revert this effect without any direct action on the paint surface (results are presented in Appendix III. v, page 86).
<table>
<thead>
<tr>
<th>Abreviaturas e Acrónimos</th>
</tr>
</thead>
<tbody>
<tr>
<td>μm</td>
</tr>
<tr>
<td>cm</td>
</tr>
<tr>
<td>EDX</td>
</tr>
<tr>
<td>ESEM</td>
</tr>
<tr>
<td>μ-FTIR</td>
</tr>
<tr>
<td>ICDD</td>
</tr>
<tr>
<td>PCA</td>
</tr>
<tr>
<td>XRD</td>
</tr>
</tbody>
</table>
Índice de Matérias

Agradecimentos 2
Dedicatória 3
Sumário 4
Abstract 5
Abreviautas e Acrónimos 6
Índice de Matérias 7
Índice de Figuras 9
Índice de Tabelas 14

1 Introduction 15
1.1 The Artist: Amadeo de Souza-Cardoso 15
1.2 The Pigment: Lead White 16
1.3 The Oils: 18
1.3.1 Definition 18
1.3.2 From Drying to Degradation 19

2 Results and Discussion 21
2.1 Lead White and Barium Sulfate 22
2.1.1 Fourier Transform Infrared Spectroscopy (FTIR) 22
2.1.2 Scanning Electron Microscopy (ESEM-EDX) 24
2.2 Oils and Oil Paint 27
2.2.1 Micro-Fourier Transform Infrared Spectroscopy (μ-FTIR) 27
2.2.2 Principal Component Analysis (PCA) 33

3 Conclusions 42
Anexos

I. Methods and Materials
   i) Oil Paint Reconstructions

II. Experimental Design
   i) Fourier Transform Infrared Spectroscopy (FTIR)
   ii) Principal Component Analysis (PCA)
   iii) Scanning Electron Microscopy (ESEM-EDX)
   iv) Colourimetry

III. Results
   i) FTIR
      - Spectra of powdered pigments
      - Spectra of Oils
      - Spectra of Lead White Oil Paint Reconstructions
      - Spectra from previous studies, used for PCA
   ii) PCA
      - Reference samples
      - Silva Porto
      - Tomás d’Anunciação
      - Gustave Courbet
   iii) ESEM-EDX
   iv) XRD
   v) Colourimetry
Índice de Figuras

<table>
<thead>
<tr>
<th>Número</th>
<th>Descripción</th>
<th>Página</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Amadeo de Souza-Cardoso, Manhufe [1913], Fundação Calouste Gulbenkian, Espólio ASC-BA: ASC 03/39</td>
<td>15</td>
</tr>
<tr>
<td>1.2</td>
<td>Hydrocerrusite unit cell</td>
<td>16</td>
</tr>
<tr>
<td>1.3</td>
<td>Shed for stacking the lead-filled jars</td>
<td>17</td>
</tr>
<tr>
<td>1.4</td>
<td>Lead rolls after the transformation into lead white, image from the HART project</td>
<td>17</td>
</tr>
<tr>
<td>1.5</td>
<td>The triglycerides are the building blocks of a drying oil matrix. The typical fatty acids present in triglycerides are here highlighted after hydrolysis – linoleic (a), linolenic (b) and stearic (c) – as well as the glycerol (d)</td>
<td>18</td>
</tr>
<tr>
<td>1.6</td>
<td>Shematic model of the drying mechanism as presented by Boon et al. [18]: a) oil matrix before drying; b) after drying; c) during maturation and degradation</td>
<td>19</td>
</tr>
<tr>
<td>2.1</td>
<td>Infrared spectra for Lead White pigment produced by the traditional Dutch process (top) and a modern Lead White (bottom). On the right is depicted a selected region of the spectrum from 1700 to 1300 cm(^{-1}) for a detailed analysis of the carbonate band</td>
<td>23</td>
</tr>
<tr>
<td>2.2</td>
<td>ESEM Images in back-scattering mode (BSED) of oil paint cross-sections - with 100(\mu)m scale: (a) Modern Lead White with 25% BaSO(_4), (b) Dutch Lead White with 25% BaSO(_4), (c) White micro-sample from Amadeo’s Mucha Painting; and with a 10(\mu)m scale: (d) Modern Lead White with 25% BaSO(_4), (e) Dutch Lead White with 25% BaSO(_4), (f) White micro-sample from Amadeo’s Mucha Painting</td>
<td>26</td>
</tr>
<tr>
<td>2.3</td>
<td>Energy-dispersive X-ray (EDX) spectra of Zone 1 corresponding to the BaSO(_4) and Zone 2 corresponding to the lead white pigment</td>
<td>27</td>
</tr>
<tr>
<td>2.4</td>
<td>Infrared spectra for a lead white paint with linseed oil after 90 hours of drying. On the left, the linseed oil used was untreated (LZK) and on the right the oil was previously heated at 300°C (LZH300K)</td>
<td>29</td>
</tr>
<tr>
<td>2.5</td>
<td>Second derivative analysis of the infrared spectra of for a lead white paint with linseed oil after 90 hours of drying. On the left, the linseed oil used was untreated (LZK) and on the right the oil was heated at 300°C (LZH300K)</td>
<td>30</td>
</tr>
<tr>
<td>2.6</td>
<td>Infrared spectra for a lead white paint with linseed oil (LZH150K) after 14 days of drying and corresponding 2(^{nd}) derivate. The linseed oil used was previously heated at 150°C</td>
<td>31</td>
</tr>
<tr>
<td>2.7</td>
<td>Infrared spectra for a lead white paint with linseed oil (LZH150K) after 280 days of drying and corresponding 2(^{nd}) derivate. The linseed oil was previously heated at 150°C</td>
<td>31</td>
</tr>
</tbody>
</table>
2.8 Infrared spectra for a lead white paint with linseed oil naturally aged for 11 years (ZH150K – from the Molart Fellowship [32]) and the corresponding 2\textsuperscript{nd} derivate. The linseed oil used was previously heated at 150\textdegree C

2.9 Calibration plot of the Principal Component Analysis of the infrared data of both sets of reference samples: oils and lead white oil paints, naturally aged for 280 days

2.10 Principal component analysis of the infrared spectra between 3100-2800 cm\textsuperscript{-1} for lead white paints with linseed oil, artificially aged (samples from the HART Project)

2.11 Principal component analysis of the infrared spectra of micro-samples from Amadeo de Souza-Cardozo’s paintings. Analysis of the section of the spectra between 3100-2850 cm\textsuperscript{-1}

2.12 Analysis of the three principal components (3-dimensional plot) of the infrared spectra of micro-samples from Amadeo de Souza-Cardozo’s paintings. Analysis of the section of the spectra between 3100-2850 cm\textsuperscript{-1}

2.13 Principal component analysis of the infrared spectra of micro-samples from Amadeo de Souza-Cardozo’s paintings. Analysis of the section of the spectra between 3010-2940 cm\textsuperscript{-1}

2.14 Principal component analysis of the infrared spectra of micro-samples from Amadeo de Souza-Cardozo’s paint tubes. Analysis of the section of the spectra between 3100-2850 cm\textsuperscript{-1}

2.15 Principal component analysis of the infrared spectra of micro-samples from Amadeo de Souza-Cardozo’s paint tubes. Analysis of the section of the spectra between 3010-2940 cm\textsuperscript{-1}

2.16 Principal component analysis of the infrared spectra of the micro-samples taken from Silva Porto’s paint box. Analysis of the section of the spectra between 3010-2940 cm\textsuperscript{-1}

Al.1 Materials and procedures for the preparation of an historically accurate oil paint: (a) – Oil presser with filters; (b) – Freshly pressed oil; (c) – Work Bench with marble slab and mortar, palette knives and drying oil; (d) – Grinding the oil with the pigment; (e) – Final product: the paint

Al.1 Scheme of the melinex® guide used for colourimetric readings; Melinex® placed on one of the artist’s boards

AlII.1 Infrared spectra of lead white pigment produced by the traditional Dutch process

AlII.2 Infrared spectra of a modern lead white pigment

AlII.3 Infrared spectra of barium sulfate pigment

AlII.4 Infrared spectra for unprocessed linseed oil (LZ) at 0 hours, 24 hours and 1 week into the drying (right) and the corresponding 2\textsuperscript{nd} derivate (left)

AlII.5 Infrared spectra for linseed oil treated with litharge (LA-2) at 0 hours, 24 hours and 1 week into the drying (right) and the corresponding 2\textsuperscript{nd} derivate (left)

AlII.6 Infrared spectra for poppy oil treated with litharge (PA-2) at 0 hours, 24 hours and 1 week into the drying (right) and the corresponding 2\textsuperscript{nd} derivate (left)
All.7 Infrared spectra for untreated poppy oil (PZ) at 24 hours, 1 week and 6 weeks into the drying (right) and the corresponding 2nd derivative (left)

All.8 Infrared spectra for lead white paint with untreated linseed oil (LZK) at 14 and 280 days into the drying, and a matching sample naturally aged for 11 years, Molart Fellowship [32] (right), and corresponding 2nd derivatives (left)

All.9 Infrared spectra for lead white paint with linseed oil heated at 150°C (LZH150K) at 14 and 280 days into the drying, and a matching sample naturally aged for 11 years, Molart Fellowship [32] (right), and corresponding 2nd derivatives (left)

