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Analysis and Treatment of a Nineteenth Century Portrait, Study of Artsorb® and a Proposal for a Microclimate Frame

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Resumo

O presente trabalho encontra-se dividido em duas partes: A Parte 1 foca-se na análise e tratamento de um retrato do século XIX de Domingos Affonso, pertencente ao Ecomuseu Municipal do Seixal; e a Parte 2, que se intitula “O Projeto da Moldura Microclima”, foca-se no estudo do Artsorb® e no planeamento de uma moldura microclima para a pintura.

Na Parte 1, foi realizado um estudo dos materiais da pintura através do uso de técnicas analíticas complementares e a condição da pintura foi cuidadosamente avaliada. A pintura exibia sinais de crescimento de fungos, tendo sido feita uma investigação mais detalhada deste assunto para perceber se a comunidade fúngica se encontrava ativa e se representava um ameaça real à pintura. Um tratamento foi proposto, apropriado à condição da pintura. A descrição do tratamento efetuado, envolvendo as opções de tratamento, encontra-se também presente nesta secção.

Dentro do estudo da moldura microclima, na Parte 2, o estudo da potencial corrosividade do Artsorb® foi um assunto central. As folhas de Artsorb® são um dos materiais mais vastamente utilizados para atenuar as flutuações de humidade relativa em molduras microclima e a sua reportada excelente performance é reforçada pela sua disponibilidade em folhas leves que podem ser facilmente colocadas dentro das molduras microclima. Contudo, têm surgido preocupações relativamente à presença do sal corrosivo cloreto de lítio na composição deste material tampão. Consequentemente, o presente trabalho também visou compreender os potenciais riscos de utilizar Artsorb® e a possibilidade de evitar a exposição das obras de arte ao cloreto de lítio através do uso de Tyvek®.

Os resultados dos testes preliminares parecem indicar que o Artsorb® liberta cloreto de lítio para o ambiente. Este estudo mostrou ainda que uma cobertura de Tyvek® sobre o Artsorb® reduz mas não elimina evidência de contaminação por cloro, além de reduzir significativamente a eficácia do material tampão. Considerando que o Artsorb® parece ser inadequado devido à libertação do sal corrosivo, que o Tyvek® não foi eficiente como barreira para a passagem do cloreto de lítio nem como material permeável para permitir o correto funcionamento do Artsorb®, o material tampão proposto para ser utilizado nas molduras microclima é a sílica gel sem indicador. Com base na escolha do material tampão, em consequência deste estudo, foi proposta uma moldura microclima.

Este trabalho resultou numa apresentação em *poster* e na submissão de um artigo:

Sá, S., Carlyle, L., Pombo Cardoso, I. 2015. *Artsorb® in microclimate frames: Oddy testing to evaluate the corrosive potential of lithium chloride and the efficacy of Tyvek® to mitigate its effects.* Poster presentation at the 1st International Conference on Science and Engineering in Arts, Heritage and Archaeology (SEAHA), University College London, 14-15 July 2015.

Sá, S., Pombo Cardoso, I., Carlyle, L., Alves, L. C. 2015. Preliminary results: Oddy testing of Artsorb® to evaluate its corrosive potential and the efficacy of Tyvek® covers. (Submetido ao Studies in Conservation)

Palavras-chave: retrato do século XIX; análise e tratamento; crescimento de fungos; flutuações de humidade relativa; folhas de Artsorb®; cloreto de lítio; Tyvek®; moldura microclima.

Abstract

The present work is divided in two parts: Part 1 is focused on the analysis and treatment of a 19th century portrait of *Domingos Affonso*, which belongs to the Ecomuseu Municipal do Seixal; and Part 2, which is entitled “The Microclimate Frame Project” is focused on the study of Artsorb® and on the planning of a microclimate frame for the painting.

In Part 1, a study of the painting’s materials was performed using complementary analytical techniques and the painting’s condition was carefully evaluated. The painting exhibited signs of mould growth, and a more detailed investigation was made of this topic to understand if the fungal community was active and if it represented a real danger to the painting. A treatment was proposed, appropriate to the painting’s condition. A description of the treatment carried out, comprising the treatment options, is also present in this section.

Within the study of the microclimate frame, in Part 2, the study of the potential corrosiveness of Artsorb® was a central subject. Artsorb® sheets are one of the most widely used materials for buffering relative humidity fluctuations in microclimate frames and its reported excellent performance is enhanced by its availability in lightweight sheets that can be easily placed inside microclimate frames. However, concerns have arisen regarding the presence of the corrosive salt lithium chloride in the composition of this buffer. Consequently, the present work also aimed to understand the potential risks of using Artsorb® and the possibility of avoiding exposure of lithium chloride to the artworks through the use of Tyvek®.

Results from the preliminary tests seem to indicate that Artsorb® releases lithium chloride into air. This study also showed that a Tyvek® cover over Artsorb® reduces but does not eliminate evidence of chlorine contamination, and it significantly reduces the effectiveness of the buffering material. Considering that Artsorb® appears to be unsuitable due to the release of the corrosive salt, that Tyvek® was not efficient as a barrier for lithium chloride or as a permeable material to enable the proper functioning of Artsorb®, the buffering material proposed for the use in the microclimate frames is silica gel without indicator. Based on the choice of buffering material, as a result of this study, a microclimate frame is proposed.

This work resulted in a poster presentation and a submitted article:

Sá, S., Carlyle, L., Pombo Cardoso, I. 2015. *Artsorb® in microclimate frames: Oddy testing to evaluate the corrosive potential of lithium chloride and the efficacy of Tyvek® to mitigate its effects.* Poster presentation at the 1st International Conference on Science and Engineering in Arts, Heritage and Archaeology (SEAHA), University College London, 14-15 July 2015.

Sá, S., Pombo Cardoso, I., Carlyle, L., Alves, L. C. 2015. Preliminary results: Oddy testing of Artsorb® to evaluate its corrosive potential and the efficacy of Tyvek® covers. (Submitted to Studies in Conservation)

Keywords: 19th century portrait; analysis and treatment; mould growth; relative humidity fluctuations; Artsorb® sheets; lithium chloride; Tyvek®; microclimate frame.

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Symbols and Abbreviations

μ-FTIR	Micro Fourier Transform Infrared Spectroscopy
μ-EDXRF	Micro Energy Dispersive X-Ray Fluorescence
SEM-EDS	Scanning Electron Microscopy equipped with Energy Dispersive Spectroscopy
BSE	Back-scattered electrons
OM	Optical Microscope
PLM	Polarized Light Microscopy
UV	Ultraviolet Light
RH	Relative Humidity
UNL-DCR	Universidade Nova de Lisboa – Departamento de Conservação e Restauro
EMS	Ecomuseu Municipal do Seixal
HART	Historically Accurate Reconstruction Techniques
W&N	Winsor & Newton
LiCl	Lithium Chloride
PDA	Potato Dextrose Agar
MC	Microclimate
PP	Polypropylene
EVA	Ethylene-vinyl acetate
®	Registered Trademark
ν	Stretching
δ	Bending

PART 1: ANALYSIS AND TREATMENT OF THE PORTRAIT OF DOMINGOS AFFONSO

1. INTRODUCTION

1.1. Description of the Image

The painting under study is a 19th century oil painting on canvas and its artist is unknown. The figure is depicted sitting in a chair, in a formal position, and against a brown flat background (Figure 1). The only particular feature of the background is the faint evidence of an archway behind and above the figure's head. The figure's hands rest on his lap and in his right hand he holds a letter with an inscription. Analysis made by Raquel Marques for her thesis (2014) revealed that the text in the letter reads: "*Domingos Affonso Vice Consul dos Estados Unidos da America. Arialva"* [1].

Figure 1 - Portrait of *Domingos Affonso*. Before treatment under normal light.

1.2. Historical Context

The painting, which portrays *Domingos Affonso,* was donated in 2009 to the Ecomuseu Municipal do Seixal together with two other paintings: a portrait of *João Luiz Lourenço* and a portrait *of Isabel Maria Lourenço Affonso*. As noted by Marques, it is known through information available in Moinho de Maré de Corroios, which currently belongs to the Ecomuseu Municipal do Seixal, that *Domingos Affonso* was the husband of *Isabel Maria Lourenço Affonso* who in turn was the daughter of *João Luiz Lourenço*. *João Luís Lourenço* bought the Tide Mill in 1836 and it was inherited by *Domingos Affonso* after the death of his father in law. *Domingos* was an influential person, mentioned as a merchant, city councilman and also vice consul of the USA [1].

Marques also noted that the couple's portraits appear to be companion pieces and both portraits were studied in her thesis in terms of style, painting materials and technique. An analysis of the figure's clothing was also previously made by Marques in order to help date the painting (see Appendix III, page 7, of her thesis) [1]. Marques was able to narrow the date range to between the 1840's and the 1860's. This period was consistent with the period in which the family lived.

For this thesis, in an attempt to narrow the date range further for this painting, an investigation of the period during which *Domingos Affonso* was vice consul of the United States of America was made. In contemporary municipal minutes and reports from the ministry of foreign business *Domingos* is mentioned as vice consul of the USA in 1851, 1855 and 1860 [2, 3]. It was not possible to trace the beginning and the end of his tenure due to the absence of lists of foreign consuls before 1855 and after 1860 in these reports.

2. EXAMINATION: CONDITION, MATERIALS AND TECHNIQUE

2.1. Examination and Condition Summary

The painting portraying *Domingos Affonso* exhibited both structural and aesthetic problems primarily due to water exposure (evident in tide line staining in the original and lining fabrics). The painting was lined in the past and one of the most prominent structural problems was the detachment between the original canvas and the lining canvas. The lining fabric showed evidence of being weak in the form of tears and deterioration at the tacking margins and was therefore not providing adequate support for the painting. Some of the deterioration appeared to have been caused by mould in areas where tide lines showed evidence of the extent of water damage. The original canvas also exhibited tears in the bottom part as well as a small missing strip of original canvas. With regard to the paint composite, the most significant problem was the areas with tenting and cupping associated with active flaking occurring at the interface of paint/ground and ground/canvas. In addition the varnish was very yellow, largely obscuring the image, and had severely blanched at the edges of the image apparently due to water damage. Apart from the dirt and dust present on the painting's surface, there was also extensive mould growth both on the front and back of the painting.

2.2. Previous Treatments

The lining canvas consisted of a single piece of plain weave fabric, slightly thinner than the original canvas, with a thread density of 16 vertical x 16 horizontal threads per cm^2 (slightly higher than the original canvas). Through observation in the Optical Microscope (OM) under crossed polarized light it was possible to identify the fibres from the lining canvas as bast fibres (probably flax) (full analysis in Appendix IV.4).

As noted above there was significant detachment between the lining and the original canvas along the margins, especially at the bottom, but the centre was generally well adhered. The tacking margins were extremely deteriorated, and the lining fabric was not attached to the stretcher in some areas along the sides in addition to being completely detached along the bottom. The metal tacks that held it to the stretcher were significantly oxidised which contributed to the deterioration of the fabric around them and to the consequent lack of adhesion of the fabric to the auxiliary support (Figure II.4). From the back, it was possible to observe that the lining fabric exhibited severe distortions in the areas corresponding to tented and cupped paint in the front of the painting (Figures II.1, II.2). In addition, both the lining and original canvas exhibited several undulations, especially in the upper part of the painting (Figures I.3, I.4). The lining fabric also exhibited dirt, mould growth and tide lines (staining) from water exposure (Figure II.3). Once the lining was removed tide lines were also evident in the original canvas (Figure V.18). The evidence of extensive mould growth (Figure V.7) and deterioration mostly in the area with tide lines suggest that the painting was saturated with water for a significant time.

The lining adhesive was analysed with µ-FTIR and identified as a glue-starch combination. Polarized Light Microscopy (PLM) on a dispersed sample of the lining adhesive confirmed the presence of starch in the glue formulation (full analysis in Appendix IV.6).

The lining adhesive was not holding the two canvases together (original and lining) since they were completely detached in the bottom of the painting. Once the lining adhesive was removed, it could be seen that the adhesive revealed a powdery consistency in this area, which may be explained by its partial dissolution or swelling and rearrangement during water exposure. There was also presence of mould growth on the adhesive itself (Figure VI.9), not only in the bottom where water may have been in contact with the painting, but also in the middle of the painting. In the areas corresponding to tenting and cupping paint, the adhesive was darker, having a melted appearance (Figure V.14). This may indicate an overheating of these two areas in the lining process which may have contributed for the tenting and cupping of the paint or may also be associated with water damage specific to these areas.

In this way, the old lining adhesive and canvas were not fulfilling their task of providing a proper support for the painting and were even providing an extra source of nutrients (present in the glue-paste adhesive and in the natural canvas fibres) for mould growth.

2.3. Auxiliary Support: Stretcher

The painting's auxiliary support is a wooden stretcher constructed with a softwood, and judging by its appearance it is likely pine. The stretcher is 86.2 cm long and 52.2 cm wide. Both vertical and horizontal bars are 2 cm thick while the cross bar is 1.7 cm. All stretcher bars have inside chamfered edges and the corner construction is a Simple Mortise & Tenon, with 2 wooden keys and 2 blind slots (Figures 2, I.2) [4].

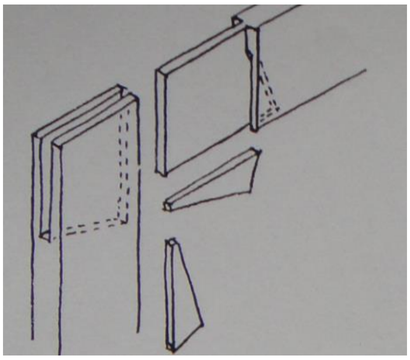

Figure 2 - Schematic of a corner construction in Simple Mortise & Tenon with 2 wooden keys and 2 blind slots. Image by Weil, 1966 [4].

The stretcher is most probably a replacement dated from the lining since the original dimensions of the painting appear to have been smaller – at the bottom and left side of the painting it is possible to see sections of the original tacking margin particularly in the x-radiograph (see chapter 2.4) (Figure I.8). At the back of the stretcher was a shipping label, placed on top of the lining canvas. All three paintings donated to the Ecomuseu Municipal do Seixal had the same label. It belongs to a British transport company named "WOODBRIDGE & Ltd." and includes the name of the family that donated the paintings, "Newberry" (see Appendix II, Figure II.5).

Regarding its condition, the stretcher is somewhat distorted since one corner is lifted when the stretcher is placed on a level surface. There is also evidence of previous insect infestation in the form of exit holes (Figure II.3).

2.4. Original Support: Fabric

The original canvas is a single piece of plain weave fabric with a thread density of 14 vertical x 14 horizontal threads per cm^2. The fabric exhibits significant imperfections (slubs) so it is possible that it was hand-woven. The fibres were observed under the OM with polarized light and were identified as bast fibres (likely hemp or flax) (full analysis in Appendix IV.4).

The current image area is 65.5 x 84.8 cm. Although it seems that the tacking margins were cut off at the time of the lining, as previously mentioned, through observation of the x-radiography of the painting it was possible to conclude that the left and bottom tacking margins are still present, due to the evidence of holes (likely tacking holes) and a turnover edge partially infilled (Figure II.9). Although slightly visible in raking light, due to an elevated wrinkle, the old tacking margins are currently covered with dark paint and the holes are infilled (Figure II.6). It was proposed that the original tacking margins were used to enlarge the painting's original size but the reason for this is not well understood since, as noted by Marques, an original tacking margin was also detected in Isabel's portrait (on the right side of the painting) and judging by the images of the companion pieces, it is likely they were always a similar size and in proportion to each other.

As far as the original fabric's condition is concerned, there are irregularities along the edges due to being cut away from the tacking margins. These irregularities were infilled with a putty by the previous restorer and dark brown paint was placed all around the edges on top of the putty. The bottom edge currently has a considerable amount of tears and small losses, in addition to a major loss in the bottom left corner with approximately 1.8 x 8.5 cm (Figure II.8).

2.5. Preparation Layers

In traditional preparations a size layer is used to seal an absorbent surface, like canvas, to prevent binder from the ground or paint layers from soaking through the threads of the fabric [5] and to fill the canvas interstices, so that no ground passes through to the back of the canvas [6]. According to PhD research by Maartje Stols Witlox on documentary evidence for ground preparations, an animal glue was often recommended in historic texts, and in some cases flour pastes or starch pastes could be used [6]. In this portrait, the size layer is not visible with the naked eye and it was not possible to identify it through the observation of cross-sections in the OM and with µ-FTIR analysis.

Figure 3 - Ground sticking out at the back of the original canvas (photography taken after the removal of the old lining canvas).

Figure 4 - Ground sticking out at the back of a canvas sample from HART Project. Ground was composed by lead white and barium sulfate in oil and the size used was fluid. Photography taken by the author.

The ground layer is used to prepare the support for the painting by creating a surface to receive the paint layers. Ideally it forms a good bond between the canvas and the paint layer above [5, 7]. It can also counter the absorbency of the support and can reduce or enhance its texture or even create a separate one [7]. In this portrait, the fabric texture is visible but not pronounced. The colour of the ground is light beige and according to the x-radiograph its application extended over the original tacking margins, since a continuation of the density of the materials from the centre of the painting to the original taking margins is visible. This indicates that the ground was applied before the fabric was stretched and that it was done either in the artist's studio or by an artist's supplier [8]. At the time of its application, the ground partially passed through the original canvas and can be seen from the back, indicating that the canvas was not well sealed by the size (Figure 3). In order to better understand the reason for the ground to pass through the canvas, comparison with samples from the HART Project was undertaken. It was seen that in the canvas samples where a fluid size or no size was used, the ground had passed through it. Figure

4 illustrates a sample from the HART Project where an oil ground with lead white and barium sulphate (same binder and pigments/fillers as the ground from the portrait of *Domingos Affonso*) was applied on top of a canvas with a fluid size. This may indicate that in the portrait under study a fluid size might have been used or no size at all [9].