All.10 Infrared spectra for lead white paint with linseed oil heated at 300°C (LZH300K) at 14 and 280 days into the drying, and a matching sample naturally aged for 11 years, Molart Fellowship [32] (right), and corresponding 2nd derivatives (left)

All.11 Infrared spectra for lead white paint with linseed oil treated with litharge (LA-2K) at 14 and 280 days into the drying, and a matching sample naturally aged for 11 years, Molart Fellowship [32] (right), and corresponding 2nd derivatives (left)

All.12 Infrared spectra for lead white paint with untreated poppy oil (PZK) at 14 and 280 days into the drying (right), and corresponding 2nd derivatives (left)

All.13 Infrared spectra for lead white paint with poppy oil heated at 150°C (PZH150K) at 14 and 280 days into the drying (right), and corresponding 2nd derivatives (left)

All.14 Infrared spectra for lead white paint with poppy oil heated at 300°C (PZH300K) at 14 and 280 days into the drying (right), and corresponding 2nd derivatives (left)

All.15 Infrared spectra for lead white paint with poppy oil treated with litharge (PA-2K) at 14 and 280 days into the drying (right), and corresponding 2nd derivatives (left)

All.16 Infrared spectra of a white micro-sample from the painting 86P19 by Amadeo de Souza-Cardoso

All.17 Infrared spectra of a white micro-sample from the painting 86P23 by Amadeo de Souza-Cardoso

All.18 Infrared spectra of a white micro-sample from the painting 91P217 by Amadeo de Souza-Cardoso

All.19 Infrared spectra of a white micro-sample from the painting 87P158 by Amadeo de Souza-Cardoso

All.20 Infrared spectra of a white micro-sample from the painting 91P220 by Amadeo de Souza-Cardoso

All.21 Infrared spectra of a white micro-sample from the painting 91P225 by Amadeo de Souza-Cardoso

All.22 Infrared spectra of a white micro-sample from the painting CP158 by Amadeo de Souza-Cardoso

All.23 Infrared spectra of a white micro-sample (B1) from the painting Mucha by Amadeo de Souza-Cardoso

All.24 Infrared spectra of a white micro-sample (s3) from the painting Guitarr by Amadeo de Souza-Cardoso
Infrared spectra of a white micro-sample (s2) from the painting *Guitarra* by Amadeo de Souza-Cardoso

Infrared spectra of a white micro-sample taken from Amadeo de Souza-Cardoso's paint box

Infrared spectra of a cadmium red oil paint tube (ASC3) belonging to Amadeo de Souza-Cardoso

Infrared spectra of a zinc white oil paint tube (ASC8) belonging to Amadeo de Souza-Cardoso

Infrared spectra of a zinc white oil paint tube (ASC8 - sample: novoB) belonging to Amadeo de Souza-Cardoso

Infrared spectra of a zinc white oil paint tube (ASC8 - sample: a2) belonging to Amadeo de Souza-Cardoso

Infrared spectra of a zinc white oil paint tube (ASC8 - sample: 2D) belonging to Amadeo de Souza-Cardoso

Infrared spectra of a cobalt violet oil paint tube (ASC13) belonging to Amadeo de Souza-Cardoso

Infrared spectra of a cobalt blue oil paint tube (MG4) belonging to Amadeo de Souza-Cardoso

Infrared spectra of an ivory black oil paint tube (MG17) belonging to Amadeo de Souza-Cardoso

Infrared spectra of an ivory black oil paint tube (MG17 - sample: a1) belonging to Amadeo de Souza-Cardoso

Infrared spectra of a blue micro-sample (azul) taken from Silva Porto’s paint box

Infrared spectra of a white micro-sample (branco) taken from Silva Porto’s paint box

Infrared spectra of a blue micro-sample (Amora-azul) taken from the painting *Vista de Amora*, by Tomás d’Anunciação

Infrared spectra of a white micro-sample (Amora-b1) taken from the painting *Vista de Amora*, by Tomás d’Anunciação

Infrared spectra of a white micro-sample (Amora-b2) taken from the painting *Vista de Amora*, by Tomás d’Anunciação

Infrared spectra of a blue micro-sample (azul) taken from the painting *Floresta Fechada*, by Gustave Courbet

Infrared spectra of a micro-sample form the preparation layer (preparação) taken from the painting *Floresta Fechada*, by Gustave Courbet

Principal component analysis of the infrared spectra of lead white oil paints naturally aged for 11 years (Molart Fellowship [32]). Analysis of the section of the spectra between 3100-2850 cm⁻¹
Principal component analysis of the infrared spectra of lead white oil paints artificially aged (HART Project [13]). Analysis of the section of spectra between 3100-2850 cm⁻¹

Principal component analysis of the infrared spectra of the micro-samples taken from Silva Porto’s paint box. Analysis of the section of the spectra between 3100-2850 cm⁻¹

Analysis of the three principal components (3-dimensional plot) of the infrared spectra of micro-samples taken from Silva Porto’s paint box. Analysis of the section of the spectra between 3100-2850 cm⁻¹

Principal component analysis of the infrared spectra of the micro-samples taken from the painting Vista de Amora, by Tomás d’Anunção. Analysis of the section of the spectra between 3100-2850 cm⁻¹

Analysis of the three principal components (3D plot) of the infrared spectra of micro-samples taken from the painting Vista de Amora, by Tomás d’Anunção. Analysis of the section of the spectra between 3100-2850 cm⁻¹

Principal component analysis of the infrared spectra of the micro-samples taken from the painting Vista de Amora, by Tomás d’Anunção. Analysis of the section of the spectra between 3100-2850 cm⁻¹

Analysis of the three principal components (3D plot) of the infrared spectra of micro-samples taken from the painting Vista de Amora, by Tomás d’Anunção. Analysis of the section of the spectra between 3010-2940 cm⁻¹

Principal component analysis of the infrared spectra of the micro-samples taken from the painting Floresta Fechada, by Gustave Courbet. Analysis of the section of the spectra between 3100-2850 cm⁻¹

Analysis of the three principal components (3D plot) of the infrared spectra of micro-samples taken from the painting Floresta Fechada, by Gustave Courbet. Analysis of the section of the spectra between 3100-2850 cm⁻¹

Principal component analysis of the infrared spectra of the micro-samples taken from the painting Floresta Fechada, by Gustave Courbet. Analysis of the section of the spectra between 3010-2940 cm⁻¹

Analysis of the three principal components (3D plot) of the infrared spectra of micro-samples taken from the painting Floresta Fechada, by Gustave Courbet. Analysis of the section of the spectra between 3010-2940 cm⁻¹

X- X-Ray Diffraction spectra for a traditional Dutch lead white (supplier: Jeff Seynave, HART Project) on the left; and of a modern lead white (supplier: Kremer Pigmente®) on the right

X-ray diffraction spectra of traditional vs. modern lead white with reference values for lead carbonate and basic lead carbonate

Evolution of the b* values over natural aging
Índice de Tabelas

1.1 Representative fatty acid composition of the most common drying oils used for traditional oil painting 19
2.1 Detailed list of oil paint reconstructions used as reference samples 21
2.2 Characteristic infrared absorptions for lead carbonate vs. basic lead carbonate 23
2.3 Morphology of the lead white and barium sulfate pigments 25
2.4 Characterization of the infrared absorption bands for a lead white oil paint 28
2.5 Main results for the identification of the oil binder in real oil paint samples by principal component analysis of the C-H stretching region of the infrared spectra 39
AII.1 ESEM Images acquired at 1000x, 4000x and 25000x magnification, for the reference samples and Amadeo’s Mucha painting sample B1 84
AII.2 Colour measurements in the L*a*b* system, for a lead white paint with untreated linseed oil (LZK) 90
AII.3 Colour measurements in the L*a*b* system for a lead white paint with linseed oil heated at 150°C (LZH150K) 90
AII.4 Colour measurements in the L*a*b* system for a lead white paint with linseed oil heated at 300°C (LZH300K) 91
AII.5 Colour measurements in the L*a*b* system for lead white paint with linseed oil treated with litharge (LA-2K) 91
AII.6 Colour measurements in the L*a*b* system for a lead white paint with untreated poppy oil (PZK) 92
AII.7 Colour measurements in the L*a*b* system for a lead white paint with poppy oil heated at 150°C (PZH150K) 92
AII.8 Colour measurements in the L*a*b* system for a lead white paint with poppy oil heated at 300°C (PZH300K) 93
AII.9 Colour measurements in the L*a*b* system for lead white paint with poppy oil treated with litharge (PA-2K) 93
1. Introduction

1.1 The Artist: Amadeo de Souza-Cardoso

Amadeu Ferreira de Sousa Cardoso was born on November 14th 1887 in Manhufe, Amarante. After dropping out of Law in Coimbra, he was admitted at the Real Academia de Belas-Artes in Lisbon. As soon as he graduated in 1906, on the day of his 19th birthday, he went to Paris to study architecture in the École des Beaux-Arts [1]. Once in Monparnasse, where he lived throughout his eight year stay in Paris, he soon realized that the universe of experimentation lied in paintings and sculpture. In 1907 he began his journey as a painter, influenced by the retrospective exhibition of Cézanne held at the Salon d’Automne and by the Kahnweiler Gallery where paintings by Braque, Picasso, Van Dongen, Juan Gris, André Derain and Vlaminck were shown [1,2].