The ground was analysed by Raquel Marques in her Master thesis (2014) in order to compare the portrait of *Domingos Affonso* with its companion piece. Marques used µ-EDXRF, µ-Raman and µ-FTIR and observed cross-sections in the Optical Microscope. In order to confirm her results and to complete the information about this painting's preparatory layers, new cross-sections were taken and observed under the OM and new samples were analysed by µ-FTIR. Marques noted that under the OM all cross-sections showed a single thick white ground but analysis with SEM revealed what appear to be two layers, although the results were not consistent throughout the samples analysed. In this thesis, it was seen that in some of the new cross-sections and some of those taken by Marques there is also a slight distinction in the ground under UV light in OM images, which suggests more than one ground application (Figure 5 a)). However, in keeping with Marques's results, this finding was not always evident.

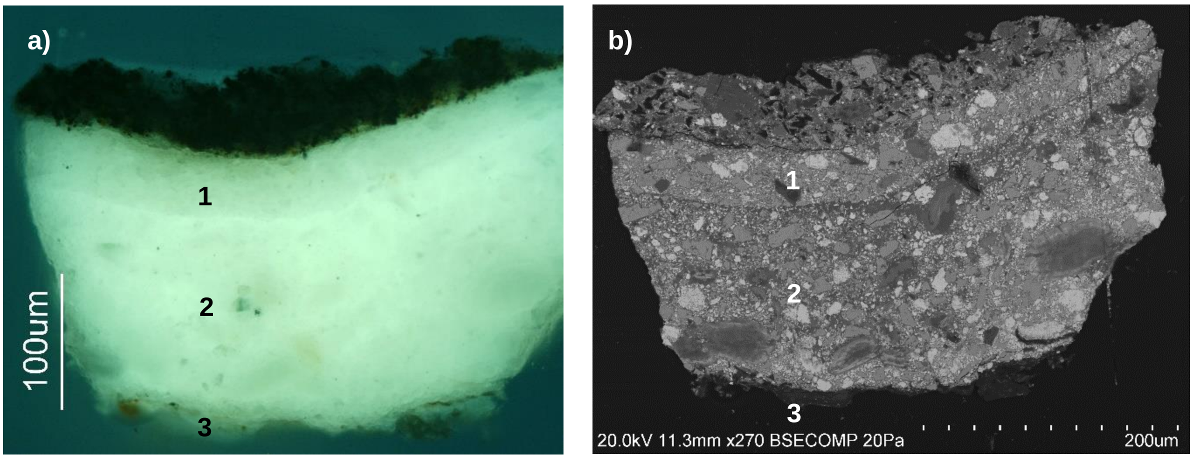

Figure 5 - **a)** OM image in UV light, of cross-section S3 (cross-section by Marques in 2014, photographed by the author for the current report); **b)** SEM-BSE micrograph of cross-section S3 (analysis and image by Marques in 2014). The three ground layers are numbered. Layers 1 and 2 correspond to ground layers composed of lead white and barium sulfate and layer 3 corresponds to the calcium carbonate.

Using the techniques referred to above, Marques found that the white ground layer or layers are composed of lead white ($2PbCO_3.Pb(OH)_2$) and barium sulphate ($BaSO_4$) in an oil binder. In the bottom of cross-section S3 she saw evidence of a thin layer in the ground, with an orange translucent colour (Figure IV.2), composed of calcium carbonate ($CaCO_3$), according to her SEM and Raman analysis (Figure 5). However, ground samples removed from the back of the original canvas (which would presumably consist of the first layer of ground applied) revealed a composition of lead white and barium sulphate, with no evidence of the orange coloured calcium carbonate. It is also noted in the current work that the cross-sections taken from areas with tenting and cupping paint exhibit a layer with the same appearance to the one found by Marques in S3 (see Appendix IV.2). In addition, cross-section S10 that corresponds to the infill around the edges of the painting, also exhibits a similar layer in the bottom.

Regarding the condition of the ground, although its adhesion to the support was good in most places, in areas with tenting the adhesion was poor (evident as flaking between the ground and canvas). In addition to these areas, at the bottom edge of the painting where it was exposed to water, the ground also exhibited poor adhesion to the support. Overall, the internal cohesion of the ground is good except for the areas of tenting and water damage, where small losses of paint indicate delamination in the ground as well. There are also some areas with local mechanical cracking that are evident in the x-radiograph (Figure II.10).

2.6. Paint Layers

Through close observation of the surface it was possible to see that the paint was applied by layering. This was confirmed in the cross-sections (Figures IV.2 to IV.7). In the darker areas the paint is generally thinly applied while areas with white paint are thicker and more buttery. This is noticeable in the figure's collar and shirt in photographs under raking light, where the texture is evident (Figures II.12, II.14). The paint from the lighter colours seems to be more opaque when compared to the darker colours, especially in the figure's face and shirt, however, detailed observation under the stereomicroscope revealed that there is some transparency in the lighter colours as well (Figure II.13).

The painting exhibits mechanical cracks overall. As noted above, there are two major areas of significant cupping associated with tenting (Figures I.1, II.1 and II.15). The paint cohesion is generally good but in some areas there are losses of paint and ground/paint (see map of damages Appendix III). In these areas there was significant flaking at the interface of the paint/ground and at the interface of the paint & ground composite which is also seen along the bottom edges of the painting. The losses along the bottom edge of the painting are significant and likely associated with the water damage described above. On the surface of the painting and in between cracks, it is possible to see small white dots that appear especially on top of the black paint (on the figure's hair and jacket). Those dots were thought to be mould growth (Figure II.16) (for the fungi identification see Appendix VI).

The paint surface exhibits signs of abrasion. Initially these were thought to be associated with a frame, however, the abrasions were not consistent with either the rebate of a frame or an extension of the inner part of the frame: the abrasions were too large to be caused by a rebate, and their shape did not follow upper curved portion of a frame (the curved image area at the top of the painting suggests a curved frame was used). Through a more detailed observation in the stereomicroscope it was possible to see that these abrasions had also green and white deposits on top, indicating that it may have been caused by the contact with another painted surface (maybe with the surface of the companion piece) (Figure II.7).

There is evidence of protrusions into the paint mainly in the flesh tones and in the white paint. These small projections have a whitish appearance (do not have paint on top) and are small and rounded in shape (Figure II.11). They are very similar to a known problem that occurs in paintings, which are the metal soap aggregates [10]. As reported by Marques, these protrusions are also seen in the other two paintings and were studied by Joana Devesa for her Master thesis [11].

Analysis of the portrait's materials was made by Raquel Marques in order for her to compare the companion portraits of husband and wife. For the portrait of *Domingos Affonso* she carried out analysis with µ-EDXRF and cross-sections were observed under OM and analysed with SEM-EDS, µ-Raman and µ-FTIR. The binder was identified as an oil and the materials found were: lead white, barium sulphate, vermillion, iron oxides (goethite and hematite), a carbon-based pigment (carbon black), Prussian blue and a red lake (likely madder) (see table of pigments identification in Appendix IV.5). For this thesis new cross-sections were taken and they were observed under the OM and some of the cross-sections (one corresponding to the figure's shirt and other to the letter) were analysed with Raman. The pigments found were consistent with the ones identified by Marques but a new pigment was found, ultramarine blue, which had not been identified in the previous cross-sections (only in the restoration). All materials found in the painting were in use in the 19th century and therefore, are consistent with a 19th century painting.

2.7. Surface Coating: Varnish

The painting has a substantial coat of varnish on the surface which was applied in a fairly even manner as evidenced in UV light. Some areas of the painting have a more matt appearance under normal light. Under UV light the varnish has a greenish fluorescence (Figure I.5) suggesting a natural resin [5] which was confirmed by µ-FTIR. Cross-sections from the background and from the jacket revealed two layers of varnish and in-between is a layer of overpaint. Significantly, the cross-sections from other areas revealed only one layer of varnish. The evidence for this will be discussed in the next topic (2.8. Previous Surface Treatments).

The varnish condition is poor due to its severe yellowing, mainly visible in the lighter areas, such as the figure's shirt. Although most visible over light paint, the yellowing may also be obscuring details in the painting, especially in the figure's clothing. As well, the heavily discolored varnish hampers the distinction of the limits between the figure and background. The uneven gloss and the presence of blanching in the corners and edges of the painting are also problems associated with the degraded varnish.

2.8. Previous Surface Treatments

As well as the previous structural treatment (lining), there were also previous surface treatments. Along the cut edges of the original canvas where it met the lining canvas, a filling material had been applied. This was presumably applied to secure the edges and create a more finished appearance after the lining. This filling material was overpainted and its colour was very similar to the colour of the background of the painting. Marques had already noted through observation of cross-sections in the OM that the background of both female and male portraits seemed to have an overpaint layer. Observation of new cross-sections and those taken by Marques in the OM showed clear evidence of an overpaint layer sandwiched between two layers of varnish (Figures IV.3 to IV.5 and IV.7).

Current findings show that this overpaint corresponds to the same paint used on top of the filling material applied by a previous restorer. This layer is very distinctive: in normal light it is an orange translucent colour with some darker particles, but under UV it has a brownish translucent appearance and some of the particles fluoresce in blue (Figure 6). Further observation made in the course of this thesis preparation showed that the overpaint layer on the male portrait is not only on top of the background but also on the figure's jacket. Figure 6 shows details of four cross-sections: S10 was taken from the painting's margins and corresponds to the filling material, S1 and S20 were taken from the background and S5 was taken from the figure's jacket. Images of cross-sections S1, S5 and S20 show that the paint layer sandwiched between the two layers of varnish is very similar to the paint layers applied during a previous restoration treatment alongside the painting's margins. The dashed lines on cross-sections S10 and S1 enhances the layer division, and the arrows indicate a possible correspondence of the layers on top of the putty to the overpaint and final varnish on the painting's surface. Although only three cross-sections are represented here to show the overpaint layer, this also appeared in the other cross-sections taken from these areas.

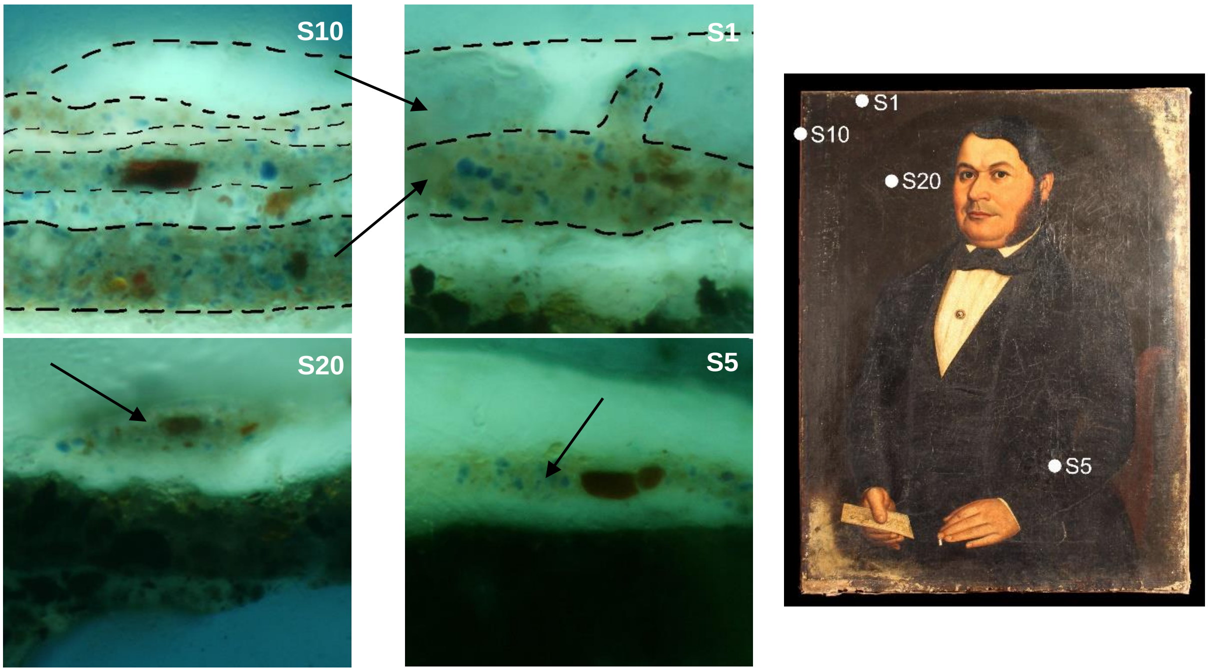

Figure 6 - **Left:** OM details from cross-sections under UV light, where the overpaint layer is seen, 500x magnification. Cross-section S5 was taken by Marques in 2014 and S1 by a DCR student in 2012. Both were photographed by the author of this thesis. Cross-sections S10 and S20 were taken and photographed by the author. **Right:** Map of sampling for the cross-sections showed on the left.

In addition there are occasional small lacunas (easily visible in the x-radiograph) which have been infilled and inpainted (see map of damages Appendix III).

2.9. Fungi Identification Summary

This part is only a summary comprising the most important findings from the fungi identification and its implications in the painting's treatment. For the complete identification see Appendix VI.

Samples were taken from the paint surface, from the lining and from the original canvas, in areas where there were visual signs of possible microorganism's activity (Appendix VI.2 and VI.3), and were inoculated, isolated and identified. The sampling on the original canvas was only possible after the lining canvas removal and was done while the remains of the old lining adhesive were still present.

Cultivation essays confirmed the presence of active microorganisms inhabiting the painting, with the following fungi identified: *Cladosporium*, *Humicola* and *Erysiphe graminis* (?). *Cladosporium* was the most common fungus, appearing in several samples from the back of the painting (both in the lining and in the original canvas). *Humicola* and *Erysiphe graminis* (fungi identification not conclusive) appeared only at the front of the painting and are associated with the small white dots on the dark paint.

The presence of active fungi at the surface of the painting emphasized the need for caution in selecting treatment options, such as the choice of the adhesive for the facing and consolidation. The active fungi in the old lining materials reinforced the need for their removal and signalled the possible danger of further mould growth in the case of using organic materials for the new lining treatment.

3. TREATMENT REPORT

3.1. Treatment Proposal Summary

Considering the various problems presented by the painting, the treatment proposed was to carry out an initial consolidation to re-adhere flaking paint, surface cleaning, facing, de-lining, lining adhesive removal from the original canvas, flattening of distortions in the paint composite and canvas, relining and re-stretching, varnish removal followed by infilling and inpainting of losses. Previous infills and inpainting would be adjusted as needed or redone if necessary. A final varnishing with an appropriate varnish would complete the treatment. This thesis reports on the work carried on up to the flattening.

3.2. Consolidation

Consolidation is carried out to re-adhere materials that have lost cohesion [12]. As previously noted, the portrait exhibited insecure areas with active flaking, in particular the two areas of tenting and cupping paint and the bottom section of the painting that suffered from water exposure. Consolidation had already been initiated by UNL-DCR students and they used BEVA® 371b in White Spirits as the adhesive, however these areas were not yet perfectly stable and secure requiring further consolidation. BEVA® 371b[1] is a synthetic resin adhesive composed of ethylene vinyl acetate copolymer (Elvax 150), an aldehyde ketone resin, ethylene vinyl acetate copolymer (A-C Copolymer), phthalate ester of hydroabietyl alcohol (Cellolyn 21), paraffin, and the solvents toluene and naphtha [13, 14]. BEVA® 371b is strong and flexible and can be heat activated after its application, with a temperature over 60ºC [12]. It is soluble in hydrocarbon solvents and can be removed either with heat or solvent [13]. In spite of being a relatively new material (introduced by Gustav Berger in 1970 [15]), it is believed that its components are not harmful to oil paintings in themselves or in combination, and tests indicate that this adhesive does not pose any obvious threat to the painting[2] [16].

Since there was significant evidence of mould growth on top of the paint layers and associated with both the original and lining canvas, the use of an aqueous adhesive (either a natural material or a synthetic resin in aqueous solution) was rejected as it would supply an initial source of water and moisture that could reactivate the mould (and a natural glue would supply nutrients) (see Appendix VI). Consequently the choice went to a non-aqueous adhesive. The advantages of BEVA® 371b stated by the literature and its good performance on this painting (seen by tests and its previous use) made this adhesive a good option for this case.

A solution of BEVA® 371b in White Spirits (1:1) was used to consolidate the unstable areas. The solution was warmed up until it became fluid and was applied with a small brush (W&N Cotman Brush 0000) between gaps and under paint islands (Figure V.1). Silicone-coated Melinex® was then placed on top of the painting (silicone side face down) and the area where the adhesive was introduced was warmed up with a hot spatula set to 60ºC to activate the adhesive (see Equipment and Suppliers in Appendix VIII). Initially a light finger pressure was applied while the adhesive was cooling and setting in

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[1] BEVA 371b is a reformulation of the BEVA 371 (Original Formula) and contains an aldehyde ketone resin instead of the Laropal K80 used in the original formula [13].

[2] BEVA 371b has not been fully tested for any possible interaction with oil painting materials and because it is a relatively new material, it was not possible to access yet its natural aging characteristics. However because of its very successful performance as a consolidant since 1970, this material is widely used internationally by painting conservators.

order to flatten the cupping paint and promote the adhesion between the paint and the support. This was followed by weights. Prior to the consolidation the stretched canvas was supported from below to allow the application of pressure without any harm to the painting (Figure 7).

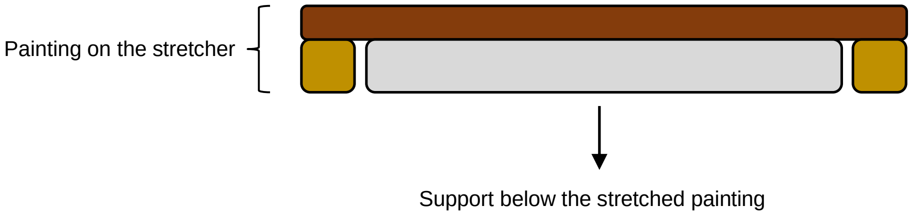

Figure 7 - Schematic of the stretched painting supported from below.

3.3. Facing

To secure and protect the paint during the removal of the stretcher, lining canvas and lining adhesive, the painting was faced. Facing is a temporary treatment done when a painting must be subjected to manipulation during treatment steps. For this procedure it is possible to use weak, viscous and non-penetrating adhesives to obtain a temporary surface facing, or thin, strong, low viscosity and penetrating adhesives to permanently consolidate flaking paint [12].