He traveled around Britain, Normandy, spends some months in Brussels and traveled across Spain on one of his journeys back to Portugal, keeping close contacts with the artistic and intellectual milieu and establishing his reputation as one who is in a constant quest for originality, reflected in the plurality of his work. In 1911 he showed some of his work in the Salon des Indépendants, in Paris, bringing him closer to artists such as Amedeo Modigliani, Constantin Brancusi, Alexander Archipenko, Juan Gris and the couple Robert and Sonia Delaunay. In 1914 he met with Antoni Gaudí in Barcelona, he then went to Madrid where he was faced with the beginning of World War I. He decided to go back to Portugal, where in 1916 he held an exhibition entitled “Abstraccionismo” with 114 paintings, regarded with novelty as well as some scandal [2,3].

Subsequently Amadeo explores cubism, abstractionism and expressionism and in his last paintings he experiments with new shapes and techniques such as collages as well.
as other forms of artistic expression. On the 25th of October 1918, he falls victim to the Spanish flu, which hit Europe during World War I, and died at the early age of 30 [3].

1.2 The Pigment: Lead White

"Lead White is, historically, the most important of all white pigments"[4]. By its current definition, lead white refers to lead carbonate hydroxide, or basic lead carbonate, with the formula 2PbCO₃·Pb(OH)₂, which is the chemical equivalent of the natural occurring mineral hydrocerrusite. Its structure is considered to be made up of two layers of lead carbonate - PbCO₃ - with one of lead hydroxide - Pb(OH)₂ – sandwiched between them [5].

Figure 1.2 illustrates the crystalline structure as presented by Bissengaliyeva [6] and based on previous crystallographic and diffraction studies [5,7]. This atomic arrangement is closely related to the other published structures of lead carbonate hydroxide and can be viewed as a sequence of the layers described above: layer A composed of Pb and CO₃ and layer B composed of Pb and OH, in this model the stacking sequence would be ...BAABAA... [5,7]. The double layer AA forms a structural backbone, repeating a slab of the cerrusite structure and acting as an ‘anchor unit’. The disorder in layer B is probably due to the long-range order built from the somewhat similar layers A and B, but of different density. This layered crystal structure may explain some physical properties of the pigment, such as the easy spreading and high covering power, much appreciated by painters [7].

Production

Since antique times, lead white as been used as plasters, ointments, cosmetic goods and as a pigment. Its manufacture is reported by Theophrastus, Vitruvius, Pliny, Theophilus and Muratori, always maintaining the same method of manufacture by exposing metallic lead to acetic acid fumes, named the dry process [8, 9, 10].

According to Pulsifer [8], before the 19th century lead white was produced mainly by these dry processes. Venice was an important production centre for lead white during the Middle ages, however, from the end of the sixteenth century, large-scale lead white production was introduced in Holland. As in earlier recipes, the Dutch used earthenware
jars, filled with a layer of vinegar on top of which lead was suspended. They optimised the process by building large stacks containing rows of lead-filled jars (figures 1.3, 1.4). The jars were covered and buried in horse dung, the fermentation of which raised the temperature and supplied the necessary carbon dioxide. The metallic lead was thus exposed to acetic acid in a carbon dioxide rich environment. The elevated temperature evaporated the acetic acid, which reacted with lead to form lead acetate, which then reacted with carbon dioxide to form basic lead carbonate. The lead white was then beaten off the rolls and processed [8,9,11,12].

![Figure 1.3 – Shed for stacking the lead-filled jars [12]](image3)

![Figure 1.4 – Lead rolls after the transformation into lead white, image from the HART project [13]](image4)

Usually a mixture of lead-containing compounds is formed, their exact proportions depending on the reaction parameters. Amongst others are formed ‘common’ basic lead carbonate or hydrocerrusite (\(2\text{PbCO}_3\cdot\text{Pb(OH)}_2\)), neutral lead carbonate (cerrusite, \(\text{PbCO}_3\)), lead acetate (\(\text{PbCH}_2\text{COOH}\)), but this can be an extremely complicated mixture of different basic lead carbonates, all with different crystal and molecular configurations [14].

In the late eighteenth century, the existence of carbon dioxide was discovered. This led to a better understanding of the formation of lead white and a more scientific approach to the stack-process became possible. In the ‘German’ process, lead was hung inside a chamber into which acetic acid fumes and carbon dioxide were introduced. Lead white produced in different manners required different grinding and cleaning processes. Stack-process and chamber-process lead whites formed a coarse, flaky powder that could still contain bits of unreached metallic lead, which had to be removed. Precipitation lead white (wet-process) had been washed during production and did not require much grinding since it consisted of fine powder [12, 14].
However the covering properties of lead white oil paints are not only dependent on the molecular formula, but at least as much on the type, shape and size of the crystals. Lead white produced from modern precipitation methods will result in small homogeneous crystals while lead white produced from metallic lead during a slow process of many weeks will give an amorphous product, that once dispersed in linseed oil appears to give a paint with better covering properties than paints made with small crystals [14].

1.3 The Oils

1.3.1 Definition

Drying oils, like linseed, walnut or poppy, are natural vegetable oils consisting of glycerol esters – triglycerides. Once hydrolysed (figure 1.5) the chains become free fatty acids – these can have between 12 and 18 carbon atoms and up to 3 unsaturations each.

![Diagram of triglycerides](image)

Figure 1.5 – The triglycerides are the building blocks of a drying oil matrix. The typical fatty acids present in triglycerides are here highlighted after hydrolysis—linoleic (a), linolenic (b) and stearic (c)—as well as the glycerol (d).

The composition and physical properties of each oil vary accordingly to its fatty acid content (Table 1.1). As will be shown, it is the unsaturations in the fatty acid chains that will propel the drying properties of these oils by playing a leading role in initializing the polymerization of the oil matrix.
Table 1.1 – Representative fatty acid composition of the most common drying oils used for traditional oil painting [15,16, 17].

<table>
<thead>
<tr>
<th></th>
<th>Linseed</th>
<th>Walnut</th>
<th>Poppy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic</td>
<td>4-10%</td>
<td>3-8%</td>
<td>9-11%</td>
</tr>
<tr>
<td>Stearic</td>
<td>2-8%</td>
<td>0.5-3%</td>
<td>1-2%</td>
</tr>
<tr>
<td>Oleic</td>
<td>10-24%</td>
<td>9-30%</td>
<td>11-18%</td>
</tr>
<tr>
<td>Linoleic</td>
<td>12-19%</td>
<td>57-76%</td>
<td>69-77%</td>
</tr>
<tr>
<td>Linolenic</td>
<td>48-60%</td>
<td>2-16%</td>
<td>3-5%</td>
</tr>
</tbody>
</table>

1.3.2 From Drying to Degradation

The drying process is a complex and continuous mechanism [16-30]. A scheme presented by Boon et al [18] illustrates (figure 1.6) the process of evolution of the oil-pigment or drier matrix, from its fresh form to the degraded state, this included the interaction with metal ions from the pigments or drier.

Figure 1.6 – Shematic model of the drying mechanism as presented by Boon et al. [18] a) oil matrix before drying; b) after drying; c) during maturation and degradation.

The initiation of oxidative chain reactions is often preceded by an induction period, due to the presence of natural antioxidants that undergo oxidation-reduction cycles, neutralizing radicals and slowing down the reactions [25]. Auto-oxidation can be influenced by external factors, such as temperature, light, radiation or the presence of transition metal ions, that will catalyze the reaction increasing the concentration of free radicals and the incorporation of oxygen by the matrix [16,17,23,25,29]. The cis double bonds present in the unsaturated fatty acids are unstable and are therefore, the most reactive centers of the molecules. They support the auto-oxidation reactions, even while present in small concentrations, forming hydroperoxides (ROOH) that respond to photo-oxidation breaking
into new reactive molecules, such as peroxide radicals (ROO·) and alcoxides (RO·), continuously forming further oxidation products – alcohols, ketones, aldehydes and carboxylic acids [16-18,20,23]. These processes are cyclic and lead to the crosslinking of the molecules to form an intricate and complex network, thus forming the polymeric matrix illustrated in figure 6b) [18,25]. Once established, this newly formed structure shows a higher stability and degradation occurs slowly, through progressive oxidation on the alkylic chains, as the film ages [14]. The hydrolysis of the initial ester of the triglyceride forms a polyanionic matrix, balanced by the positively charged metallic ions of the pigments or driers and filled with free fatty acids, diacids and glycerol – figure 6c) [21,24].

As the paint slowly ages in prolonged light exposure, with the presence of oxygen and under the influence of the metal ions, several simultaneous photodegradation reactions can occur, the radicals will continuously interact with the fatty acids, producing numerous degradation products, rendering the film increasingly sensitive to conservation treatments [20]. The metal ions play an important role in this matrix, interacting with the resulting carboxylic acids to form carboxylates, which are metallic soaps. These can migrate to the surface of the paint, creating a lot of damage and interfering with the physical stability and appearance of the painting [21, 26-30].
2. Results and Discussion

The aim of this study was to characterize oil paints and, at the same time, develop methodologies to identify and differentiate their constituents.

As a basis for that intent, historically accurate oil paint reconstructions were produced to be used as reference samples in multiple analytical approaches. For the binder, two types of oils were chosen, linseed oil and poppy seed oil, those being the most commonly used drying oils in the formulation of paints [31]. The use of the lead white pigment was due to its historical importance, wide application in oil paints throughout Europe and constant presence in Amadeo’s paintings. Although these reconstructions can be considered fairly fresh paints, with a polymeric matrix quite different from what can be found in real aged samples, they will help to distinguish between the types of oil present. Aside from the freshly prepared paints, previously made oil paint reconstructions from the Molart Report 1999 [32] and the HART Project 2005 [13] were also used as reference.

Table 2.1 - Detailed list of oil paint reconstructions used as reference samples.

<table>
<thead>
<tr>
<th>Reference Sample</th>
<th>Modern Lead White (g.)</th>
<th>Traditional Lead White (g.)</th>
<th>Linseed Oil (g.)</th>
<th>Poppy Oil (g.)</th>
<th>Percent Oil by weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Current (2009)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LZK</td>
<td>12,502</td>
<td>-</td>
<td>3,500</td>
<td>-</td>
<td>21.87</td>
</tr>
<tr>
<td>LZH150K</td>
<td>12,498</td>
<td>-</td>
<td>3,460</td>
<td>-</td>
<td>21.68</td>
</tr>
<tr>
<td>LZH300K</td>
<td>12,500</td>
<td>-</td>
<td>3,200</td>
<td>-</td>
<td>20.38</td>
</tr>
<tr>
<td>LA-2K</td>
<td>12,480</td>
<td>-</td>
<td>3,490</td>
<td>-</td>
<td>21.85</td>
</tr>
<tr>
<td>PZK</td>
<td>12,504</td>
<td>-</td>
<td>-</td>
<td>2,380</td>
<td>15.99</td>
</tr>
<tr>
<td>PZH150K</td>
<td>12,506</td>
<td>-</td>
<td>-</td>
<td>3,040</td>
<td>20.55</td>
</tr>
<tr>
<td>PZH300K</td>
<td>12,494</td>
<td>-</td>
<td>-</td>
<td>2,510</td>
<td>16.73</td>
</tr>
<tr>
<td>PA-2K</td>
<td>12,530</td>
<td>-</td>
<td>-</td>
<td>2,900</td>
<td>18.79</td>
</tr>
<tr>
<td><strong>Molart (1999)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-XK</td>
<td>25,100</td>
<td>-</td>
<td>7,300</td>
<td>-</td>
<td>22.50</td>
</tr>
<tr>
<td>M-ZK</td>
<td>25,300</td>
<td>-</td>
<td>7,200</td>
<td>-</td>
<td>23.30</td>
</tr>
<tr>
<td>M-ZH150K</td>
<td>25,100</td>
<td>-</td>
<td>7,200</td>
<td>-</td>
<td>22.20</td>
</tr>
<tr>
<td>M-ZH300K</td>
<td>25,000</td>
<td>-</td>
<td>x</td>
<td>-</td>
<td>x</td>
</tr>
<tr>
<td>M-A-2K</td>
<td>25,000</td>
<td>-</td>
<td>7,000</td>
<td>-</td>
<td>21.80</td>
</tr>
<tr>
<td>Reference Sample</td>
<td>Modern Lead White (g.)</td>
<td>Traditional Lead White (g.)</td>
<td>Linseed Oil (g.)</td>
<td>Poppy Oil (g.)</td>
<td>Percent Oil by weight (%)</td>
</tr>
<tr>
<td>------------------</td>
<td>------------------------</td>
<td>-----------------------------</td>
<td>-----------------</td>
<td>---------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>HART (2005)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KB3-11-25</td>
<td>18,760</td>
<td>-</td>
<td>6,060</td>
<td>-</td>
<td>19.50</td>
</tr>
<tr>
<td>SWAB3-11-25</td>
<td></td>
<td>3,125</td>
<td>1,432</td>
<td>-</td>
<td>10.30</td>
</tr>
<tr>
<td>B3-11</td>
<td>-</td>
<td>-</td>
<td>3,55</td>
<td>-</td>
<td>12.40</td>
</tr>
<tr>
<td>SWA-14</td>
<td>-</td>
<td>12,501</td>
<td>1,446</td>
<td>-</td>
<td>10.40</td>
</tr>
<tr>
<td>SWA14/15a</td>
<td>-</td>
<td>12,501</td>
<td>0,631</td>
<td>0,631</td>
<td>9.20</td>
</tr>
<tr>
<td>SWA-15a</td>
<td>-</td>
<td>12,502</td>
<td>-</td>
<td>1,450</td>
<td>10.40</td>
</tr>
<tr>
<td>SWA-A-2P</td>
<td>-</td>
<td>12,500</td>
<td>-</td>
<td>1,767</td>
<td>12.40</td>
</tr>
<tr>
<td>SWA-AH2L</td>
<td>-</td>
<td>12,500</td>
<td>1,211</td>
<td>-</td>
<td>8.80</td>
</tr>
<tr>
<td>SWA-AH2P</td>
<td>-</td>
<td>12,500</td>
<td>-</td>
<td>1,605</td>
<td>11.40</td>
</tr>
<tr>
<td>SWA-POUT</td>
<td>-</td>
<td>12,500</td>
<td>-</td>
<td>2,312</td>
<td>15.60</td>
</tr>
<tr>
<td>SWA01D*</td>
<td>-</td>
<td>12,500</td>
<td>1,030</td>
<td>-</td>
<td>7.60</td>
</tr>
<tr>
<td>SWA11D*</td>
<td>-</td>
<td>12,500</td>
<td>1,400</td>
<td>-</td>
<td>10.10</td>
</tr>
</tbody>
</table>

**Legend:**
- L, P – Linseed or Poppy Oils
- Z – Untreated Oil
- X – Water washed Oil
- H150, H300 – Oils Heated at 150 and 300°C
- A-2 – Oil dried with litharge
- K – Kremer Lead White
- M – MoLart Samples
- SWA – Dutch Lead White (Seynæve Water Washed)
- 14 – Linseed Oil
- 15a – Poppy Oil
- AH2 – Oil dried with litharge under heat
- POUT – Poppy Oil Untreated
- 01 – Water washed Linseed Oil
- 11 – Untreated Linseed Oil
- B3 – Barium sulfate
- 25 – percentage of barium sulfate – B3 (25%)
- * – Samples submitted to artificial aging

### 2.1 Lead White and Barium Sulfate

#### 2.1.1 Fourier Transform Infrared Spectroscopy (FTIR)

To better understand the effect that pigments have when studying a paint, FTIR analysis on powdered samples was carried out on two types of lead white and also on barium sulfate, an extender commonly added to lead white oil paints since the 19th century [31]:

- Traditional Dutch Process Lead White (HART Project, Seynæve Lead White [13])
- Modern Lead White (Kremer Pigmente®)
- Barium Sulfate (Daniel Smith® Barytes)

Since the lead white pigment’s composition is usually a combination of carbonates – primarily basic lead carbonate, with a small percentage of the neutral carbonate [14] – all the absorption bands attributed to each carbonate, or a combination of them, are expected
to show in the Traditional Dutch Process and Modern lead white samples. The differences in the infrared absorptions between the carbonates are listed in Table 2.2.

### Table 2.2 – Characteristic infrared absorptions for lead carbonate vs. basic lead carbonate [4,6,19,20].

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Intensity</th>
<th>Wavenumber (cm⁻¹)</th>
<th>Lead Carbonate</th>
<th>Basic Lead Carbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H stretch</td>
<td>medium</td>
<td>-</td>
<td>-</td>
<td>3530</td>
</tr>
<tr>
<td>C=O stretch</td>
<td>weak</td>
<td>1735</td>
<td>1735</td>
<td></td>
</tr>
<tr>
<td>C-O stretch</td>
<td>very strong, broad</td>
<td>1435-1400</td>
<td>1400</td>
<td></td>
</tr>
<tr>
<td>CO₂ symmetric stretch</td>
<td>medium</td>
<td>1052</td>
<td>1045</td>
<td></td>
</tr>
<tr>
<td>CO₂ out of plane rocking</td>
<td>medium</td>
<td>838</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>CO₂ in plane rocking</td>
<td>strong</td>
<td>682</td>
<td>693-683</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.1 presents the spectra for the both lead white pigments and the distinct presence of a 838 cm⁻¹ absorption in the Traditional lead white, indicating a higher content of the neutral form of the carbonate, suggests that a more heterogeneous product is formed by the traditional method.

![Spectra](image)

**Figure 2.1** – Infrared spectra for Lead White pigment produced by the traditional Dutch process (top) and a modern Lead White (bottom). On the right is depicted a selected region of the spectrum from 1700 to 1300 cm⁻¹ for a detailed analysis of the carbonate band.
A modern pigment, obtained by precipitation methods, would form a more crystalline compound hence the less evident absorption of the CO$_3$ out of plane rocking, and also a narrower peak of the C-O stretch, as seen in the close up in figure 2.1. As for the Dutch process, the different carbonates reveal a broader band and the maximum value is slightly shifted to lower wavenumbers. These characteristics will also be stable and visible in the oil paints, regardless of their age.

As further characterization of both pigments, the X-Ray Diffraction results are presented in Appendix III, iv., page 87.