In the case of the portrait under study, the choice of the adhesive for the facing also took into consideration the fact that the painting had mould growth in its front, so aqueous adhesives were not considered. BEVA® 371b was tested in a small area and it presented good results. In order to take advantage of consolidation during the facing treatment, this was the adhesive chosen. It was used in a 60:40 solution by volume of BEVA® 371b in White Spirits.

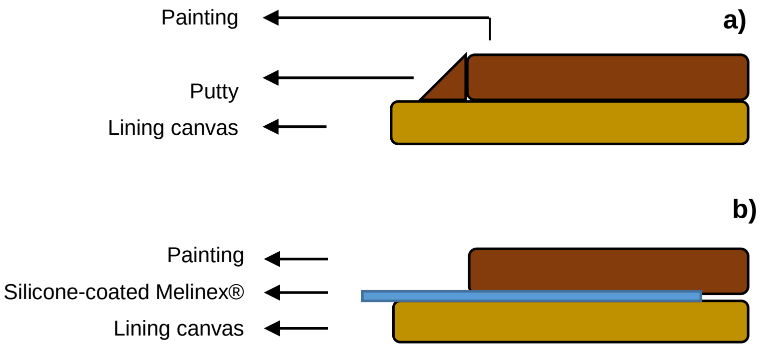

Figure 8 - **a)** Before the margins separation: the margins were adhered and the putty was making a transition between the two canvases; **b)** After the margins separation: removal of the putty and insertion of the silicone-coated Melinex® between the two canvases.

Prior to facing, in anticipation of the strip lining following the facing, the putty around the painting was removed and the margins of the original canvas were separated from the lining canvas. Strips of silicone-coated Melinex® were placed between the two so they would not re-adhere during the application of the facing adhesive (Figure 8).

Squares of Japanese tissue (see Suppliers in Appendix VIII.2) were prepared by applying lines on the tissue with a water brush then pulling apart the tissue to obtain feathered edges. Generally squares of 10 x 10 cm were used, except for the margins of the painting where larger pieces were required and in the areas of tenting and cupping, where larger squares were made to avoid having a transition line in the middle of an unstable area.

Wood planks with the same depth as that of the painting on its stretcher were placed around the painting such that the facing tissues around the edges of the painting formed a bridge across the paint surface and the wood (Figure V.2). This secured the edges of the painting while the adhesive dried, thus avoiding possible the distortions (e.g. curling) at the edges during the evaporation of the solvent from the facing adhesive.

Before the application of facing tissue onto the painting's surface, the tissue had been slightly moistened with distilled water and placed between layers of Melinex® allowing it to equilibrate and relax the fibres. This pre-treatment of the tissue avoided the formation of air bubbles at the time of the application of the adhesive since the relaxed fibres achieved a close conformation to the paint surface. Just before use, the tissue was taken from the Melinex®, placed on top of the painting and the adhesive was applied on top of the tissue with a brush (Figure V.3). It was important that the facing obtained a good conformation to the paintings surface in order to properly secure the paint layers (Figure V.4). Squares of Japanese tissue were applied in a pattern that alternated wet and dry areas on the painting in order to minimise the surface area exposed to solvent in any one area of the painting. The margins of the squares of tissue overlapped slightly to avoid unsupported areas (Figure V.5).

3.4. Removal of the Stretcher and Lining Canvas

Once the facing dried (approximately 24 hours), the tissue that was making the bridge between the painting and the wood planks was cut and the planks were removed. At this stage the painting on its stretcher was ready to be worked on from the back and it was laid face down on cushioning material (thin foam) to support the paint and canvas deformations. The old lining canvas could be detached from the stretcher along the tacking margins by gently pulling it away from the oxidized tacks (Figure V.6). After the stretcher was lifted off the back of the painting, the degradation of the bottom of the lining canvas became more apparent: apart from the already visible tears, the fabric was in decomposition and completely infested by mould (Figure V.7). It was then necessary to perform a surface cleaning of the lining canvas with a soft brush (debris was brushed towards the nozzle of a vacuum cleaner) to remove the significant amount of dirt, dust, mould, and remains of insects (Figure V.8).

To remove the lining canvas, it was gently peeled back at a low angle while the original canvas was being held down (Figure V.9). After the removal of the lining canvas, the back of the original canvas was cleaned by brushing dust into the nozzle of the vacuum cleaner (as above) to remove the loose remains of lining adhesive and extensive mould.

3.5. Strip Lining and Looming

Since the painting was no longer under tension, to avoid distortions while under treatment, it was necessary to place the painting in a temporary loom. This would also allow the access to the front and back of the painting, at the same time, for the flattening treatments. To stretch the painting in the loom, strips of fabric must be temporarily attached to the painting's margins. For this procedure, strips of polyester fabric with BEVA® 371 film were used (see Suppliers in Appendix VIII.2). Strips of BEVA® 371 film were applied first to the polyester fabric strips with a hot spatula (temperature approximately 70ºC). The width of the BEVA® 371 film strips varied according to the needs of the painting. For example, along the painting's edges where the original tacking margins were still present, a wider strip was required in order to not concentrate pressure in these fragile areas. Considering that the painting already had a significant loss at the edge of the old tacking margin, indicating the fragility of these areas, it was decided that the BEVA® 371 film strip would cover a wider area of the canvas, passing the tacking margins and reaching the healthier parts, and for that the strip had a width of 3.5 cm. At the other edge of the painting with the original tacking margin (left side) a strip 2.5 cm wide was used, and for the remaining sides of the painting, a strip with 2 cm was considered sufficient.

Once the strips were ready they were adhered to the back of the painting using the hot spatula (approximately 65ºC) (Figure V.10). The old lining adhesive had previously been removed in these areas to ensure good adhesion of the strip lining. Weights were placed on top of the strips over the adhesive areas during the cooling process to encourage the adhesion of the lining strips to the original canvas. The painting was then stretched onto the loom, where pushpins were used to attach the polyester fabric to the wood (Figure V.11). The use of pushpins instead of staples has the advantage of allowing any necessary adjustments to the tension of the painting during the initial stretching and during treatment, as well as they can be easily removed and replaced when it is necessary to change the orientation of the painting in the loom (Figure V.12).

3.6. Removal of the Lining Adhesive

Removing an old lining adhesive is very time consuming and involves a considerable risk (minor local damage to the original canvas can occur from inconsistent scraping and wetting the canvas to facilitate adhesive removal can cause severe distortion or paint loss) [12], however, it is an important step to prepare the original canvas for the new lining. The surface of the original canvas must be even and the residues of the old adhesive removed in order to obtain good adhesion and conformation between the original canvas and the new lining canvas. However, few improvements have been made regarding methods of de-lining [17]. The removal of an old lining adhesive is usually done by mechanical methods, which involves scraping the adhesive from the back of the canvas. Some new methods involving enzymes and Femtosecond lasers were proposed for the removal of glue-paste adhesives, however these methods are still very difficult to control [17].

For this painting, the adhesive proved to be relatively easy to remove by scraping. Despite the long time required to remove the adhesive (94 hours), this method proved to be effective. The removal was performed using two dentist tools, a scaler and a pick tool, and they were used according to the state of the adhesive. The old adhesive was in two states: in some areas it was powdery and pasty (especially in areas that suffered from water exposure) and in other areas it was in thick and concreted pieces. The powdery areas were scraped using the pick tool and were cleaned by brushing residue into the vacuum nozzle. The thick and concreted pieces were lifted either with the pick tool or the scaler. For these cases, the thin tip of the tool was carefully placed under the piece of adhesive to lever it off the canvas (Figure V.16).

In an attempt to obtain faster results for the removal of the thick and concreted pieces, at the suggestion of Raquel Marques, a Dremel® tool was tested. The Dremel® tool was used with a 0.8 mm engraving cutter and the rotation speed was controlled by a potentiometer based on an adapted dimmer switch [1]. While giving good results with the companion piece restored by Marques, in this case, the time consumed to remove the concreted adhesive with the Dremel® tool was very similar to the removal with the dentist tools. Therefore, this method was used only for the few areas that were showing more resistance to the dentist tools (Figure V.17).

The whole process of removing the adhesive was done under the stereomicroscope to observe closely what was happening on the surface of the original canvas and to better control the delicate work (Figures V.15, V.18, V.19).

3.7. Removal of the Facing and Surface Cleaning

Once the treatment on the back of the painting was completed (old lining canvas and adhesive removal), the facing could be taken off. Since the painting needed to be worked from the front, its orientation in the loom had to be changed (Figures V.12, V.13).

The literature states that BEVA® 371b has a good solubility in hydrocarbon solvents [13]. Prior tests of the facing removal in a small area revealed that the solvent used to dilute the solution of BEVA® 371b, White Spirits, could also be used to remove the facing. However, at the time of the actual facing removal, White Spirits was only gelling the adhesive, not dissolving it, and the removal required too much mechanical action. Two other hydrocarbon solvents were tested: Shellsol® D40 (an aliphatic solvent) and Shellsol® A100 (an aromatic solvent with an aromatic content higher than 99%) [18]. While BEVA® 371b was easily removed with aliphatic solvents or low aromatic solvents when it was freshly applied, after the adhesive had been in place for a longer time (12 weeks), a higher content of aromatic compounds was required to easily remove the adhesive.

Although Shellsol® D40 could remove the adhesive, it was taking a long time to have any effect and required extra mechanical action which was not considered safe for the painting. On the other hand, Shellsol® A100 removed the facing tissue and adhesive much more quickly. Therefore the solvent Shellsol® A was used. A cotton swab was moistened with the solvent and rolled on top of the facing tissue to activate the adhesive and loosen the tissue from the surface (Figure V.20). A piece of dry cotton followed the adhesive removal to absorb the excess solvent from the painting's surface. Due to the toxic nature of the solvent used, filter masks for organic solvents (see Suppliers in Appendix VIII.2) were used during this procedure and air exhaust units were positioned near the work area.

3.8. Local Flattening

An early attempt was made to flatten the paint tenting and distortions with moisture treatments (at the same time of the consolidation step) while the lining canvas was still in place, however, the painting was not responding and the plasticization of the materials was not occurring in the desired extent. For that reason, the flattening treatments were left to be performed after the lining canvas and adhesive removal.

After the painting was free from its lining canvas and adhesive, its response to the flattening treatments was much more encouraging. Several methods were explored to plasticize the paint but the most efficient was the combination of introducing moisture to the back of the canvas with a pre-conditioned slightly moist blotting paper cut to the size of the areas of distortion (Figure V.21), followed by a moisture tent which was created on the front of the painting. A sheet of thin Melinex® was placed over the moisture tent and sealed with light weights to avoid the dissipation of the humidity (Figure V.22). During the first treatments, the painting's response was monitored with finger pressure in short time intervals (the back was monitored in the first 30 seconds and the front in the first 2 minutes) to ensure that no harm was posed to the painting and to evaluate the level of plasticization (flexibility) being conferred by the moisture treatment. It was important to closely monitor the effect of the moisture in order to determine how long the painting was taking to respond. It was seen that 2 minutes of moistening for the back of the canvas and 10 minutes for the front were long enough to efficiently plasticize the materials. After the painting became ductile, weights were placed on top of it, with a Melinex® sheet, foam and foam-core board (to uniformly distribute the weight) with chamfered edges[3] between the painting and the weights (Figure 9) (see Suppliers in Appendix VIII.2). The painting's surface was monitored after 1 hour and heavier weights were placed on top of the painting for a longer period of time (usually overnight). The local flattening treatments were done gradually with the weights being heavier in progression with the treatment and the cushioning foam being removed once the most severe paint distortions were flattened. The plasticization of the painting before the flattening with weights is a fundamental step since the absence of flexibility in the painting at the time of pressure application through the weights may cause the paint to fracture and/or shatter.

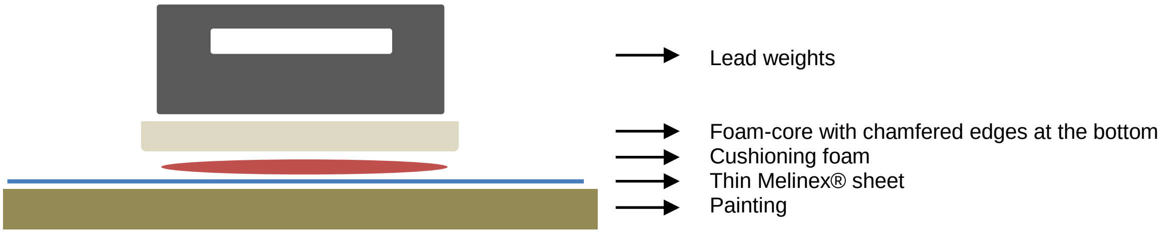

Figure 9 - Schematic of the flattening system with weights.

In areas where the paint was severely tented and cupped and the moisture treatments were not enough to restore the painting to plane, the painting was plasticized through the use of heat (with a heat spatula) and solvents introduced through the use of fresh BEVA® 371b applied to the crack lines (Figure V.23).

3.9. Further Treatment

In the time available it was not possible to complete the painting's restoration treatment. The remaining steps will involve: the removal of the yellowed varnish; the re-lining of the painting using the mist-lining technique; the stretching of the lined painting onto its new stretcher; the infilling and inpainting of losses; and the application of a final varnish.

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[3] Placing weights on top of sharp edged boards on a plasticized paint may cause a deformation on the painting's surface, hence the need for chamfered edges.

PART 2: THE MICROCLIMATE FRAME PROJECT

1. INTRODUCTION

1.1. Objectives

The three paintings from the Ecomuseu Municipal do Seixal (EMS) will be exhibited at the Tide Mill due to the relationship of this building with the family portrayed, and will be later stored at Quinta da Trindade. The museum had already reported that these buildings, due to their historic character, have an uncontrolled environment, hence the need of microclimate frames to protect the paintings. To better understand the environment in which the paintings are going to be exhibited and stored, RH and temperature values were collected for 11 months with Lascar® dataloggers (see Instrument Description in Appendix VII.1). It was confirmed that both places have strong fluctuations in temperature and relative humidity with the Tide Mill showing the worst conditions (Figures VII.10 and VII.11). In this way, the Microclimate Frame Project aimed to solve a practical problem for the EMS, offering a solution for the continued preservation of their three paintings after conservation treatments at DCR-UNL. A microclimate frame was proposed, considering their known efficacy, the characteristics of the exhibition and storage areas, the needs of the works of art, and the available budget. Since a material for buffering RH fluctuations inside the microclimate frames is required, this study also aimed to understand which available buffer is the most suitable to protect the paintings.

1.2. Literature review

It is well known that artworks can be negatively affected by daily, weekly and annual fluctuations in temperature and relative humidity (RH) [19]. To understand the potential problems caused by these fluctuations, it is important to consider the relationship between temperature and relative humidity. Relative humidity is expressed as a percentage and it can be defined as follows [20]:

$$RH = \frac{amount\ of\ water\ in\ a\ given\ quantity\ of air}{maximum\ amount\ of\ water\ which\ the\ air\ can\ hold\ at\ that\ temperature} \times 100$$

As the equation demonstrates, RH is dependent and inversely proportional to temperature, meaning that, with a given quantity of water in the air, as the temperature rises, the RH lowers because hot air has a greater capacity to hold water than cold air [20]. But how do RH and temperature fluctuations affect artworks? As reported by Toishi (1958), objects made of materials susceptible to humidity variations, such as wood, paste and glue or other organic materials, give out moisture when the air becomes drier and absorb moisture when the air becomes more humid [21].

Thomson (1964) warns that substances which contain very little free water, such as linseed oil paint, will change in size very slightly as a result of an RH change, but all cellulosic materials, such as linen, and many proteinaceous substances, such as glue, may undergo considerable dimensional changes [22]. Mecklenburg's research demonstrated that the different response of the materials in a paint composite to the environment may cause several problems such as cracking, tenting and cupping [17, 23]. He also showed that at high RH (above 80%) there is a dramatic increase in the stress of a canvas that results in severe shrinkage, and the glue size layer loses his strength and therefore the ability to maintain the bond between the canvas and the ground layer (hide glue was used in the tests) [23]. Thus, it is crucial to control the RH to which paintings are exposed, and it has been established that this control can be obtained with the use of a microclimate box or frame [24].

As well as reducing RH fluctuations and controlling the RH inside (through the use of desiccant or buffering materials), microclimate frames offer protection for the artefact against vandalism and any direct damage that could come from visitors [25] and they can protect the paintings during exhibition, storage or transit [24]. When a glazing is not desired (i.e. due to the problem of reflections or additional weight from the glass for example), a backing board alone can be used. As shown in the extensive literature search by Dina Reis in her Master thesis (2011) although a backing board offers some degree of protection (depending on the material used), the use of a glazed frame with a backing board combined greatly provides a significant buffering to RH fluctuations [26]. This was confirmed by the study of 12 model paintings installed at the Palácio da Pena initially reported in her thesis [26] which continued for a full year (unpublished report, DCR).

There are different types of microclimate frames for paintings: some can enclose both the painting and the frame, others can enclose a painting that does not have a frame, and others are built inside the frame [24]. These microclimate frames usually consist of a backing board and a glass front enclosed in a more or less air tight frame [27] with some characteristics varying from frame to frame. This model is usually preferred since it is aesthetically more pleasant and less distracting [24]. These microclimate frames can also be classified according to their content: frames with an active buffering material to stabilize the internal relative humidity, frames containing no added buffer material (but well-sealed) and frames with an altered gas content [24, 28].

Microclimates frames with an altered gas content have been mainly constructed in order to reduce de deteriorating effects of oxygen. Purging with N_2 and the use of oxygen scavengers are ways of obtaining a low oxygen content [28]. However, there are colorants that undergo changes in colour in such atmospheres: Prussian blue, vermillion and purple madder have been reported to be less stable in vacuum and/ or with nitrogen environments [29]. Townsend et al. (2008) warn that some materials in particular, such as the pigments listed above, should be investigated before they are exposed to anoxia [29].

Well-sealed cases provide some level of protection against the RH fluctuations taking place outside the case. The rate of interior RH change depends on the amount of air leakage of the case. According to Weintraub, in a case with an air leakage of one air exchange per day but with a considerable amount of hygroscopic materials, the interior RH will barely change [30]. Microclimate frames containing no added buffering material take advantage of the hygroscopic behaviour of the frame and the artwork itself as a stabilizing factor within a small air volume [28]. Thomson (1964) states that since wood holds much more water that air, considering volume for volume, its effect, though slower, will finally predominate unless there is only a very small quantity present [22].