Barium Sulfate was included in this analysis due to its constant presence in the Amadeo’s samples previously analysed [30,33]. Nineteenth and early twentieth century oil paint formulations would often include several additives, barium sulfate being the most common in lead white oil tubes [31]. The spectrum (figure ALIII.3, Appendix III. i., page 51) shows the typical absorptions at 1186 (medium shoulder), 1120 (strong) and 1085 cm$^{-1}$ (very strong) of the sulfate (SO$_4^{2-}$) asymmetrical stretching and at 984 cm$^{-1}$ for the symmetrical stretching [34]. Two other characteristics bands around 637 and 611 cm$^{-1}$ are expected for the bending vibrations but are not visible in the spectrum due to the normalization of the collections acquired from 4000 to 650 cm$^{-1}$.

2.1.2 Scanning Electron Microscopy (ESEM-EDX)

Environmental Scanning Electron Microscopy with Energy-dispersive X-ray Spectroscopy (ESEM-EDX) analysis will enable us to differentiate between the manufacturing processes of the lead white pigment. The traditional Dutch process is known to produce a pigment with globular flakes ranging from large particles (25 µm) to very small ones (0.1 µm); as opposed to the modern precipitation methods that generate laminar structured particles of a more regular size [4,13,14].

In order to create a set of reference samples four things were taken into consideration: the process of manufacture of the pigments (traditional Dutch process and modern precipitation); the extenders present and their percentage (in this case, only barium sulfate, BaSO$_4$, was studied); the vehicle that could interfere with the readings (samples with the oil binder or simply in powder); and the angle of observation (a top view of the paint or in cross-section). They were chosen amongst the HART Project [13] samples, listed in Table 2.1.

1 For more information on the experimental setup and the ESEM-EDX analysis, see Appendix II. iii, page 50.
The different observations done on the samples proved to be very useful:

- **cross-sections**: were the best method to compare with real samples, as it was possible to clearly see the dimension, morphology and distribution of the particles in the layers;

- **top view**: although it was interesting to explore this kind of observation, since it is the visible layer and the surface that will be dealt with in conservation treatments (cleaning, consolidations, etc.), it provided misleading information regarding the composition of the mixture and particle size – the larger particles were camouflaged by smaller ones at the surface – and an occasional area of oil binder at the surface makes it hard to focus the pigments, hence making it harder to identify; one advantage seemed to be a better visualization of the particle shape, in higher resolutions each particle can be fully characterized;

- **powder**: the observation is very similar to the one in cross-section, where it is possible to see the larger particles and there is no oil interference, although with the advantage of being able to see the real shape of each particle, as in the top view observation.

It was possible to analyse the two main characteristics that can be easily recognized and help identify whether the production is achieved by the traditional Dutch stack process or by the modern method of precipitation. Starting with the particle shape, the traditional process reveals rounded particles whereas the modern presents a thin plate structure often with geometrical edges. The range in particle size is also to be considered, with the traditional process consisting of particles ranging from a very small size (0.5μm) up to quite large aggregates (20-65μm). In the samples made with the modern lead white we see a more regular size, ranging from 0.8 to 10μm.

The observations were also made on samples of barium sulphate (BaSO₄) in powder and oil paint. The results are summarized in Table 2.3.

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Particle Shape</th>
<th>Range of Particle Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modern Lead White</td>
<td>Flat; Geometrical plates</td>
<td>0.8 – 10 μm</td>
</tr>
<tr>
<td>Dutch Process Lead White</td>
<td>Round; Globular</td>
<td>0.5 – 5 μm + 25 – 65 μm</td>
</tr>
<tr>
<td>Barium Sulfate</td>
<td>Parallelepiped</td>
<td>0.2 – 25 μm</td>
</tr>
</tbody>
</table>
Figures 2.2 (a) to (f) represent two reference samples with lead white pigments from both processes and a chosen sample from one of Amadeo de Souza-Cardoso paintings, named Mucha, previously studied [30,33,35], in a scale of 100µm and 10µm (for the remaining images see table AIII.1, Appendix III. iii, page 84). The morphology of the particles found in Amadeo’s Mucha sample – (c) and (f) – closely resembles the characteristics mentioned for traditional Dutch process – (b) and (e) – and although some of the particles have a longer and more geometrical shape similar to the modern lead white – (a) and (d) –, the evident larger particles and a rounder shape even in the smaller ones leads to thinking that the pigment was manufactured by the traditional method.

Although they already exhibited distinctive morphologies, with the help of energy-dispersive x-ray spectroscopy (EDX) it was possible to undoubtedly differentiate the barium sulfate particles from the lead white pigment (figures 2.2 (d) and 2.3).


Figure 2.2 – ESEM Images in back-scattering mode (BSED) of oil paint cross-sections - with 100µm scale: (a) Modern Lead White with 25% BaSO₄, (b) Dutch Lead White with 25% BaSO₄, (c) White micro-sample from Amadeo’s Mucha Painting and with a 10µm scale: (d) Modern Lead White with 25% BaSO₄, (e) Dutch Lead White with 25% BaSO₄, (f) White micro-sample from Amadeo’s Mucha Painting.
2.2 Oils and Oil Paint

A series of paints were manufactured according to 19th century recipes as described in the Molart Report [32] in order to achieve historical accuracy for a better understanding of the behaviour of drying oil matrixes and the characterization of its constituents. For the first time, infrared data was submitted to principal component analysis to assess the discrimination between the different types of oils, using the current reconstructions as a calibration and former reconstructions to test the method. Five sets of real paint samples were analysed to determine their composition: several paintings from Amadeo de Souza-Cardoso; Amadeo’s oil paint tubes; Silva Porto’s paint box; Tomás d’Anunciação “Vista de Amora” painting from 1852 and Gustave Courbet’s “Floresta Fechada” from the mid 19th century.

2.2.1 Micro-Fourier Transform Infrared Spectroscopy (μ-FTIR)

→ Oils

In all the spectra (figures AII.4 – AII.7, Appendix II.iii, pages 52 to 55) the left part is dominated by a series of aliphatic vibrations caused by the large amount of CH₂ and CH₃ groups in the fatty acids. The broad band at around 3400 cm⁻¹ can indicate the presence of alcohol or hydroperoxide vibrations – both products of oxidation of the oil [20,23].

It is reported [18] that an increased absorption in the background of the spectral region between 3200-3000 cm⁻¹ can be caused by carboxylic acids. Their presence is confirmed by the absorption band at 1414 cm⁻¹ and the broadening of the carbonyl band.
There is a visible shift to lower wavenumbers of the peak attributed to the C=O bond of the ester (from 1745 to ~1730 cm⁻¹) and a broadening on its right side, due to the presence of carboxylic acids (1710 cm⁻¹), as mentioned before, produced during the drying process – and a shoulder at around 1655 cm⁻¹, assigned to the C=C bond of remaining unsaturations. Other types of carbonyls (e.g., ketones, aldehydes, lactones and anhydrides) might also contribute to the broadening of the carbonyl band [20].

The ester triplet shows at ~1240, 1170 and 1099 cm⁻¹, the following peak at ~977 cm⁻¹ suggests the cis double bonds visible at 724 cm⁻¹ are being isomerized to trans configuration [20].

→ Lead White Oil Paints

The absorption bands expected for lead white oil paint samples are listed in Table 2.4 in approximate values, according to the literature [16,19,20,21,23,29], identifying the peaks attributed to the oil matrix and the lead white pigment.

Table 2.4 – Characterization of the infrared absorption bands for a lead white oil paint.

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Assignment</th>
<th>Intensity</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>3540</td>
<td>O-H stretch</td>
<td>medium</td>
<td>Pigment – Hydroxyl</td>
</tr>
<tr>
<td>3010</td>
<td>C=O-H (cis) stretch</td>
<td>medium</td>
<td>Oil – Fatty acid</td>
</tr>
<tr>
<td>2958</td>
<td>CH₃ stretch</td>
<td>shoulder</td>
<td>Oil – Fatty acid</td>
</tr>
<tr>
<td>2926</td>
<td>CH₃ stretch</td>
<td>strong</td>
<td>Oil – Fatty acid</td>
</tr>
<tr>
<td>2855</td>
<td>CH₃ stretch</td>
<td>medium</td>
<td>Oil – Fatty acid</td>
</tr>
<tr>
<td>1745</td>
<td>C=O stretch</td>
<td>strong</td>
<td>Oil – Ester bond</td>
</tr>
<tr>
<td>1745</td>
<td></td>
<td>strong</td>
<td>Pigment – Carbonate</td>
</tr>
<tr>
<td>1655</td>
<td>C=C</td>
<td>weak</td>
<td>Oil – Fatty acid</td>
</tr>
<tr>
<td>1464</td>
<td>CH₃ asymm. bend</td>
<td>medium</td>
<td>Oil – Fatty acid</td>
</tr>
<tr>
<td>1456</td>
<td>CH₂ scissors</td>
<td>medium</td>
<td>Oil – Fatty acid</td>
</tr>
<tr>
<td>1418</td>
<td>(CH₃)-CO-O- wag</td>
<td>weak</td>
<td>Oil – Fatty acid</td>
</tr>
<tr>
<td>1400</td>
<td>C-O stretch</td>
<td>very strong, broad</td>
<td>Pigment – Carbonate</td>
</tr>
<tr>
<td>1374</td>
<td>CH₃ wag (umbrella mode)</td>
<td>weak</td>
<td>Oil – Fatty acid</td>
</tr>
<tr>
<td>1239</td>
<td></td>
<td>medium</td>
<td></td>
</tr>
<tr>
<td>1164</td>
<td>C=O</td>
<td>strong</td>
<td>Oil – Ester triplet</td>
</tr>
<tr>
<td>1100</td>
<td></td>
<td>medium</td>
<td></td>
</tr>
<tr>
<td>1045</td>
<td>CO₂ symmetric stretch</td>
<td>medium</td>
<td>Pigment – Carbonate</td>
</tr>
<tr>
<td>977</td>
<td>C=O-H (trans) bend</td>
<td>very weak</td>
<td>Oil – Fatty acid</td>
</tr>
<tr>
<td>847</td>
<td>CO₂ out of plane</td>
<td>very weak</td>
<td>Pigment – Neutral Carbonate</td>
</tr>
<tr>
<td>722</td>
<td>CH₃ rocking</td>
<td>medium</td>
<td>Oil – Fatty acid</td>
</tr>
<tr>
<td></td>
<td>C=C-H (cis) bend</td>
<td>medium</td>
<td>Oil – Fatty acid</td>
</tr>
<tr>
<td>682</td>
<td>CO₂ in plane rocking</td>
<td>strong</td>
<td>Pigment – Carbonate</td>
</tr>
</tbody>
</table>
90 hours – the initial stages of drying

The following spectra were acquired after the paint had been drying on glass slides for 90 hours (figure 2.4). The peak around 3010 cm\(^{-1}\) is still visible in these early stages of drying since it is due to the C-H stretching of the C=CH bond, and as the C=C double bonds are among the first to break in order to start the oil matrix polymerization, this absorption will gradually diminish and eventually disappear. But the degradation that occurs during heat treatment at 300°C accelerates the drying process by providing enough energy to break the double bonds and, therefore, the peak is considerably smaller – almost not visible – compared to the untreated oil. The most intense peak is due to the C-O stretch of the carbonates present in lead white (between 1500-1300 cm\(^{-1}\)) camouflaging many absorptions attributed to the oil’s fatty acid chains.

![Figure 2.4](image)

Figure 2.4 – Infrared spectra for a lead white paint with linseed oil after 90 hours of drying. On the left, the linseed oil used was untreated (LZK) and on the right the oil was previously heated at 300°C (LZH300K) – for more details see text.

![Figure 2.5](image)

Figure 2.5 – Second derivative analysis of the infrared spectra of for a lead white paint with linseed oil after 90 hours of drying. On the left, the linseed oil used was untreated (LZK) and on the right the oil was heated at 300°C (LZH300K).
All the peaks present in the spectra correspond to the expected absorptions already described in Table 2.4, although there is a consistent peak at 847 cm\(^{-1}\) that maybe be attributed to the neutral form of the carbonate from the lead white pigment – which is a common component of lead white [4,14], as seen in the previous chapter. A shoulder in the short wavelength side of the intense carbonate band (around 1530 cm\(^{-1}\)), may already be a sign of the metal carboxylates' formation [30].

The second derivative analysis (figure 2.5) was done to define the peaks in the finger print area (1500–600 cm\(^{-1}\)), mainly those that were "camouflaged" by the strong broad peak between 1500 and 1300 cm\(^{-1}\) and to resolve the peaks from the carboxylic acid (1710 cm\(^{-1}\)) from the ester carbonyl band (1745 cm\(^{-1}\)).

In these spectra we can now clearly identify the weak absorption bands between 1470 and 1414 cm\(^{-1}\) and the carboxylate absorption at \(\sim\)1530 cm\(^{-1}\) is resolved into the peaks of the different coordination structures (approx. 1580 to 1510 cm\(^{-1}\)). Although not visible in these selected close ups, the CO\(_3\) symmetric stretch peak at 1045 cm\(^{-1}\) has been separated by the 2\(^{rd}\) derivative analysis from the ester triplet absorptions; the peak at 847 cm\(^{-1}\) attributed to the neutral form of the carbonate from the lead white pigment was resolved into two peaks at 867 and 845 cm\(^{-1}\); and the 725 cm\(^{-1}\) cis double bond peak is also visible. The 970 cm\(^{-1}\) absorption of the heated oil reveals the isomerization to the trans configuration caused by the high temperature treatment.

**Drying and Aging**

The comparison between the heights of the C-H and C=O peaks is common [20,30] in order to establish a qualitative analysis of the degradation of the initial ester, but this may not be accurate in paints prepared with lead white pigment due to the presence of an additional C=O absorption from the carbonate (CO\(_3^{2-}\)) of the pigment, especially since different amounts of lead white were added to make the paints. Furthermore, the exact amount of organic material in the light path during analysis is unknown [20] – making it impossible to ensure the pigment to oil ratio being analysed.

Figures 2.6 and 2.7 represent the IR spectra and respective second derivative of the lead white oil paint prepared for this study, with an heat treated linseed oil at 150\(^\circ\)C (LZH150K). For this set of paint, two readings are presented, followed by a lead white oil paint sample from the Molart Report (figure 2.8) with similar composition, manufactured with the same pigment and oil and has been naturally aging for 11 years.
We can follow the evolution of the drying process beginning with the disappearance of the 3010 cm$^{-1}$ absorption caused by the breakage of the C=C double bonds that characterizes the initial stages of the polymerization. The gradual increase of the absorption in the background of the spectral region between 3200-3000 cm$^{-1}$ can be caused by carboxylic acids. Close to it, at around 3400 cm$^{-1}$, a weak and broad band also emerges and that can indicate the presence of alcohol or hydroperoxide vibrations – both products of oxidation of the oil [20, 23].

Figure 2.6 – Infrared spectra for a lead white paint with linseed oil (LZH150K) after 14 days of drying and the corresponding 2$^{nd}$ derivative. The linseed oil used was previously heated at 150°C – for more details see text.

Figure 2.7 – Infrared spectra for a lead white paint with linseed oil (LZH150K) after 280 days of drying and the corresponding 2$^{nd}$ derivate. The linseed oil used was previously heated at 150°C.
Figure 2.8 – Infrared spectra for a lead white paint with linseed oil naturally aged for 11 years (ZHI50K – from the Molart Fellowship [32]) and the corresponding 2nd derivate. The linseed oil used was previously heated at 150°C.

It is noticeable early on (figure 2.7) that the broadening of the base of the C=O peak occurs towards lower wavenumbers, owing to the degradation of the initial ester present in the oil triglycerides and the resulting formation of other carbonyl species with lower absorptions, such as carboxylic acids (1710 cm⁻¹), ketones, aldehydes, lactones and anhydrides. At approximately 1530 cm⁻¹ we can identify the carboxylates that have formed with the metal ions from the lead white pigment. Even with the IR spectra alone we can clearly see a small peak forming at that wavenumber and consistently increasing until reaching a considerable size in the last spectra (figure 2.8 – 11 years old), already apart from the strong and broad band of the C-O stretch. With the second derivative analysis we can further resolve the peak and identify the several small absorptions (1628, 1553, 1531, 1524 cm⁻¹), that correspond to the different coordination structures of the lead carboxylates. The presence of multiple absorptions, ranging from 1480-1340 cm⁻¹, found in all of the above spectra, is consistent in various lead white oil paints, but they are yet to be attributed to a specific compound [20].

In Appendix III, i.e., pages 56 to 63, are all the spectra for the remaining paint sets, varying in oil composition. Distinction between the different treatments is only possible at the first stages, with the pre-polymerization of heated oils, as the differences fade with aging. Regarding the type of oil, polymerization is clearly happening early on for linseed oil paints, as expected, but using this characteristic to tell them apart in real aged samples is also not feasible, with just that approach.
2.2.2 Principal Component Analysis (PCA)

With the aim of being able to distinguish the oils as to their type (linseeds or poppy seeds) the former μ-FTIR spectra were submitted to Principal Component Analysis (PCA). For this analysis the current paint reconstructions, after 9 months of drying, as well as the oils that were used to produce them, dried for approximately 6 months, were used as reference samples to calibrate the results.

Analyzing the full spectrum of both sets of samples (4000-650 cm⁻¹), no differentiation could be established, probably due to the strong influence of the pigment’s absorptions. But since the two oils can be identified by their fatty acid content, the analysis was then performed focusing only on a section of the aliphatic region (3100-2800 cm⁻¹) of the 2ⁿᵈ derivative of the spectrum, and a clear separation between them was obtained using the first two principal components – PC1 and PC2 – adding up to a total of approximately 80% of the spectral characteristics.

The results for both sets – oils and paints – were plotted together to create a calibration space, clearly showing a propensity to have the Linseed samples (whether in oil or in paint) above the horizontal axis (PC2) and the Poppy samples below it. This space (figure 2.9) was then used to analyze the remaining sets projecting the results onto the calibration plot.