Sozzani (1997), in a study that involved microclimate frames both with and without wooden panels and silica gel, submitted to cycles of fluctuating temperature and constant RH, proposed that the moisture released by a wooden panel due to a rise in temperature, will be absorbed by the silica gel in order for it to maintain its preconditioned RH. He warned that in a period of sustained elevated temperature the wood can continue to give off moisture that in turn, is absorbed by the silica gel, inducing further dimensional change in the panel. However, he emphasized that only in well-sealed microclimate frames with minimal internal air volume can the object come into a moisture equilibrium with the surrounding air with inconsequential moisture exchange between the air and object [19].

There have been differing opinions regarding whether a microclimate case or frame should include an added buffer or not. Although tests show that enclosures with no added buffer material perform well for a case containing wood (Sozzani 1997, Thomson 1964) [19, 22], it should be noted that Toishi and Gotoh (1994) warn of damage resulting from enclosing objects containing a minor component with different hygrometric properties in such way [31]. They state that when an object is composed of different materials – such as paintings – moisture moves between these materials and there may be instances where moisture moves from a minor to a major component, damaging the former. Their evidence for this came from a painting that suffered noticeable flaking in the gouache retouching after traveling in an airplane. They showed that the use of a buffering material, by releasing moisture, would counteract the tendency of the minor component to desiccate [31].

By having a high water capacity and responding quickly, these buffering materials are the first to react to the introduction or loss of moisture in an enclosed system, thus reducing the response of the artefact they are there to protect [21]. This type of passive humidity control within the cases are very simple and seem to be a cost-efficient method of protecting the artworks from damage induced by relative humidity variations [30].

Apart from the problem of the RH and temperature variations, there is also another cause of concern related to microclimate frames. Enclosing a painting in a microclimate frame can protect the painting from pollutants generated outside (mainly inorganic), but can lead to the build-up of pollutants generated inside (mainly organic) [25, 27]. Research related to this topic has just recently been developed; the most extensive is the PROPAINT project published in 2010. As a results of this research, the recommendations of López-Aparicio, S. et al. (2010) (study in the course of PROPAINT project) is to make the microclimate frames as tight as possible to avoid infiltration of oxidizing pollutants and possible reactions with organic compounds, but to avoid the use of construction materials in the frames with high emissions of organic compounds. They also advise observing a significant period of time between the construction of the microclimate frame and the installation of the painting. SIT International Transporters (an international transporting and frame design company) advise at least three months for this [28]. The PROPAINT report states that mitigation measures can be the application of absorbing materials, installation of barrier films to cover construction materials that emit pollutant gases, such as wood, or changing the composition of the atmospheres inside the microclimate frames.

Another cause of concern which adds to the previous issues is the possibility of mould growth [32, 33]. As stated by Michalski (2004), the use of backing boards in warm and humid countries have been avoided due to the fear of mould growth at the back of the paintings, but many of the advantages of enclosed systems were also being lost [32]. The cause for this mould growth at the back of the painting would be the maintenance of a stable environment with high relative humidity for a prolonged period of time. An example provided by Michalski is that for a painting placed in a room with 90% RH at night and 50% RH during the day, mould will not grow because the work of art dries during the day. It could be assumed that the environment inside a microclimate frame with the painting, placed in that same environment would reach a stable average of the day/night cycle, 70% RH. However, studies had shown that porous materials, such as wood and plywood, are much more permeable to moisture at 100% HR than at 50% RH (up to 20-50 times). In this way, the humidity would enter into the microclimate frame much more easily than it would come out, and in a microclimate frame placed in an environment with 50%RH during the day and 90% during the night, the average RH would not be 70% but higher. This would make the risk of mould growth much greater, especially if the painting's canvas was coated with vulnerable materials such as old glue paste linings. In order to prevent this situation Michalski advises the use of ventilation holes at the bottom and top of the frame so that the humidity could escape from the microclimate much more easily during the day [32].

A practical study by Toledo et al. (2007) performed in warm and humid museums, showed that greater mould growth occurred on the paintings that were not protected by a glass box. It was also seen that dust and dirt deposition was much more frequent on unprotected paintings, as it would be expected [34] and it is possible that the presence of dust and dirt could promote mould growth.

As this discussion of the current literature indicates, the use of microclimate frames for paintings can bring numerous advantages for the protection of the work of art, but only as long as these framing systems are well planned and constructed with carefully selected materials [28].

1.2.1. Materials used and the construction of a microclimate frame

Methods for the construction of microclimate frames can vary in detail but are very similar in general. Generally, glazing is mounted in the frame rabbet and a backing board is attached to the back of the frame. A build-up at the back of the frame may be necessary either to accommodate a buffering material or the backing board itself (Figure 10). Older methods could consist of the use of a glass "door" at the front of the painting. However these were generally added to existing frames and had the disadvantage of requiring the alteration of the original frame, leaving it frequently heavy and complicated in appearance [33].

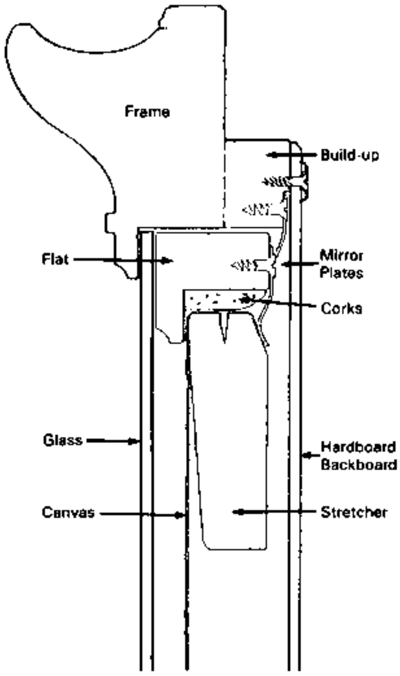

Figure 10 - Schematic example of a microclimate frame, in cross-section view. Image by Stephen Hackney, from "Framing for conservation at the Tate Gallery", 1990 [33].

The materials used for the construction of microclimate frames have been varied [28]. Glass, acrylic sheets, polycarbonate, and other similar materials have been used for the glazing. Acrylic sheets have the advantage of being less breakable than glass, with polycarbonate being even stronger. The disadvantage of both is that they can have a high reflection unless treated and are relatively easy to scratch [33]. Recently high quality acrylic sheets for glazing of paintings have been developed (Optium acrylic®), and according to the manufacturer it is lightweight, non-reflective, anti-static, and clear-coated but they are currently expensive. It is possible to find good quality low reflecting glass but glass has the disadvantage of being fragile and very heavy. Laminated glass, which is impact resistant, is safer for framing systems and is also available with low reflecting glass treatments [33].

As for the backing board, oil tempered hardboard has been one of the most widely used materials. It is reasonably impact resistant, a good moisture barrier and not expensive but is also heavy, distorts in high humidity and it is not an archival quality material. In order to prevent acidic materials from the hardboard from entering into the microclimate frame it is advisable to cover the inside surface with a layer of Melinex® (polyester film) or polyethylene film [33]. In the PROPAINT report, Marvelseal® 360 (an aluminized polyethylene and nylon barrier film) is also mentioned to cover the backing board and the inner part of the wooden frame. Aluminium tape is also referred to as a material to seal the wooden frame [28]. Other more expensive materials are referred to in the literature as core boards containing polystyrene foam, honeycomb laminates made with glass fibre or aluminium skins, and polyethylene laminated cardboard [33]. Aluminium sheets have also been used. Some authors defend that visual inspection of the back of the painting is also important and for that, a transparent backing material can be useful, such as polycarbonate sheets [28]. The materials used in these frames can be held together by aluminium tape and brass or steel screws [28].

The PROPAINT report provided some guidelines that should be considered for the construction of a microclimate frame: its design should ensure an efficient and simple mounting process and attention must be paid to the visual appearance of the system. The size and weight of the microclimate frame must also be considered in relation to its handling. All materials should be conditioned at the same temperature and RH prior to installing the painting [28].

1.2.2. Materials for buffering relative humidity fluctuations

When it is necessary to protect artefacts that are enclosed in a case or a microclimate from relative humidity fluctuations, a buffering material is usually recommended. As noted above buffering materials quickly absorb moisture as the air grows humid and emit it as the air becomes dry [21]. Some of these buffering materials (such as silica gel) are used as dehumidifying agents. For that purpose, they are first heated to drive off all possible moisture. When used as a passive buffer it is necessary to condition them before use at the humidity desired [21]. A great variety of substances and products have been used to buffer RH fluctuations. These materials include clay, saturated salt solutions, silica gel and a variety of commercial products.

Silica gel is a well-known material for buffering RH fluctuations. It was first recommended by Toishi in 1959 for museum applications [30]. This chemically inert and non-toxic material is composed of amorphous silicon dioxide (SiO_2) and has an internal network of interconnecting microscopic pores, yielding a typical surface area of 700-800 square meters per gram [30]. The water molecules are adsorbed or desorbed by these micro-capillaries until a vapour pressure equilibrium is achieved with the relative humidity of the surrounding air [30]. Nevertheless, a considerable amount of the material is needed (20Kg/m^3) in order to achieve its best performance (the amount required was determined by Thomson) [20, 25]. Therefore in recent years other materials have been tested and developed for buffering RH fluctuations with the aim of being a better alternative to silica gel, either by having a faster response to fluctuations, or by requiring less material, or both.

Artsorb®[4] is one of the popular alternative materials to silica gel. It consists of an aqueous solution of lithium chloride embedded in silica gel pores [35 - 37]. Lithium chloride is a highly corrosive salt with a pronounced desiccative property [20, 38]. Artsorb® is sold in three different forms: beads, cassette or sheet [37]. It has the advantage of having a water capacity in the range of 50-60% RH which is twice that of the best silica gels [36]. Supplied in lightweight sheets is undoubtedly convenient to control RH fluctuations inside narrow spaces such as in microclimate frames. According to the manufacturer, the required amount of Artsorb® sheet in a well-sealed case is 1 sheet for $0.099m^3$, corresponding to 10.1 sheets per cubic meter, while the amount required of Artsorb® beads is $1kg/m^3$.

According to Weintraub (2002), the reason for the discrepancy for the amounts required of Artsorb® and silica gel is not based on a comparison of buffering capacity, but relies on the different formulas used for determining the quantity [30]. Thomson calculated the amount of silica required to buffer the RH in an average case over a full year so that it would never require reconditioning. The case would be self-correcting and maintenance free [20, 30]. The interior would be buffered against low winter RH and high summer RH in the surrounding air (of Britain). As stated by Weintraub, the source of the recommendation for the amount of Artsorb® is not known, but it is thought that Artsorb®'s recommendation of $1kg/m^3$ is based on protection against RH fluctuations caused by rapid changes in temperature, a short-term effect. In this way, for protection against long-term leakage, Weintraub suggests that much more Artsorb® would be required [30].

Another well-known buffering material is Prosorb®, a commercial product similar in formulation to Artsorb® but instead of having lithium chloride it contains aluminium oxide (Al_2O_3) [35]. Prosorb® is recommended for buffering RH fluctuations at lower relative humidities (compared to Artsorb®), specifically in the range of 35-60% [37]. An experimental method developed by Melin in 2007 which compared two silica gels, Artsorb® and Prosorb® showed that when conditioned at 50% RH, Artsorb® presents better results in a humid climate and Prosorb® in a dry climate [35].

Other materials have been recommended for buffering RH fluctuations but it is not possible to describe all of them in detail in the present study.

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[4] Other synonyms for Artsorb are Art-Sorb, ART-SORB, ART SORB and Art Sorb.

2. THE CHOICE OF A MATERIAL FOR BUFFERING RH FLUCTUATIONS

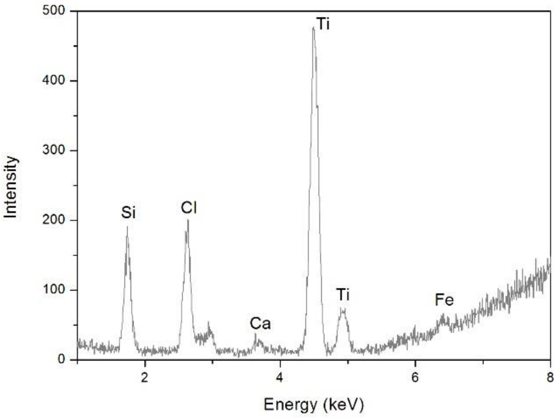

Figure 11 - µ-EDXRF spectra of an Artsorb® sheet.

Lightweight and thin, Artsorb® sheets appear to be an excellent choice for buffering RH fluctuations in microclimate frames for paintings. However, there are concerns regarding the presence of the corrosive salt lithium chloride in the composition of Artsorb® [37]. Lithium chloride (LiCl) is used for various commercial applications such as air conditioning and industrial drying systems [38]. In dehumidification systems its corrosive properties on metals is recognized [39].

To mitigate contamination to artworks, the use of a permeable but dustproof material, such as Tyvek® (non-woven fibres of 100% high density polyethylene), has been suggested [37]. Due to the strong fluctuations and frequent high RH in the Tide Mill, it is desirable to use a buffering material inside the microclimate frames. Considering the advantages of Artsorb® and the availability of this material in the Ecomuseu Municipal do Seixal, for whom the microclimate frames are being planned, it was not ruled out without some tests being made. Therefore, the present study set out to test Artsorb® in relation to its corrosive potential and to establish whether Tyvek® effectively limits the spread out of LiCl without significantly reducing its efficacy. The presence of chlorine in the Artsorb® sheets had already been identified by Melin (2007) [35] and was confirmed in the current thesis through µ-EDXRF analysis. Other elements such as Si, Ti, Ca and Fe were also found (Figure 11).

Two Oddy tests and a third adapted test were performed in order to establish whether Artsorb® releases LiCl. The Oddy test is an accelerated corrosion test for the effects of display or storage materials on metals, however, as explained by Thickett and Lee (2004), it is also possible to deduce from the Oddy test the effects of a display or storage material on non-metallic artefacts, since the pollutants that cause corrosion on certain metals are also known to be the cause of deterioration on various non-metallic substrates [40]. For this work, the objective was to look for the effects of the corrosive salt lithium chloride.

To evaluate whether Tyvek® would reduce the efficiency of Artsorb® as a humidity buffer, sets of framed and glazed model paintings with both covered and uncovered Artsorb® were placed at the Tide Mill. Since it was anticipated that a substitute material will be required if Artsorb® was found to be unsuitable, the experiment at the Tide Mill also included framed and glazed model paintings with silica gel as the buffering material. The silica gel was also included in the Oddy test.

2.1. Preliminary tests of the potentially corrosive Artsorb®

2.1.1. Experimental design

Three tests involving metal coupons to investigate the potential corrosiveness of Artsorb®'s lithium chloride were performed. Each test is described below.

Test 1: Oddy test

Coupons, 1 x 1.5 cm, of silver, copper and lead 0.1mm thick as specified in the Oddy test protocol [40] were polished with a glass bristle brush to expose a reactive surface and then degreased with acetone. As required by the test, 2g of each test material (orange silica gel, Artsorb®, and Artsorb® in a Tyvek® bag) were placed in 50ml glass bottles with a coupon of each metal. Another 50ml glass bottle with no material to be tested was used as a control (Figure VII.1). A small glass container with 0,5ml of distilled water was placed inside each sealed bottle to obtain an environment with 100% RH. The test was placed in an oven at 60ºC for a period of 28 days (see Equipment and Suppliers in Appendix VIII).

Test 2: Oddy test

The Oddy test was repeated with the buffers preconditioned to 100%RH so that the buffering materials would not remove the humidity from the environment inside the bottles. Due to problems with the use of the glass bristle brush in the previous test (polishing over such a small area was found to be dangerous to the researcher) for this test, a paste of calcium carbonate in water was used to polish the coupons. The orange silica gel used in Test 1 was replaced with a silica gel without indicator. Preconditioning involved placing the buffering materials inside a sealed box with a metal container to contain the water (Figure VII.2). The boxes were placed in the oven at 60ºC and the weights of the buffering materials were monitored periodically until they stabilized, indicating that the material reached its maximum absorption for that temperature. After the preconditioning, the buffering materials were placed inside the glass bottles as per Test 1 and the second Oddy test took place. The test period was 28 days as in Test 1.

Test 3: Adapted test

Copper coupons with the same dimensions as the ones in the previous tests were polished with a 1500 Micro-mesh cushioned abrasive to create a reactive surface and were degreased with acetone. The coupons were placed in 250ml bottles (50ml bottles were unavailable) containing 10g of Artsorb®. Both the control bottle (with no Artsorb®) and the one with Artsorb® contained 2.5 ml of water to have the same ratio of water per volume of air as the first Oddy test. The remaining bottle contained 6.5 ml of water. The 6.5 ml of water was calculated based on the maximum absorption of Artsorb®. It is known through the Artsorb® isotherm that at 100% RH, Artsorb® has 40% of absorption capacity, meaning that it can absorb 40% of its weight [37]. Therefore considering that 10g of Artsorb® were being used in each bottle, 4 ml of water were added to the 2.5 ml of water that was going to evaporate into the environment. This amount of water aimed to reproduce the pre-conditioning at 100%RH of the buffering material but this time, inside its own bottle. These three bottles were placed in the oven, at 60ºC, and another three bottles reproducing the exact same conditions were placed at ambient temperature (~25ºC). The test ran for 42 days.

At the end of each test, coupons were digitalized for a better observation of the surface using a flatbed scanner[5] (see Instrument Description in Appendix VII.1). The visual analysis of the metal

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[5] This method was suggested by Wolfram, J., Brüggerhoff, S. and Eggert, G. in 2010 in the paper: Better than Paraloid B-72? Testing Poligen waxes as coatings for metal objects. Thanks to Leonor Oliveira for sharing this reference.

coupons were complemented with µ-EDXRF and SEM-EDS analysis for the presence of chlorine. The differences and variables between each test are summarized in Table 1.

Table 1 - Differences between Test 1, 2 and 3.

Test	**Variables**				
	RH of the buffering materials		**Polishing method**	**Duration time of the experience**	**Observations**
	Artsorb	***Silica gel***			
Test 1 (Oddy test)	50% RH	0% RH[6] ?	Glass bristle brush	28 days	Materials to be tested placed directly in the test containers.
Test 2 (Oddy test)	100% RH	100%RH	Calcium carbonate	28 days	Materials first pre-conditioned in a separate container.
Test 3 (Adapted test)	50% and 100% RH	-	Polishing cloth	42 days	Materials to be tested placed directly in the test containers.

2.1.2. Results and discussion

At the end of the first Oddy test (Test 1) it was seen that the coupons had corroded by different mechanisms: while the control corroded by a wet process, the other coupons corroded by a dry process. It was then proposed that the buffers may have extracted the water from the environment since the Artsorb® was pre-conditioned at 50% RH and the silica gel was dry. All the coupons enclosed with the buffers exhibited a green or yellow colour contrasting with the copper coupon from the control which had an orange colour. Although visual comparison between the control and the other coupons from the first Oddy Test was difficult, it was possible to observe a higher degree of corrosion in the ones exposed to the orange silica gel and Artsorb® (Figure 12). The copper coupons were the easiest to evaluate visually. The silver and lead coupons did not show significant evidence of corrosion (only a few localized corroded areas were seen in the silver) (see Table VII.1 Appendix VII.3).

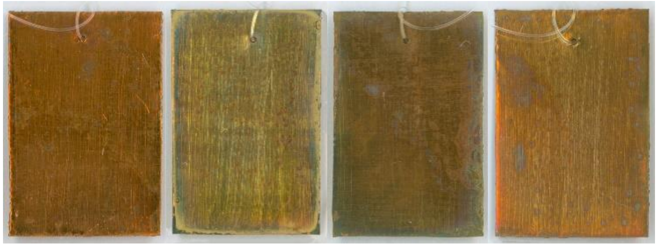

Figure 12 - Copper coupons from the left to right: control, orange silica gel, Artsorb®, Artsorb® with Tyvek® cover.

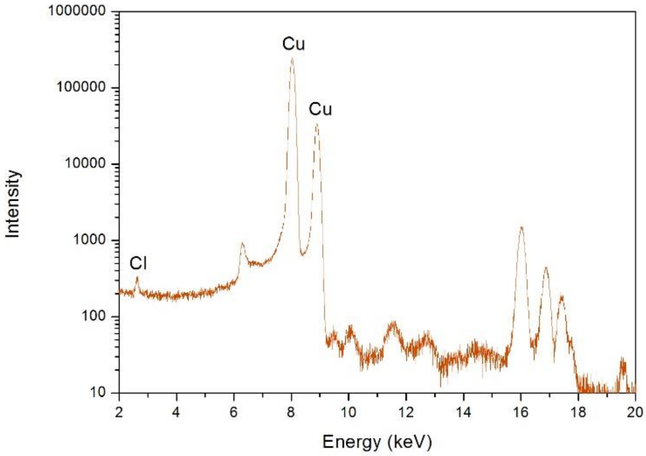

Figure 13 - µ-EDXRF spectra from the copper coupon with Artsorb® (first Oddy test).

µ-EDXRF analysis of the copper coupons revealed the presence of chlorine on those exposed to Artsorb® and Tyvek® covered Artsorb®, although chlorine appeared in lesser extent in the one with Tyvek® (Figure 13) (silver and lead coupons were eliminated

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[6] The RH at which the orange silica gel was pre-conditioned is not known. It was supposed to be dry but the container from where it was taken was no longer sealed.

from µ-EDXRF because the Cl peak K-Alpha overlaps with a secondary peak from silver, and the lead overwhelms lighter elements such as chlorine).

In the second Oddy test (Test 2), none of the coupons revealed corrosion to a higher degree than the control with the exception of the lead coupon from the silica gel. Even the copper coupons that were the easiest to evaluate visually in the first Oddy test did not show any significant corrosion (see Table VII.2 Appendix VII.3). These coupons were also analysed with µ-EDXRF but no chlorine was observed in the spectra for any of them. On the lead coupon from the silica gel a few white spots were seen on the surface. It is not clear the reason for this slight corrosion since silica gel is chemically non-reactive [20, 30] and in the first Oddy test no corrosion was seen in the lead coupon from the silica gel. It is proposed that the corrosion might be related with water condensation on top of the coupon since in some bottles condensation occurred.

Test 3 was done as an attempt to understand the reason chlorine was detected in the first Oddy test but not in the second. It may be that the absence of chlorine in Test 2 could lie in the different polishing methods used for the coupons or in the fact that the material was first pre-conditioned in a separate container. The glass bristle brush leaves a more reactive surface on the metal due to the striations left in the surface of the metal which increase the surface area available for reaction presumably leading to its greater response to pollutants or contaminants versus the surfaces polished with calcium carbonate. As for the pre-conditioning two theories are proposed: that the hygroscopic salt lithium chloride left the Artsorb® when it was exposed to 100% RH leaving a smaller amount in the Artsorb® sheets to react during the test, or that the lithium chloride, when exposed to such a high level of RH, was not available to react with the remaining materials due to its high affinity with the water. For that reason, in Test 3 the metal coupons were polished with a coarse polishing cloth to create striations and expose a more reactive surface, and the amount of water in the test bottles was varied to see how the salt would behave when saturated and not saturated with water. This test also included a variation in the temperature to see if that would have an influence on the salt reactivity. However, at the end of the test, none of the coupons exhibited a significant degree of corrosion and no chlorine was found in µ-EDXRF analysis (see Table VII.3 Appendix VII.3).

Since the reason for the lack of chlorine in the two last tests was unclear, SEM-EDS analysis on the coupons were performed. EDS spot analysis were done based on visual evidence of corrosion areas

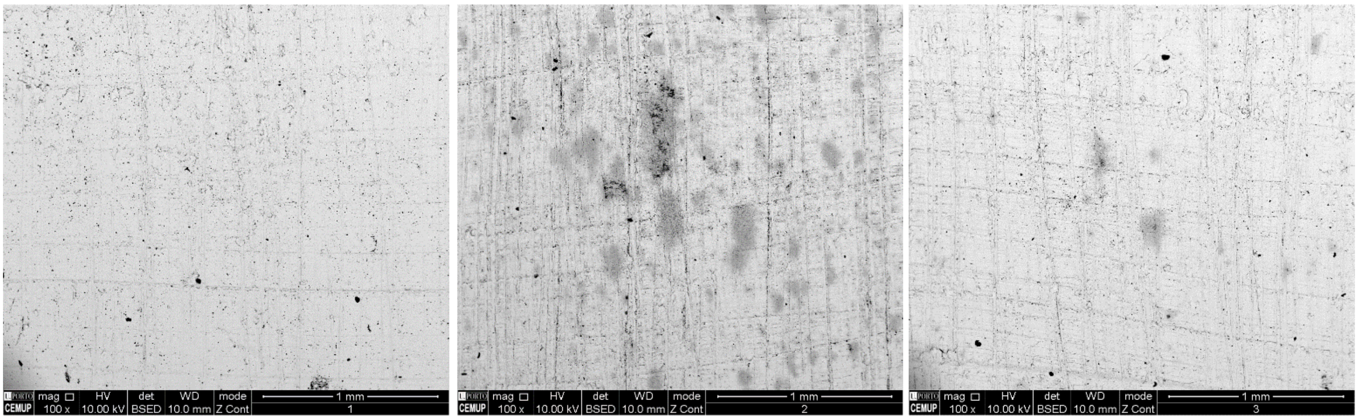

Figure 14 - SEM-BSE micrographs, 100x magnification of silver coupons from the first Oddy Test.
Left: Control; **Centre:** Artsorb®; **Right:** Artsorb® with Tyvek® cover.

on the metal. Results of the silver coupons from the first Oddy test were consistent with µ-EDXRF on the copper coupons: the control showed no presence of chlorine while the coupon from the Artsorb® environment had a significant amount. This was seen as dark stains in the SEM-BSE micrographs and EDS analysis confirmed the presence of chlorine on these spots (Figure 14) (see Appendix VII.4, Figure VII.3). These stains are likely to be reaction products of the metal with the chlorine. The coupon from the environment of Artsorb® with Tyvek® cover revealed some stains but to a much lesser extent (Figure 14). These findings support that a Tyvek® cover over Artsorb® reduces but does not eliminate chlorine contamination from the Artsorb® sheets.

However, analysis of the coupons from Test 2 and 3 showed less consistent results. From the second Oddy test only the copper coupons from the control and the Artsorb® could be analysed due to time limitations. On the control coupon, in one of the several spot analysis, a very small peak of chlorine was identified. In the Artsorb® coupon, chlorine appeared more pronounced and more frequently than in the control. Yet, the presence of chlorine on this coupon from Artsorb® was not as significant as in the silver coupons from the first Oddy test.

From Test 3, one coupon from each environment was analysed. On the control exposed to 60ºC no chlorine was found. On the coupons exposed to that same temperature and confined to an environment with Artsorb® with 2.5ml and 6.5ml of water, chlorine was identified but its occurrence was very small. In contrast, on the coupons exposed to ambient temperature, chlorine was found on all of them including in the control, although in this last one it was restricted to a drop mark that resembled an accidental contamination.

Although the presence of chlorine on the control from Test 2 is insignificant and on Test 3 it appears to be explained by an external contamination, it is necessary to consider the possibility of contamination by the distilled water used. However, this theory raises questions regarding the source of chlorine in the remaining coupons. On Test 1 it is highly unlikely that the chlorine found on the coupons exposed to Artsorb® and Tyvek® covered Artsorb® was due to water contamination since chlorine was not found on the controls. In addition, the fact that chlorine was more easily found on the coupons exposed to Artsorb® than in the controls on Test 2 and 3, supports that even if contamination occurred, the Artsorb® contributes to the release of chlorine that attacked the metal coupons.

It is not fully understood why the occurrence of chlorine on coupons from the environment with Artsorb® in Test 2 and 3 was much reduced in comparison to Test 1. It had already been proposed that the absence of chlorine on Test 2 may be due to the surface polished with calcium carbonate not being as reactive as the surface polished with the glass bristle brush due to the striations created on the material by this last method. However, the presence of chlorine on Test 3, where striations were created on the surface of the coupons with the coarse polishing cloth, was still not nearly as evident as in Test 1. With the results at this point it is only possible to propose that perhaps polishing cloths do not provide a metal surface as reactive as that produced by the glass bristle brush. Further testing will be undertaken to explain these differences and to confirm the release of chlorine by Artsorb® sheets.

2.2. Preliminary tests on the efficiency of Artsorb® with and without a Tyvek® cover

2.2.1. Experimental design

Four microclimate (MC) frames with two replicates (in a total of eight frames) were installed at the Tide Mill. All the MC frames were made in the same way, so that the only variable is the buffering material placed inside. Each MC frame enclosed a model painting[7], made by Dina Reis (2011) for her thesis, in order to simulate the conditions inside a real microclimate frame.

For this study the minimum amount of buffering material required for each case was calculated, based on the volume of the case, in order to establish the amount of material required for adequate performance. However, as previously mentioned, the recommended amount of the two buffering materials is not comparable since the amount for silica gel is based on the long term efficiency of a microclimate frame while the recommended amount for Artsorb® is based on the attenuation of short term fluctuations. Therefore, the amount of buffering material used was the maximum amount possible for the available volume in order to obtain the best performance for the system. Both silica gel and Artsorb® were pre-conditioned at 50% RH.

Control MC frame: This MC frame does not include any material for buffering RH fluctuations, to compare the buffering capacity of the buffers in relation to an empty MC frame. The control also allows the assessment of the buffering capacity of the frame itself, through the comparison of RH measurements inside with the measurements from the room.

MC frame with Artsorb®: This MC frame includes an Artsorb® sheet (with 25 x 35 cm) adhered with double sided tape to the polypropylene (PP) backing board. The sheet has a square of 7 x 7 cm in the middle to accommodate the datalogger (Figure VII.4). The amount of Artsorb® that fitted in the microclimate frame was 6.14 times more than the amount recommended by the manufacturer.

MC frame with Tyvek® covered Artsorb®: This frame has the same amount of Artsorb® as the previous MC frame but the buffer is wrapped in a Tyvek® cover (Figure VII.7). This frame was included to evaluate whether Artsorb® covered with Tyvek® would still perform efficiently (Figure VII.5).

MC frame with Silica gel: In this frame, silica gel was placed in a Reemay® bag, designed to hold as much silica gel as possible and to gain maximum surface area exposure. As in the other microclimate frames, a 7 x 7 cm square was left open in the silica gel's bag for the datalogger. A second layer of Reemay® (a random non-woven polyester) was placed between the silica gel's bag and the inner space of the microclimate frame to avoid any silica gel dust from falling into the back of the painting and to prevent spillage in case the bag tears. The amount of silica gel that fitted in the microclimate frame (approximately 400g dry weight) was 3.51 times more than that recommended by Thomson [20, 30]. This buffer was chosen as an alternative to Artsorb® should it be proven unsuitable and it was also tested to compare its efficiency against that of Artsorb® (Figure VII.6).

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[7] Model paintings were composed of linen canvas stretched on wooden strainers. The canvas was gel-sized with rabbit skin glue, then coated with layers of pigmented dammar varnish to simulate a painted surface [26].

2.2.2. Construction of the model frames and installation

Each MC frame was composed of a wooden frame with a glass glazing and a polypropylene hollow sheet backing board. Spacers, to create a gap between the model paintings and the glass were constructed with 4mm thick cardboard with PEL archival quality rabbet foam attached (see Suppliers in Appendix VIII.2). In each MC frame, a datalogger was hung inside such as the detector was situated at the center back of the painting (accommodated in the open space left in the buffers). Four archival cardboard triangles were placed in the corners at the back of the frame to work as a spacer between the painting and the backing board in order to prevent the painting from falling back. The backing board was held in place with mending plates and brass screws (see Suppliers in Appendix VIII.2). Cork spacers 2cm thick were nailed into the bottom of the frame to keep it from contact with the wall in order to avoid any condensation at the back of the frame (Figure VII.9) [41].

The eight MC frames were hung at the Tide Mill on the same wall, in the room where the three paintings will be exhibited (Figure VII.8).

2.2.3. Results and discussion

Due to a technical problem (an insufficient number of dataloggers available), the duplicate set was not available in the first two months. After that time, on the 8th of August, custom-made dataloggers were used which provided the required number for the eight frames, such that replicas were installed for each MC frame and the test could then run with duplicates. These dataloggers have the advantage of enabling the downloading of the data without the need to open the frames (for details see Appendix VII.1).

The RH and temperature inside the first set of MC frames was measured from the 20th of April until the 1st of September with an interval from the 16th of June until the 8th of July where no readings were performed. In this period of time the MC frames were removed from the Tide Mill to download the data from the dataloggers and to expose them to the same RH and temperature conditions as the set of duplicates before they were all placed again at the Tide Mill. As well as the custom-made dataloggers being used, the ones from Lascar® remained inside the first set of MC frames to confirm the readings. The RH and temperature data from the Lascar® dataloggers (from 20th of April until the 8th of August) are presented in Figure VII.12. Data from the custom-made dataloggers in Set 1 and Set 2 (from the 8th of August until the 1st of September) for each MC frame is presented and compared separately in Figure VII.13. This data was not considered for the conclusions in this work because the results from the two sets were not consistent throughout. In spite of following the same curve, RH values from the control MC frame and from the one with Artsorb® had a difference of approximately 5% RH in the readings (Figure VII.13). It is not possible to know yet if this difference is due to a failure in the accuracy of the sensors or if the RH variation is real. This will only be ascertained when data from the Lascar® dataloggers is accessed and compared with data from the custom-made dataloggers placed inside the same MC frames. To avoid opening the frames an extra time, this comparison will only take place further ahead in this experiment.

In spite of this problem in the readings from the new dataloggers, the experiment revealed important findings. Results from the microclimate frames show that all systems effectively reduce daily RH fluctuations (Figure VII.12). Silica gel proved to be the most effective buffering material followed by

Artsorb®. Figure VII.12 shows that the microclimate frame with no buffering agent behaves very similarly to the one with Tyvek® covered Artsorb® meaning that Tyvek® greatly reduces the effectiveness of the buffering material. A full year of data will confirm whether these initial results hold, and whether the buffering materials continue to perform well. However, it is notable that as previous studies conclude [19, 22] simply placing a painting in a glazed frame with a backing board does reduce daily fluctuations, although the effect is improved with a buffer.

2.3. Conclusions and proposal for a microclimate frame

Results from the preliminary tests of Artsorb® indicate that it releases chlorine from the lithium chloride salt into air (based on Cl contamination on the metallic coupons). It was seen that a Tyvek® cover over Artsorb® reduces but does not eliminate evidence of chlorine contamination but also significantly reduces the buffering capacity of Artsorb®. Therefore Artsorb® or Tyvek® covered Artsorb® is not recommended for the MC frames that are being planned for the three paintings of EMS.

Silica gel without indicator showed no significant negative effects on metal coupons (based on visual evidence and µ-EDXRF analysis) and the literature refers to this compound as being chemically inert [20, 30]. In addition it was the most efficient material to buffer RH fluctuations, as well as maintaining the RH inside the MC frames below the critical value of 65% during the period of time in which the experiment took place. As a result of this study, silica gel is the buffering material recommended[8] for use in the microclimate frames.

One of the microclimate frames will be built at the UNL-DCR and it will consist of a simple system that could be easily assembled by the museum staff. It will follow the most common microclimate frames, composed of anti-glare glazing and a backing board mounted on a wooden frame. Since the RH at the Tide Mill is frequently high, it may be advisable to cover the inner part of the wooden frame with an aluminium foil such as Marvelseal® 360 to avoid infiltration of water vapour in the microclimate frame by diffusion through the wood. As for the backing board, since the painting was at some point infested by mould, it is suggested a transparent material such as polycarbonate, to enable the inspection of the back of the portrait. The available budget of the museum for its construction is 1499.37€, however, since the museum is a public institution with very limited resources, efforts will be done to reduce the cost of the microclimate frame.

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[8] Further research should be carried out on the effect of dust from silica gel since it is unlikely to have chemical consequences but might induce mechanical changes in the cellulosic materials (e.g. canvas). Ideally, a barrier material for dust (such as Gore-tex®) should be used. Gore-tex® is made of polytetrafluoroethylene, is chemically inert, air permeable and has been used for filtration in industry to reduce air pollution [42].