![Figure 2.9 – Calibration plot of the Principal Component Analysis of the infrared data of both sets of reference samples: unpigmented oils and lead white oil paints, naturally aged for 280 days.](image-url)
The samples from the Molart Report – that closely resemble the formulation of the current reconstructions, only using linseed oil paints and currently 11 years old – are clearly clustered in the section above the horizontal axis, making this the first step to confirm the validity of the analysis (figure AIII.43, Appendix III. ii, page 78). As for the HART samples, the results were still according to what was expected, with all the linseed oil paints clustered well above the horizontal axis whereas the poppy oil paints are below it. The paint samples prepared with a mixture of linseed and poppy oil (50-50%) can be found between the other two clusters. Since they still placed close enough to the linseed samples this could mean the distinction between mixtures and pure linseed oil paints could be ambiguous (fig. 2.10).

The groups of paints are visibly more clustered as opposed to the more scattered pattern exhibited by the oil samples. This phenomenon could be caused by the lower amount of oil present in the paint samples – the average percentage of oil in paint formulation is approx. 21% for the current reconstructions and the Molart Samples and 10% for the HART samples.

Following the tests on the calibration plot, another set of HART samples made with linseed oil, that had been artificially aged, was projected in order to establish if degraded oil matrixes could still be viable for analysis. Figure AIII.44, Appendix III, p. 78, shows that all the samples, even the most aged ones, are well clustered and placed within the calibration space for linseed oils, ensuring that degraded samples can still be discriminated.

![Principal component analysis of the infrared spectra between 3100-2800 cm⁻¹ for lead white paints with linseed oil, artificially aged (samples from the HART Project [13] – for more details see text).](image-url)

Figure 2.10 – Principal component analysis of the infrared spectra between 3100-2800 cm⁻¹ for lead white paints with linseed oil, artificially aged (samples from the HART Project [13] – for more details see text).
When analysing μ-FTIR data from real samples (the spectra can be found in Appendix III. i., page 64) the data obtained for the previously selected region of the spectra presented a few misleading results and a careful examination of the $2^{\text{nd}}$ derivative showed that the wavenumbers from 2940 to 2850 cm$^{-1}$ were contributing to the higher discrepancy. A second analysis of these samples was optimized by narrowing down the range of wavenumbers to 3010-2940 cm$^{-1}$. A new calibration was plotted using the same reference samples and the horizontal axis (PC2) is still the delimitating differentiation. The results for both sections will be presented, highlighting the similarities and differences between them.

**Amadeo de Souza-Cardoso, beginning of the 20th century**

The results obtained for Amadeo’s paintings (figure 2.11) indicate that the predominant binder for these white paints is likely poppy seed oil. Since this drying oil is known to yellow less, in comparison with linseed oil, these results are not unexpected. Some of the points projected were clearly off the calibration region and this can be due to a number of reasons: aging and degradation; additives in the paint formulation (stearates or oleates, suspension agents, etc.); a varnish layer over the paint; and possibly another type of oil or a mixture of oils.

When adding a third component to the analysis (figure 2.12), we can see that some of the samples are not in the same plane of analysis as the calibration and remaining samples. This $3^{\text{rd}}$ component, although representing only 5% of the spectra, indicates that these samples contain features not compatible with the features in calibration samples and therefore the results may not be conclusive.

![Figure 2.11 – Principal component analysis of the infrared spectra of micro-samples from Amadeo de Souza-Cardozo’s paintings. Analysis of the section of the spectra between 3100-2850 cm$^{-1}$](image-url)

- ▼ Linseed and Poppy Oils
- ★ Linseed and Poppy Oil Paints
- ● Paintings by Amadeo de Souza-Cardoso
Figure 2.12 – Analysis of the three principal components (3-dimensional plot) of the infrared spectra of microsamples from Amadeo de Souza-Cardozo’s paintings. Analysis of the section of the spectra between 3100-2850 cm\(^{-1}\)

- Linseed and Poppy Oils
- Linseed and Poppy Oil Paints
- Paintings by Amadeo de Souza-Cardoso

Figure 2.13 illustrates the results for the analysis done on the second section of the spectra, between 3010-2940 cm\(^{-1}\). The samples that were previously not in the same plane by the PC3, but laid on the linseed region are now outside the calibration region but on the poppy side of the plot, indicating, once again, that they may contain data not compatible with the calibration.

Figure 2.13 – Principal component analysis of the infrared spectra of microsamples from Amadeo de Souza-Cardozo’s paintings. Analysis of the section of the spectra between 3010-2940 cm\(^{-1}\)

- Linseed and Poppy Oils
- Linseed and Poppy Oil Paints
- Paintings by Amadeo Souza-Cardoso
As well as samples from the actual paintings, a series of paint tubes belonging to the artist were also analysed. The results (figures 2.14, 2.15) were quite consistent for both sections analysed with only one (ASC8_a2) being visibly outside the parameters. Since the same paint tube was sampled four times and only this sample showed this behaviour it is possible to assume that an experimental error in acquiring the infrared data could have occurred. As for the remaining eight paint tube samples, poppy oil seems to be the binder present in all of them except in the MG17 (Ivory Black, Winsor&Newton) which appears in the linseed oil region.

![Figure 2.14](image1)

**Figure 2.14** – Principal component analysis of the infrared spectra of micro-samples from Amadeo de Souza-Cardozo’s paint tubes. Analysis of the section of the spectra between 3100-2850 cm\(^{-1}\)

- ▼ Linseed and Poppy Oils
- ▶ Linseed and Poppy Oil Paints
- ● Oil Paint tubes belonging to Amadeo de Souza-Cardozo

![Figure 2.15](image2)

**Figure 2.15** – Principal component analysis of the infrared spectra of micro-samples from Amadeo de Souza-Cardozo’s paint tubes. Analysis of the section of the spectra between 3010-2940 cm\(^{-1}\)

- ▼ Linseed and Poppy Oils
- ▶ Linseed and Poppy Oil Paints
- ● Oil Paint Tubes belonging to Amadeo de Souza-Cardoso
**Silva Porto, late 19th century**

The results obtained by plotting both samples taken from Silva Porto’s paint box were inconclusive (figure 2.16), placing quite far from the calibration values. Again this can be caused by the presence of numerous additives that were part of the paint formulation (stearates, oleates, suspension agents, coatings, etc.), the binder used could possibly be from another origin (for example, walnut oil) or a mixture between different oils. Nonetheless, it can be concluded that some similarity between “Silva Porto azul” sample and poppy oil reference samples exists and is statistically valid, as shown in figure 2.16, for the section between 3010-2940 cm\(^{-1}\). On the other hand, based on the spectral analysis no conclusion can be drawn for the “Silva Porto branco” sample.

![Graph showing principal component analysis of infrared spectra](image)

**Figure 2.16** – Principal component analysis of the infrared spectra of the micro-samples taken from Silva Porto’s paint box. Analysis of the section of the spectrum between 3010-2940 cm\(^{-1}\).
*Tomás d’Anunciação – “Vista da Amora”, 1852*

Although this was a particularly difficult painting to analyze by μ-FTIR spectroscopy, exhibiting almost no evidence of a binding medium, three samples did have a good definition in the aliphatic region with the characteristic C-H peaks being studied here. The results are presented in figures AIII.47 and AIII.48, Appendix III. ii, page 80, and show a tendency towards a linseed oil medium, even though only one of the samples (Amora_azul) is placed within the calibration values.

Analysing the second section of the spectra (figures AIII.49, AIII.50, Appendix III. ii, page 81), the results conflict with the previous. Now in the calibration plane are the samples “Amora_b1” and “Amora_b2” and all lay in or near the poppy region.

*Gustave Courbet – “Floresta Fechada”, mid 19th century*

Analysis of the first section of the spectra (figure AIII.51, AIII.52, Appendix III. ii, page 82) shows that both samples lie in the linseed region and in the second section (figure AIII.53, AIII.54, Appendix III. ii, page 83), the only two samples viable for this analysis are neatly distributed in the calibration plot, one for each oil type. The sample from the blue area (Courbet_azul) lies in the linseed oil region and the sample from the preparation (Courbet_prep) lies in the poppy oil region. Again, some samples have a deviation in the 3rd principal component and the different results for each of the regions analysed make these results inconclusive.