FINAL CONCLUSIONS

The treatment of the portrait of *Domingos Affonso* was planned based on the prior study of its materials and condition, which helped to ascertain the most appropriate treatment options for this painting. For example, the study of the fungal community present on the paint surface and on the original and lining canvas revealed the presence of active microorganisms and strongly influenced the choice of materials to be used during the restoration treatment. Also, the finding of an overpaint layer over the background and the figure's jacket is important in interpreting the current image and for understanding the varnish layers present which will help in the development of a controlled method for varnish removal.

The treatment of the painting was a rewarding experience which contributed for the improvement of the student's manual dexterity, for the understanding of the materials' behaviour and response to the treatments, and highlighted the importance of a preliminary study of the painting's materials and condition.

In addition to the treatment, this thesis also focused on the portrait's after care. One year of data collected at the exhibition and storage areas revealed strong fluctuations in RH and temperature and emphasized the need for a microclimate frame to protect the painting. The identification of active mould on the painting established the need for monitoring after its conservation treatment and influenced the planning of the microclimate frame where a transparent backing board is proposed to facilitate the inspection of the back.

Findings from the tests of Artsorb® confirm the potential danger of enclosing this material with artworks. The use of a Tyvek® cover to eliminate lithium chloride contamination was not effective, in addition to hamper the performance of Artsorb®, thus ruling out the possibility of using Artsorb® safely. These findings are not only relevant for this particular case but also for the conservators' community in general since this buffering material is widely used. The good performance of the silica gel without indicator in the tests led to its being proposed as the material to buffer RH fluctuations. Future work will involve the construction of the microclimate frame with the challenge of a design to support the silica gel.

Further study is required to understand the real dangers of Artsorb® for paintings and to confirm that it is not suitable for use in the conservation field.

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APPENDICES

For a better resolution of the images see the digital Appendix (DVD) attached to this thesis.

APPENDIX I – Overall Before Treatment Images

Figure I.1 – Normal light, front.

Figure I.2 – Normal light, back.

Figure I.3 – Raking light from the right side, front, showing painting and canvas deformations.

Figure I.4 – Raking light from the right side, back, showing canvas deformations.

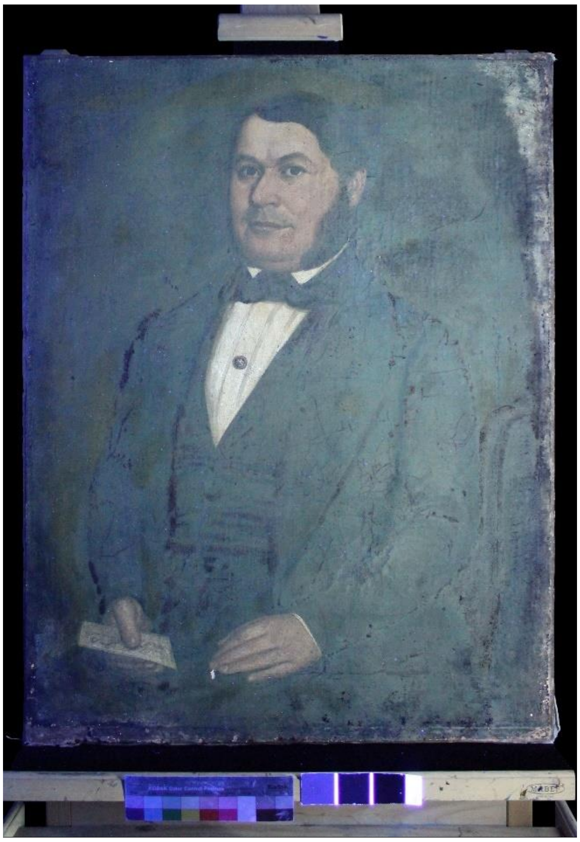


Figure I.5 – Ultraviolet light, front, showing varnish fluorescence.

Figure I.6 – Ultraviolet light, back, showing canvas staining.

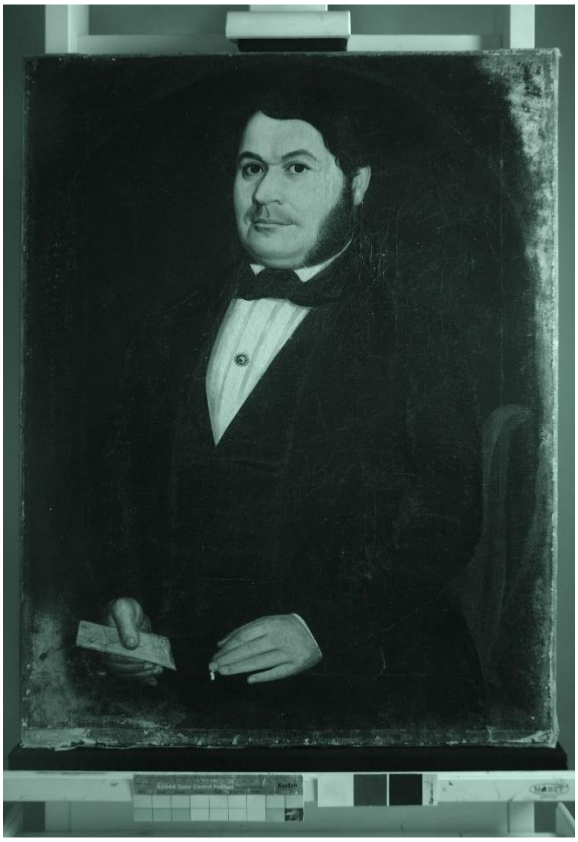


Figure I.7 – Infrared light, front.

Figure I.8 –X-radiograph.

APPENDIX II – Before Treatment Detailed Images

Figure II.1 – Tenting and cupping paint in the figure's arm.

Figure II.2 – Distortions on the canvas, visible from the back of the painting, corresponding to the area of tenting and cupping paint at the front.

Figure II.3 –Water mark in the stretcher and canvas and mould growth on the canvas. The arrow indicates one of the insect exit holes present in the stretcher.

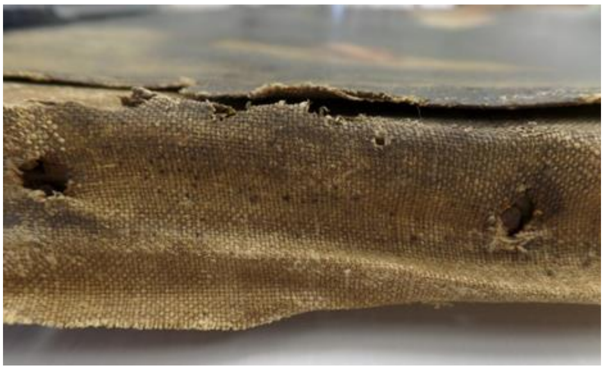
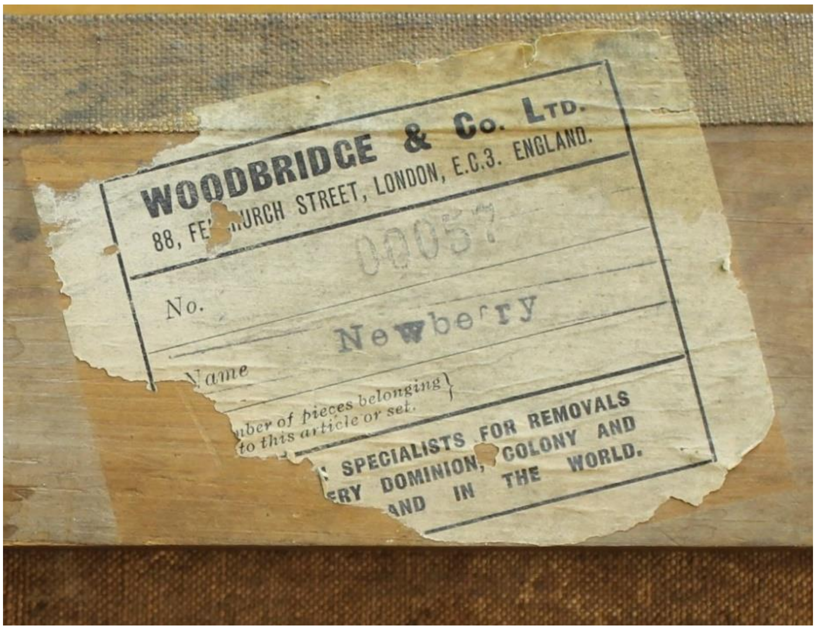


Figure II.4 – Oxidized tacks and torn lining canvas. The lining canvas was completely detached in the bottom.



WOODBRIDGE & Co. LTD.
88, FE URCH STREET, LONDON, E.C.3. ENGLAND.
No. 00057
Name Newberry
ber of pieces belonging to this article or set.
SPECIALISTS FOR REMOVALS
ERY DOMINION, COLONY AND
AND IN THE WORLD.

Figure II.5 – Label of the British transport company placed on the painting's stretcher.

The information on the label was completed in Marques's thesis by comparing the information from all three labels on each painting donated. Full text:

WOODBRIDGE & Co. Ltd.
88, Fenchurch Street, London, E.C.3. England.
No. 00057
Name Newberry
Number of pieces belonging to this article or set.
British specialists for removals to every dominion, colony and foreign land in the world.

Figure II.6 – Arrow indicates distortions at the turnover edge of the original left tacking margin.

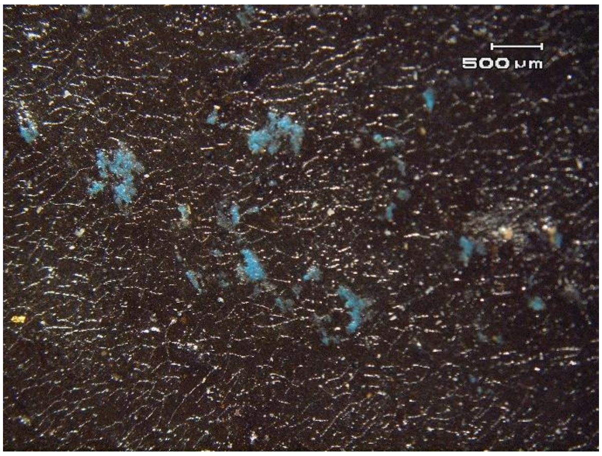


Figure II.7 – Stereomicroscopic image of abrasions and green and white deposits on the painting's surface (see Figure II.17).

Figure II.8 – Blanched varnish and missing original canvas. The lining canvas is visible underneath.

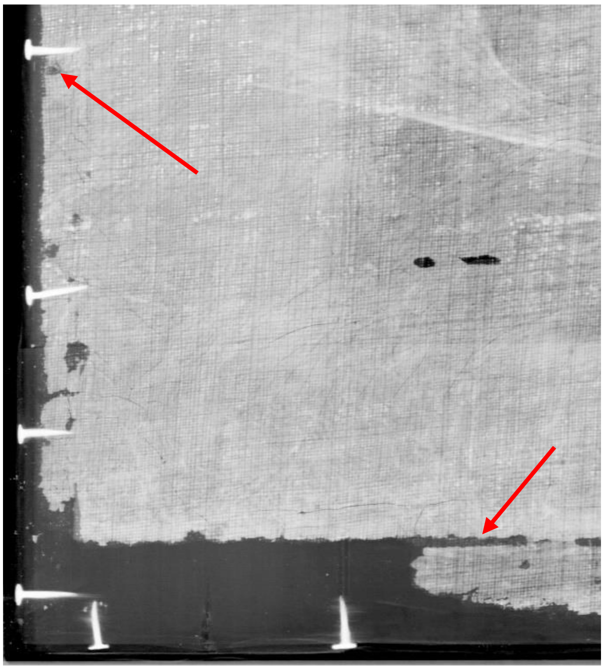


Figure II.9 – X-radiography detail. Original tacking margins at the left and bottom of the painting. The left arrow indicates a tack hole and the right arrow indicates the infilled turnover edge.

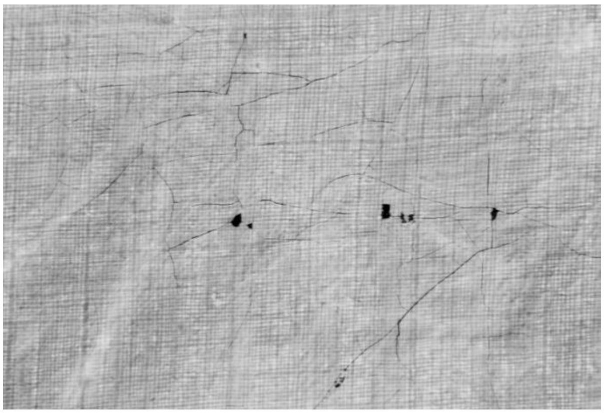


Figure II.10 – X-radiography detail where cracks in the ground are evident.

Figure II.11 – Stereomicroscopic image of protrusions in the flesh paint from the finger (see Figure II.17).

Figure II.12 – Raking light detail, textured white paint.

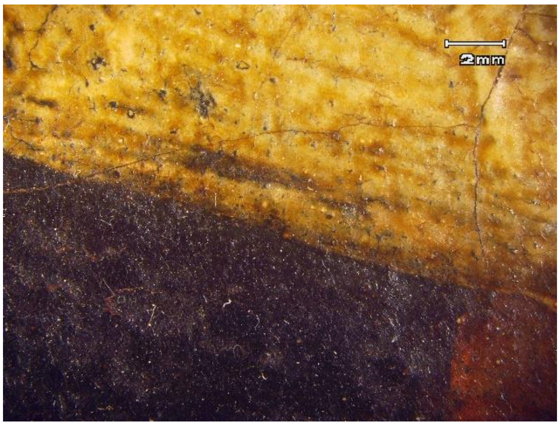


Figure II.13 – Stereomicroscopic image of transparency of the white paint (see Figure II.17).

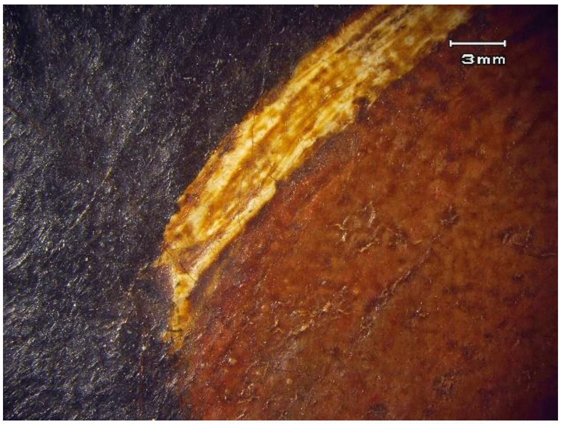


Figure II.14 – Stereomicroscopic image of white buttery paint (see Figure II.17).

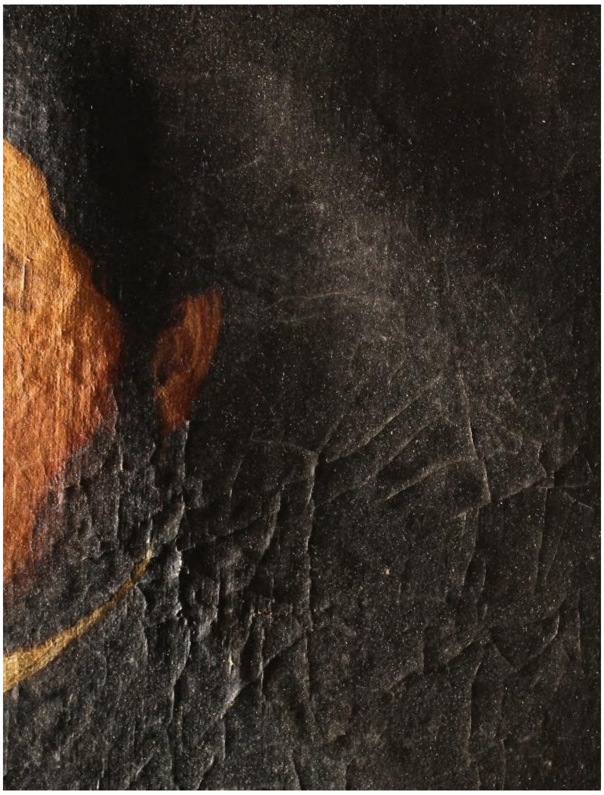


Figure II.15 – Tenting and cupping paint at the top, near the figure's head.

Figure II.16 – White spots, thought to be mould, in the black paint.

Figure II.17 – Mapping of the location of stereomicroscopic images.

APPENDIX III – Map of Damages

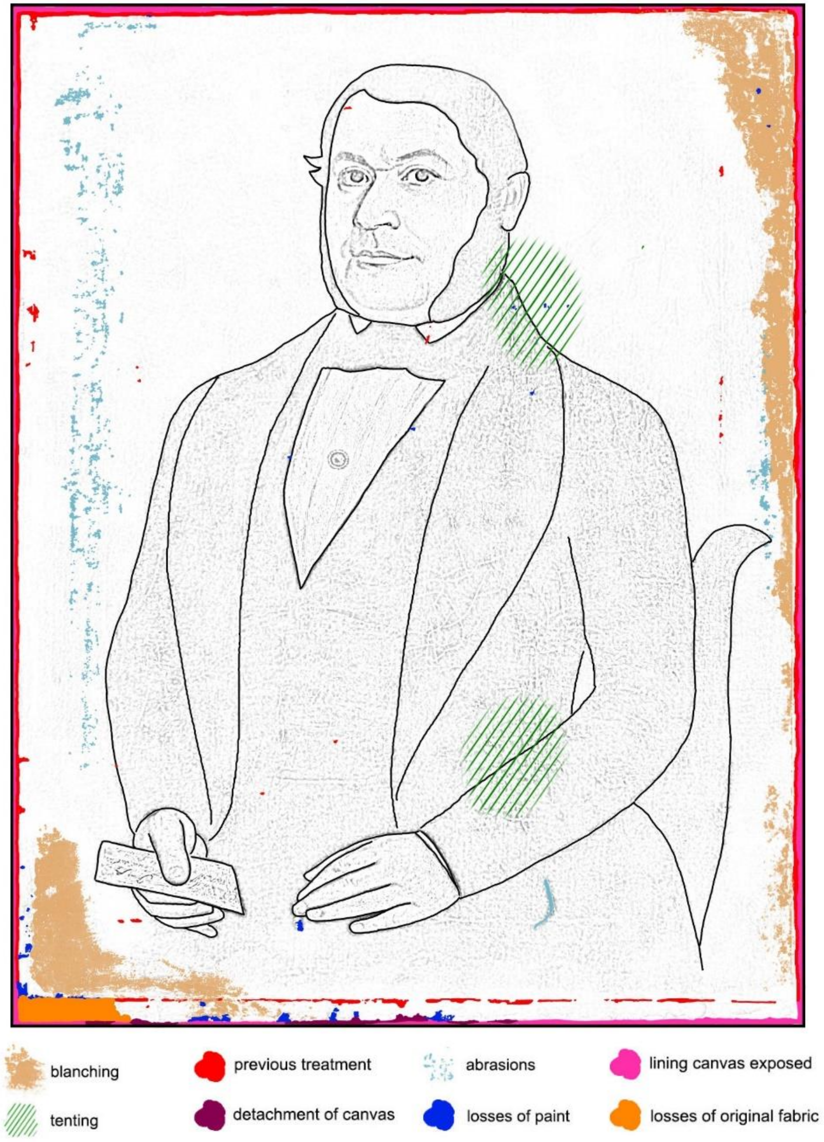


Figure III.1 – Mapping of the painting condition.

APPENDIX IV – Material Analysis

Appendix IV.1 – Instrument Description

Photographic Documentation

Photographic documentation was performed with a Canon digital camera (EOS 1100D, with a zoom lens EF-S 18-55mm f/3.5-5.6 IS II, 12.2 Mega-pixels). Ultraviolet (UV) and Infrared light photography was carried out using a Sony digital camera, model DSC-F828 cyber-shot; for UV a Pro1 Digital UV (0) Hoya filter was used and for IR an Infrared (R72) Hoya filter.

X-radiograph

X-radiographs were taken using an 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-radiographs the following conditions were used: 60 kV and 2.4mA with 100ms of integration time. The digital images acquired were processed with iX-Pect software.

Optical Microscopy (OM)

The optical microscope used is an Axioplan 2ie Zeiss microscope equipped with transmitted and incident halogen light illuminator (tungsten light source, HAL 100); UV light (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 a total optical magnification of 50x, 100x, 200x, and 500x).

For the incident and transmitted light the samples were analysed under crossed polars –polariser and analyser filters; and for UV light the Zeiss filter set 05 [BP 395-440, FT 460, LP 470] and set 2 [BP 300-400, FT 395, LP 420] were used. The scales for all objectives were calibrated within the Nikon ACT-1 software.

Energy Dispersive X-ray Fluorescence (µ-EDXRF)

X-ray fluorescence spectra were obtained using an ArtTAX spectrometer from Intax GmbH. Operating with a molybdenum (Mo) X-ray tube, focusing polycapillary lens and silicon drift electro-thermally cooled detector and a xFlash (Si drift) detector, with 170 eV resolution. The accurate positioning system and polycapillary optics enable a small area of primary radiation (ø ~70 µm) at the painting's surface. Elemental compositions were obtained from the average of three independent spots, analysed with a tube voltage of 40KV and a current intensity of 600µA and live time 100s.

µ-Raman

Micro-Raman microscopy was carried out using a Labram 300 Jobin Yvon spectrometer, equipped with a He-Ne laser of 17 mW power operating at 632.8 nm and an external laser of 50mW power operating at 532 nm. Spectra were recorded as an extended scan. The laser beam was focused with a 506 Olympus objective lens (50x). The laser power at the surface of the samples was varied with the aid of a set of neutral density filters (optical densities 0.3, 0.6, 1).

Fourier Transform Infrared Spectroscopy (μ-FTIR)

Infrared spectra were 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 4000-650 cm^{-1}, resolution setting 4cm^{-1} and 128 scans, using a Thermo diamond anvil compression cell. The spectra are shown here as acquired, without corrections or any further manipulations, except for the removal of the CO_2 absorption at ca. 2300-2400 cm^{-1}.

Electron Scanning Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS)

SEM micrographs were obtained using a FEI Quanta 400 FEG ESEM, with a Schottky emitter field emission gun, operating at low vacuum conditions and at 15 kV, equipped with an EDAX Genesis X4M detector. Micrographs were acquired using secondary (SE) and backscattered (BSE) electron detectors. SEM was performed within the Portuguese microscopy network REM, at CEMUP - Centro de Materiais, Universidade do Porto.

Stereomicroscope

Detail photographs were taken with an Olympus SZX12 stereomicroscope with a 7x to 90x zoom range, equipped with an integrated Olympus DP12 digital camera and a Schott KL 200 external cold light source with two flexible optic fibre cables.

Appendix IV.2 – Map of Sampling Areas for Cross-sections and μ-EDXRF

Figure IV.1 – Mapping of cross-sections and point analysis by μ-EDXRF.
Only the cross-sections mentioned in this thesis are present in this map.

Appendix IV.3 – Cross-sections under Normal and Ultraviolet Light

Cross-section S3 (corresponding to Figure IV.2) was taken by Marques and re-photographed for this thesis. The remaining cross-sections were both taken and photographed in the current thesis.

Normal light: **Ultraviolet light:**

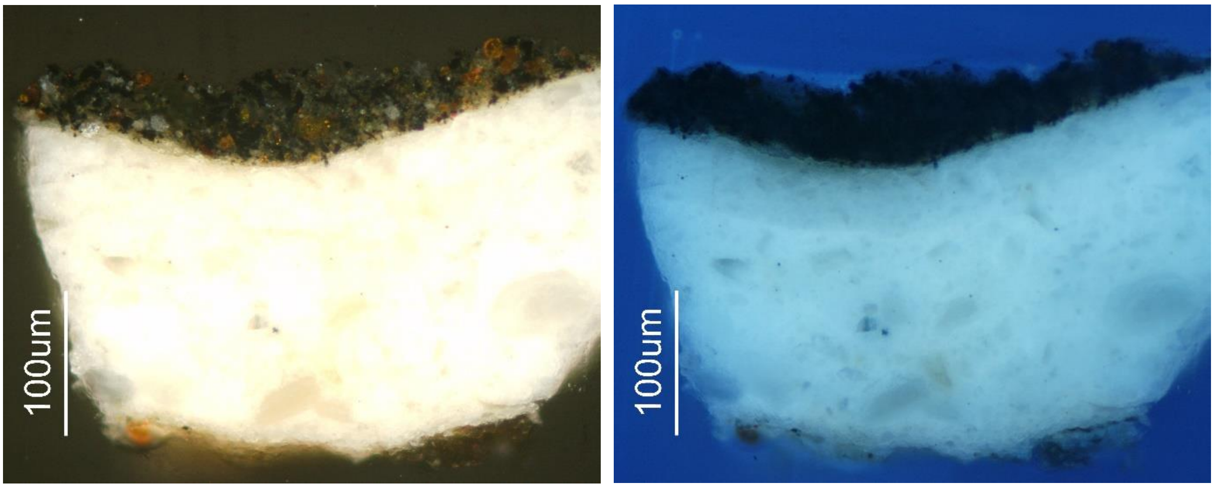


Figure IV.2 – Cross-section S3 taken from the background showing three layers in the ground.

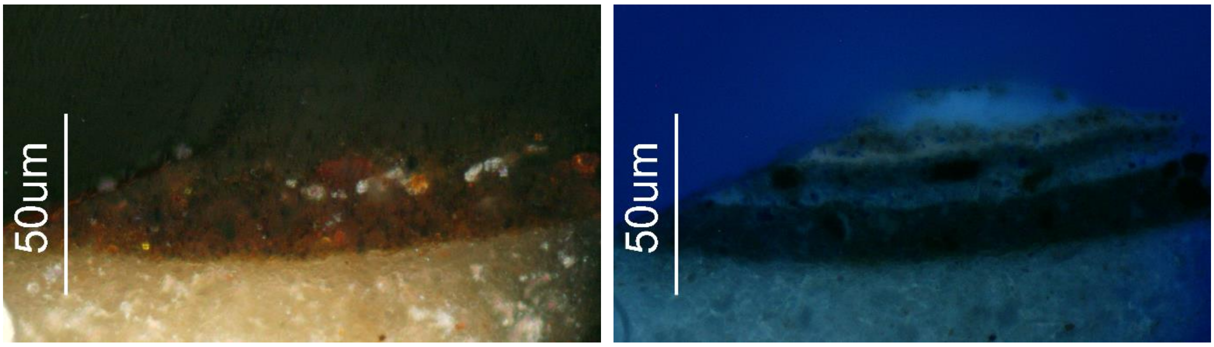


Figure IV.3 – Cross-section S10 taken from the infill in the painting's margins, showing 6 layers of paint and varnish above the putty.

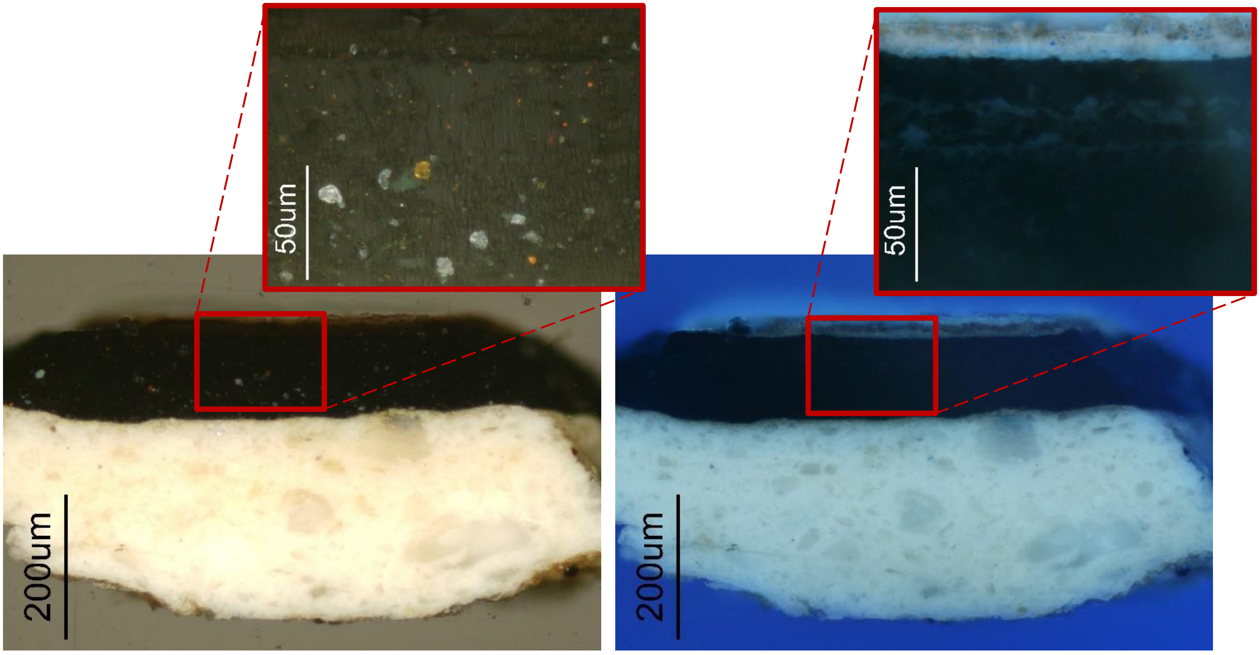


Figure IV.4 – Cross-section S13 taken from the figure's jacket showing the overpaint sandwiched between two layers of varnish. Note the particles in the bottom of the sample. The detail images show the three layers of paint with what is thought to be a layer of resin/varnish between the paint layers.

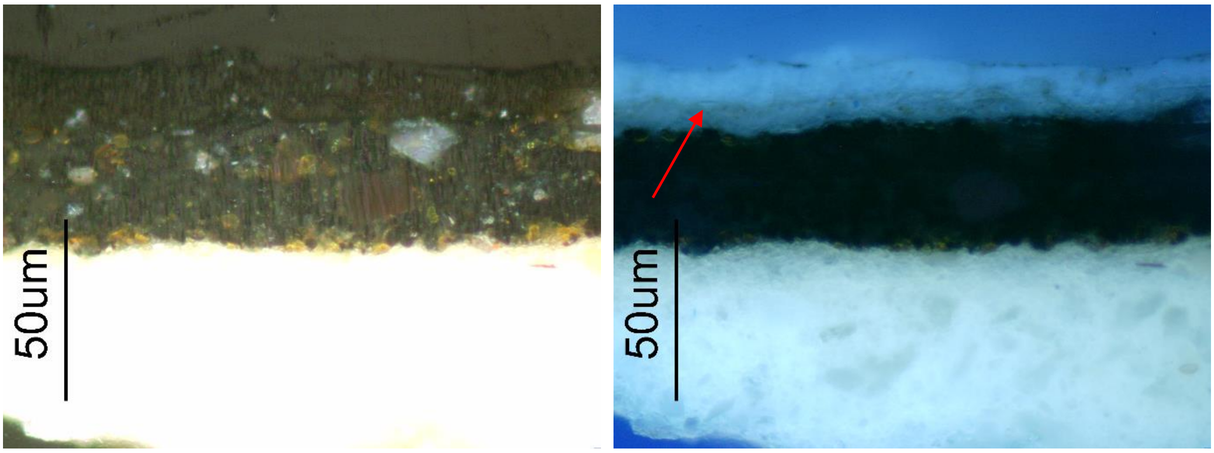


Figure IV.5 – Cross-section S15 taken from the background showing two layers of paint and the overpaint sandwiched between two layers of varnish. The arrow indicates the overpaint layer.

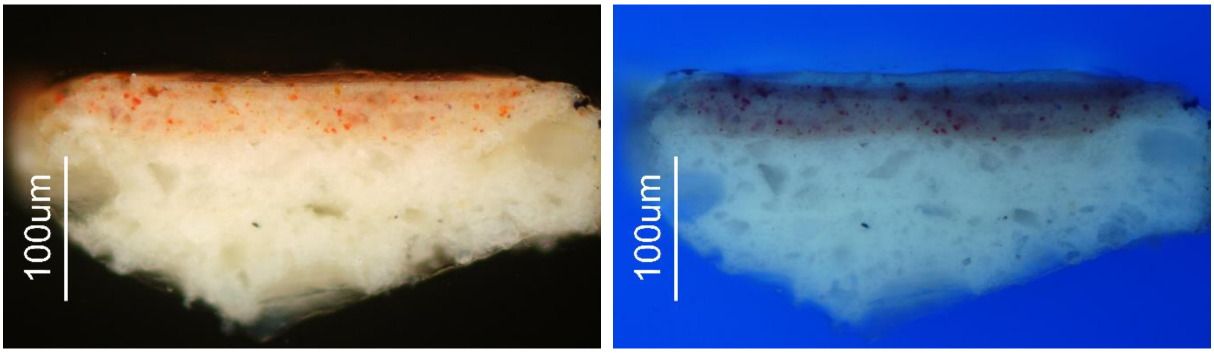


Figure IV.6 – Cross-section S19 taken from the face showing two layers of paint and on top what seems to be a glaze layer.

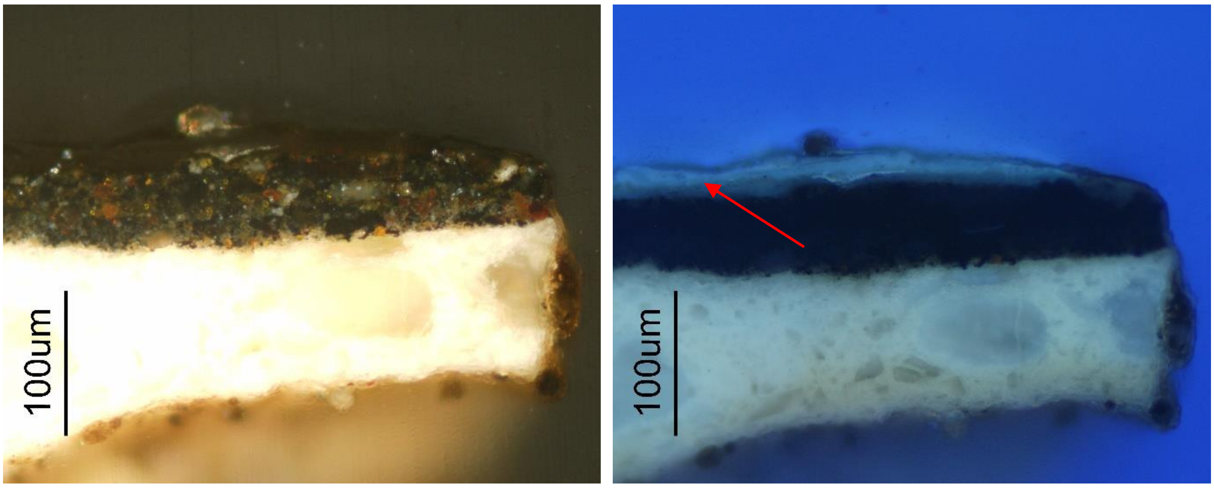


Figure IV.7 – Cross-section S21 taken from the background showing the overpaint sandwiched between two layers of varnish. The arrow indicates the overpaint layer. Note the particles in the bottom of the sample.

Appendix IV.4 – Fibre Identification: Original and Lining Canvas

Figure IV.8 – Transversal view of the original canvas fibre under cross polarized light. The arrow indicates the cross marks.

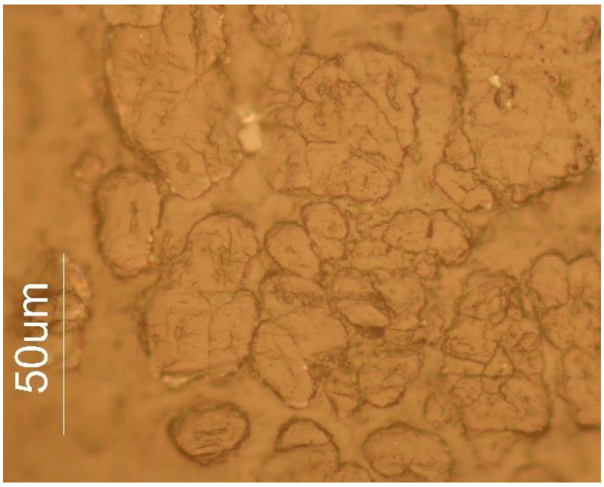


Figure IV.9 – Original canvas fibres in cross-section.