The following table summarizes the results obtained for each set of real samples, according to the section of the spectra analysed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Main pigment present</th>
<th>3100-2850 cm⁻¹</th>
<th>3010-2940 cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Amadeo de Souza-Cardoso – Paintings</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>86P19</td>
<td>Lead white</td>
<td>Poppy</td>
<td>Poppy</td>
</tr>
<tr>
<td>86P23</td>
<td>Lead white</td>
<td>Poppy</td>
<td>Poppy</td>
</tr>
<tr>
<td>91P217</td>
<td>Lead white</td>
<td>Poppy</td>
<td>Poppy</td>
</tr>
<tr>
<td>87P158</td>
<td>Lead white</td>
<td>Poppy</td>
<td>Poppy</td>
</tr>
<tr>
<td>91P220</td>
<td>Lead white</td>
<td>Poppy</td>
<td>Poppy</td>
</tr>
<tr>
<td>91P225</td>
<td>Lead white</td>
<td>Linseed + o.p.3</td>
<td>o.c.</td>
</tr>
<tr>
<td>CPU158</td>
<td>Lead white</td>
<td>h. a.</td>
<td>Poppy</td>
</tr>
<tr>
<td>Mucha (B1)</td>
<td>Lead white</td>
<td>Poppy</td>
<td>Poppy</td>
</tr>
<tr>
<td>Guitarra (s3)</td>
<td>Lead white</td>
<td>Linseed + o.p.3</td>
<td>Poppy</td>
</tr>
<tr>
<td>Guitarra (s2)</td>
<td>Lead white</td>
<td>Linseed + o.p.3</td>
<td>o.c.</td>
</tr>
<tr>
<td>Caixa</td>
<td>Lead white (paint box)</td>
<td>h. a.</td>
<td>o.c.</td>
</tr>
<tr>
<td>Sample</td>
<td>Main pigment present</td>
<td>3100-2850 cm⁻¹</td>
<td>3010-2940 cm⁻¹</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------</td>
<td>----------------</td>
<td>----------------</td>
</tr>
<tr>
<td>Amadeo de Souza-Cardoso – Paint Tubes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASC3</td>
<td>Rouge Cadmium – Lefranc</td>
<td>Poppy</td>
<td>Poppy</td>
</tr>
<tr>
<td>ASC8_novo</td>
<td>Blanc de Zinc – Lefranc</td>
<td>Poppy</td>
<td>Poppy</td>
</tr>
<tr>
<td>ASC8_novoB</td>
<td>Blanc de Zinc – Lefranc</td>
<td>Poppy</td>
<td>Poppy</td>
</tr>
<tr>
<td>ASC8_a2</td>
<td>Blanc de Zinc – Lefranc</td>
<td>Poppy + o.p.3</td>
<td>o.c.</td>
</tr>
<tr>
<td>ASC8_2D</td>
<td>Blanc de Zinc – Lefranc</td>
<td>Poppy</td>
<td>Poppy</td>
</tr>
<tr>
<td>ASC13</td>
<td>Violet de Cobalt – Lefranc</td>
<td>h.a.</td>
<td>Poppy</td>
</tr>
<tr>
<td>MG4</td>
<td>Cobalt Blue – Winsor&amp;Newton</td>
<td>Poppy</td>
<td>Poppy</td>
</tr>
<tr>
<td>MG17</td>
<td>Ivory Black – Winsor&amp;Newton</td>
<td>Linseed</td>
<td>Linseed</td>
</tr>
<tr>
<td>MG17_a1</td>
<td>Ivory Black – Winsor&amp;Newton</td>
<td>Linseed</td>
<td>Linseed</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silva Porto – Paint Box</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silva Porto azul</td>
<td>Cobalt blue</td>
<td>Poppy + o.p.3</td>
<td>Poppy + o.c. + o.p.3</td>
</tr>
<tr>
<td>Silva Porto branco</td>
<td>Lead white</td>
<td>o.c. + o.p.3</td>
<td>o.c. + o.p.3</td>
</tr>
<tr>
<td>Tomás d’Anunciação – “Vista de Amora”, 1852</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amora-azul</td>
<td>Lead white</td>
<td>Linseed</td>
<td>Poppy + o.p.3</td>
</tr>
<tr>
<td>Amora-b1</td>
<td>Lead white</td>
<td>Linseed + o.p.3</td>
<td>Poppy</td>
</tr>
<tr>
<td>Amora-b2</td>
<td>Lead white</td>
<td>Linseed + o.p.3</td>
<td>Poppy + o.c.</td>
</tr>
<tr>
<td>Gustave Courbet – &quot;Floresta Fechada&quot;, mid 19th century</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Courbet azul</td>
<td>Lead white</td>
<td>Linseed + o.p.3</td>
<td>Linseed</td>
</tr>
<tr>
<td>Courbet prep</td>
<td>Lead white</td>
<td>Linseed + o.p.3</td>
<td>Poppy + o.p.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>h.a.</th>
<th>on the horizontal axis</th>
<th>Matching positive results</th>
</tr>
</thead>
<tbody>
<tr>
<td>o.c.</td>
<td>outside calibration space</td>
<td>At least 1 positive result</td>
</tr>
<tr>
<td>o.p.3</td>
<td>in calibration but out of plane by PC3</td>
<td>Inconclusive results</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Contradictory results</td>
</tr>
</tbody>
</table>

As a new approach to the differentiation of the type of oil present in real oil paint samples, the results obtained seem very promising. The best results were the ones from Amadeo’s oil paint tubes, as expected, since the degradation inside the tubes is retarded due to the lack of oxygen for the oxidation reactions, but also because no varnishes are in evidence to interfere with the reading of the aliphatic region of the infrared spectra. The results indicate that most of the paints from this set are made with poppy oil, with the exception of the Ivory Black from Winsor&Newton (MG17) which is indicated as a linseed oil paint.

A lot of matching positive results were also obtained from Amadeo’s paintings. For six of the samples (86P19, 86P23, 91P217, 87P158, 91P220, Mucha -B1) the projected results lay in the poppy oil region for the both sections analysed. The “CPU158” sample results indicated a strong tendency towards the poppy region, but for “91P225”, “Guitarra s2” and “Caixa” the results were uncertain. The “Guitarra s3” sample gave contradictory results and no attribution can be made in this case.
The analyses done on Silva Porto’s paint box, Tomás d’Anunciação’s painting and Gustave Courbet’s painting were inconclusive for now, although Courbet’s sample “Courbet_azul” could indicate the presence of a linseed oil.
3. Conclusions

Infrared Spectroscopy is one of the most important techniques in the elucidation of the polymerization and degradation processes that occur within an oil paint. A series of oils and lead white oil paints were prepared for this study in order to follow these processes, identify the degradation products and characterize each sample so that they could be used as references.

Following the aging of the oil paints and analyzing the molecular changes that occur during this process will enable us to understand the chemical influences of the pigments and the physical consequences on the paint’s properties for a better comprehension of the core of artworks.

A degradation pattern previously published [20,23,30] was observed, following the transformation of the carbonyl bond of the initial ester into carboxylic acids and then further into metal carboxylates (lead, in the case of the studied pigment). A broadening of the carbonyl band is visible within the lower wavenumbers and also a slight shift in the absorption maxima – no longer at 1745 cm\(^{-1}\) due to the absorption at 1710 cm\(^{-1}\) of the carboxylic acids and other carbonyl species. Emerging peaks at 1628 and 1530 cm\(^{-1}\) reveal the presence of carboxylates and the second derivative analysis is able to resolve the peaks and identify the different absorptions for the several coordination structures.

The formation of other degradation products and transformations was also detected:
- 1\(^{\text{st}}\): loss of the 3010 cm\(^{-1}\) absorption – breakage of the C=C-H double bond;
- 2\(^{\text{nd}}\): small peak at 967 cm\(^{-1}\) – isomerization from cis to trans of the C=C-H bend;
- 3\(^{\text{rd}}\): increase in background absorption 3200-3000 cm\(^{-1}\) – carboxylic acids;
- 4\(^{\text{th}}\): weak and broad band at \(\sim\)3400 cm\(^{-1}\) – alcohols or hydroperoxides.

Further analysis was considered necessary for a method that would be able to distinguish between the different types of oil. For that purpose, a chemometric approach with principal component analysis (PCA) was applied to the acquired FTIR spectra of the reference samples to create a calibration plot. Naturally and artificially aged oil paint reconstructions, from the Molart Report and HART Project, were projected onto the previous results to test the calibration and then real samples from paintings and oil paint tubes were
analyzed, showing for the first time that a differentiation is possible with this multi-analytical approach and results are promising.

Additional analysis of Amadeo’s paint tubes and Silva Porto’s paint box samples by other analytical techniques, such as gas-chromatography mass-spectrometry (GC-MS), could establish if the results obtained by PCA are accurate and, if so, enable us to further develop this tool in the identification of lipidic binding media.

As for the characterization of the Lead White pigments, the ESEM-EDX technique proves to be very useful in the differentiation of the manufacturing technique, being consistent with previous results [4,13] and allowing a clear identification of the particle shape and size distribution. By creating reference samples it was possible to separate the categories into two main characteristics that can be easily recognized and help identify whether the production is achieved by the traditional Dutch stack process or by the modern method of precipitation.

Observing the particle shape, the traditional process reveals rounded particles whereas the modern presents a thin plate structure often with geometrical edges. The range in particle size is also to be considered, with the traditional process consisting of particles ranging from a very small size (0.5 μm) up to quite large isolated bunches of particles (20-65 μm). In the samples made with the modern lead white we see a more regular size, from 0.8 to 10 μm.

The sample from the top layer of Amadeo’s Mucha painting – corresponding to the white paint layer consisting of lead white and barium sulfate – was identified has being composed by traditional Dutch stack process Lead White, since the particle’s shape and size matched the characteristics mentioned above for that type of production.

In addition, ESEM analysis could also be a helpful tool for the identification of extenders and their proportions by comparison with reference samples. Relying on the samples with stepped proportions of barium sulfate to lead white from the HART Project, it is possible to calibrate software in order to characterize the mixture present in Amadeo’s samples, or visual analysis by comparison.

As a side study, colourimetry measurements taken for the oil paint reconstructions revealed a shift in the bleaching tendency, attributed to the ongoing chemical drying of the polymeric matrix. To establish a quantitative measurement of the light (lux) required for each paint to reach its maximum bleaching after yellowing in a dark environment, further tracking of the colour readings is needed as well as tests on aged samples (details and results are presented in Appendix III. v, page 86).
Bibliografia