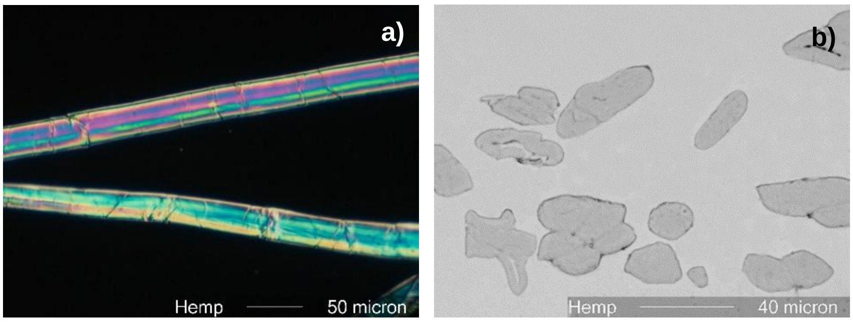


Figure IV.10 – Reference images for hemp fibres: a) Transversal view; b) Cross-section. Image from www.microlabgallery.com.

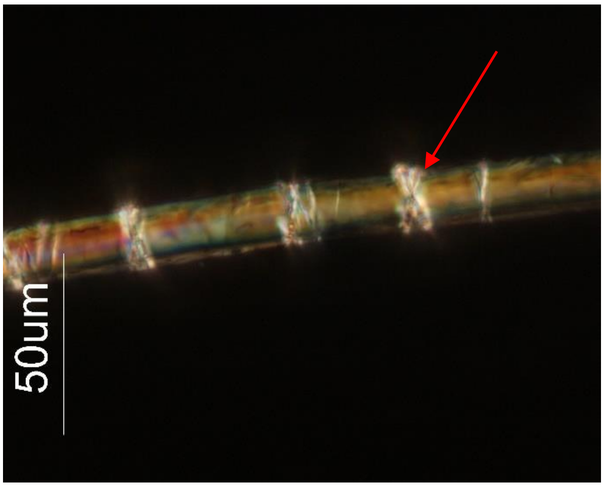


Figure IV.11 – Transversal view of the lining canvas fibre under cross polarized light. The arrow indicates the cross marks.

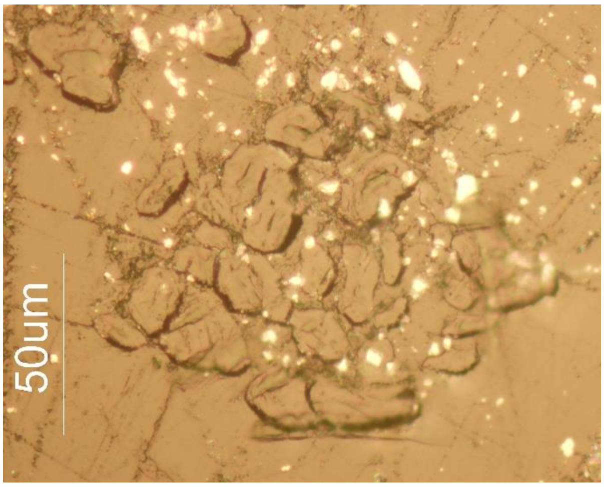


Figure IV.12 – Lining canvas fibres in cross-section.

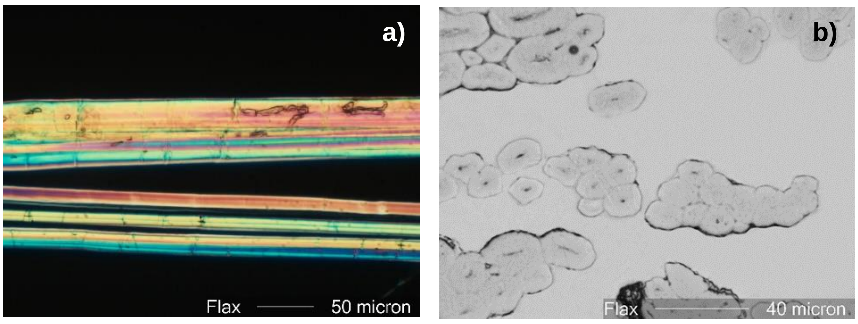


Figure IV.13 – Reference images for flax fibres: a) Transversal view; b) Cross-section. Image from www.microlabgallery.com.

Fibres from the original and lining canvas were observed with the Optical Microscope and exhibit very similar features. Transversal view of the fibres, under crossed polarized light, show transverse cross-marks and rainbow interference colours, which are characteristic of bast fibres [43]. The contour and lumen of the fibres indicates that they may be flax or hemp [44]. Fibres from the original canvas were already identified by Marques (2014) as bast fibres, likely linen or hemp, and this was confirmed in this thesis [1].

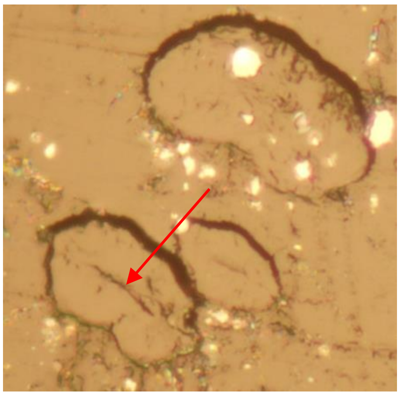


Figure IV.14 – Detail of lining canvas fibres in cross-section. The arrow indicates the lumen.

In this thesis, further comparison between fibres from the original and lining canvas show that despite being very similar, slight differences are seen in cross-section. The cell wall of the lining canvas fibre is thicker than the one from the original canvas and the lumen is narrower (Figures IV.14 and IV.15). According to the literature, the cell wall of a flax fibre is thick and the lumen is narrow, often line-like and indistinct, while hemp lumen is often broad compared to the narrow lumen of flax [43]. It is then possible that the lining fibre is flax and the original canvas fibre is hemp, however, the identification is not certain since differences between flax and hemp fibres are subtle and not always distinguishable microscopically [43]. Other methods of identification such as micro-chemical tests and drying twist tests would be needed to confirm this possibility [43].

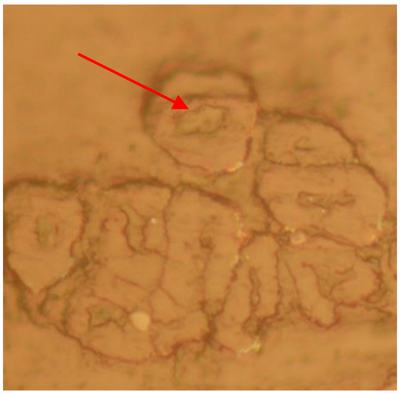


Figure IV.15 – Detail of original canvas fibres in cross-section. The arrow indicates the lumen.

Appendix IV.5 – Pigment Identification Table

The ground and pigments identification tables presented below were originally made by Marques (2014) for her thesis [see reference 1, Appendices, pp. 17-18]. It has been copied here with new information from the current thesis marked by # before the cross-section name.

Table IV.1 - Table of ground analysis.

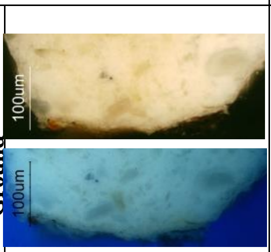
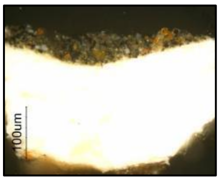
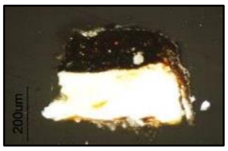
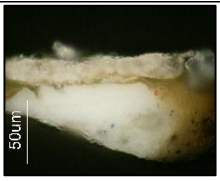
Sample		μ-EDXRF	SEM-EDX	μ-Raman		μ-FTIR		Identified Pigments
				Wavenumber (cm^{-1})	Assignment	Wavenumber (cm^{-1})	Assignment	
Ground	 Normal and UV light image from Cross-Section S3 ground layers.	(Ca), **Ba**, (Mn), **Fe**, (Cu), **Pb**	**C, Ca**	1085vs	v$_s$(CO$_3^{2-}$)	-	-	Calcium Carbonate CaCO$_3$
			Pb, C, O	1050vs-1054s	v$_s$(CO$_3^{2-}$)	3534w 1401vs 835vw 682s	v (OH) v$_{as}$(CO$_3^{2-}$) δ$_{out\text{-}of\text{-}plane}$(CO$_3^{2-}$) δ $_{in\text{-}plane}$(CO$_3^{2-}$)	Lead White 2PbCO$_3$.Pb(OH)$_2$
			Ba, S, O, Pb	459m 987s	- v$_s$(SO$_4^{2-}$)	1176m;1113s;1083vs; 982w	v$_{as}$(SO$_4^{2-}$) v$_s$(SO$_4^{2-}$)	Barium Sulphate BaSO$_4$

Table IV.2 - Table of pigment analysis.

Sample		µ-EDXRF	SEM-EDX	µ-Raman		Identified Pigments
				Wavenumber (cm^{-1})	Assignment	
S4 - Flesh Paint (Left hand)		(K), (Ca), Ba, (Mn), **Fe**, Cu, Hg, **Pb**	C, Pb, Fe, Al, S, Si, Ca, Cu, P, K	1048s-1052s	-	Lead White $2PbCO_3.Pb(OH)_2$
				460m; 988s	-	Barium Sulphate $BaSO_4$
				253vs; 282w 342m	δ (S-Hg-S) ν (Hg-S)	Vermilion HgS
				1325vs (br) 1582vs (br)	sp^3 (C-C) sp^2 (C-C)	Carbon Black C
				244vw 298w; 397vs; 478vw 551w	- δ_s(Fe-O) δ_{as}(Fe-O) ν_{as}(Fe-O)	Yellow ochre (Goethite) α-FeOOH
				-	-	Lake pigment **?**
S3 e S7 – Background		Ca, Ba, (Mn), **Fe**, **Cu,** (Hg), **Pb**	Pb, Ba, Fe, As, Cu, S, Al, Si, Ca, P, K	243vw; 298m 393vs; 555w	-	Yellow ochre (Goethite) α-FeOOH
				223vs 291-299vs 408m 611w	- δ_s(Fe-O) δ_s(Fe-O) ν_s(Fe-O)	Red ochre (Hematite) α-Fe_2O_3
				253vs; 280w; 343m	-	Vermilion HgS
				1325vs (br) 1590vs (br)	-	Carbon Black C
				276w 531s 2093w; 2128w (sh); 2154vs	δ (C-Fe-C) δ(Fe-C≡N) ν (C≡N)	Prussian Blue $Fe_4[Fe(CN)_6]_3$
				1048s-1052s	-	Lead White $2PbCO_3.Pb(OH)_2$
				452w; 988s	-	Barium Sulphate $BaSO_4$
				-	-	Orpiment As_2S_3 ?
				-	-	Emerald Green $Cu(C_2H_3O_2).3Cu(AsO_2)_2$?
S5 – Black Jacket		Ca, (**Ba**), (Mn), **Fe**, **Cu**, (Hg), **Pb**	Ca, Pb, P, Fe, Ba, Hg, Al, Si, Cu, Mg, S, As, P, K	1326vs (br); 1580vs (br)	-	Carbon Black C
				276w; 531s; 2091w 2123w (sh); 2154vs	-	Prussian Blue $Fe_4[Fe(CN)_6]_3$
				245vw; 298m; 395s 478vw; 553m	-	Yellow ochre (Goethite) α-FeOOH
				252vs; 282w (sh) 342m	-	Vermilion HgS
				1049s-1053s	-	Lead White $2PbCO_3.Pb(OH)_2$
				451m-461m; 617w; 646w; 988vs	-	Barium Sulphate $BaSO_4$
S9 – Infill Backgroumd		(K), **Ca**, (Mn), **Fe**, (Cu), (Zn), **Pb**	**C, Ca,** Si, Mg, Al	1085vs	-	Calcium Carbonate $CaCO_3$
			-	1326vs (br) 1591vs (br)	-	Carbon Black C
			Si, Al, S, Fe, **Na,** Ca, K, Cd, Mg, Mn	258w 548vs 820w 1093m	δ (S_3^-) ν_s (S_3^-) - overtone	Ultramarine Blue (probably the synthetic form) $Na_8[Al_6Si_6O_{24}]S_n$

			-	224 (vs) 292 (s); 408 (m)	-	Red ochre (Hematite) α-Fe_2O_3
#S16 – Shirt	 50um	(Ca), **Ba**, (Fe), (Cu), **Pb**	-	1047s-1053s	-	Lead White $2PbCO_3.Pb(OH)_2$
				451m-461m; 985s	-	Barium Sulphate $BaSO_4$
				259w 545vs 810w 1094m	-	Ultramarine Blue (probably the synthetic form) $Na_8[Al_6Si_6O_{24}]S_n$
#S17 – Letter	 50um	(Ca), **Ba**, (Fe), (Cu), **Pb**	-	1331vs (br) 1598vs (br)	-	Carbon Black C
				450m-460m 617w; 646w; 985vs	-	Barium Sulphate $BaSO_4$

Appendix IV.6 – µ-FTIR Spectra Analysis

µ-FTIR analysis were made by UNL-DCR students. Only the data of the spectra attained in their work was copied. The spectra was redesigned and the interpretation is from the work in the current thesis.

- **Ground**

The pigments and/or fillers in the ground were identified through infrared spectra (Figure IV.16). The three bands between 1200 and 1050cm^{-1} (1178, 1116 and 1083cm^{-1}), which correspond to the asymmetric SO_4^{2-} stretching bands, indicate the presence of barium sulphate ($BaSO_4$). Lead white ($2PbCO_3.Pb(OH)_2$) was also identified by the vibrational band at 3531cm^{-1} (ν (OH)), the strong CO_3^{2-} stretching band at 1403cm^{-1} and the CO_3^{2-} bending band at 679cm^{-1} [45]. The band at 838cm^{-1} is due to the neutral lead carbonate which is a common component of lead white [46].

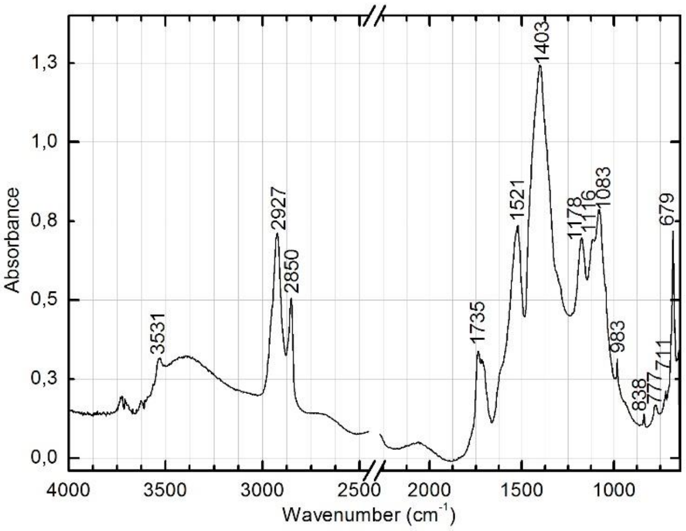


Figure IV.16 – Infrared spectra of the ground.

The binder was identified as a drying oil. The characteristic bands at 2927cm^{-1} and 2850cm^{-1} (ν (C-H)), and at 1735cm^{-1} (ν (C=O)) are evidence of the presence of a drying oil. Oils also show bands between 1300 and 900cm^{-1} that are attributed to C-O stretching, however, since this sample is a mixture of compounds, these bands may be overlapped with the ones from barium sulphate. The bands between 750-700cm^{-1} correspond to C-H torsion bands [45]. The band at 1521cm^{-1} is attributed to a metal carboxylate [46].

- **Old lining adhesive**

The lining adhesive was identified through µ-FTIR analysis (Figure IV.17) as a glue-starch combination. The glue (a protein) is characterized by the bands at 1651cm^{-1} (ν(C=O)) and 1539cm^{-1} (δ (C-N-H)) attributed to amid I and amid II, respectively, and by the band at 1454 cm^{-1} (δ (C-H)) which is referred to as amid III [45]. The presence of amid groups is confirmed by the band near 3330cm^{-1} which corresponds to the N-H stretching. The starch, a carbohydrate, has two strong characteristic bands, one around 3300cm^{-1} which corresponds to the O-H stretching, and one at 1086cm^{-1} corresponding to the C-O stretching. Bands between 1480 and 1300cm^{-1} are attributed to C-H bending bands and the ones between 1300 and 900cm^{-1} are attributed to C-O stretching bands [45].

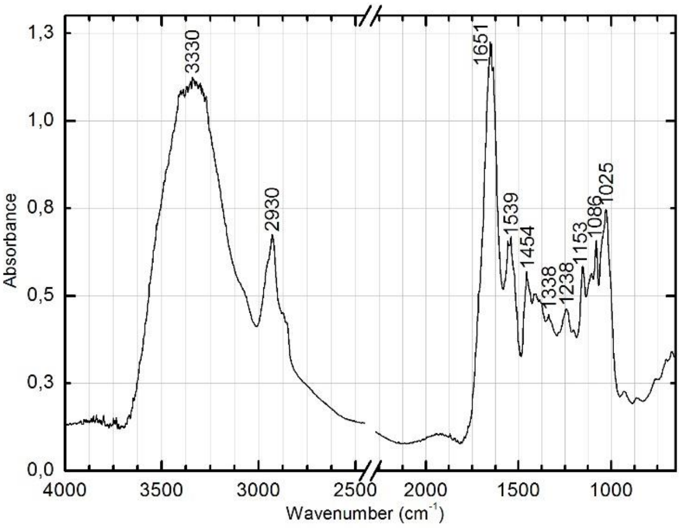


Figure IV.17 – Infrared spectra of the lining adhesive.

The presence of starch in the adhesive formulation was confirmed by the observation of a dispersed sample of the lining adhesive with polarized light, in the OM and the resulting image was compared with reference images from the *Pigment Compendium* (Figure IV.19). In polarized light, starch grains have a characteristic extinction cross, centred (Figure IV.18) [47].

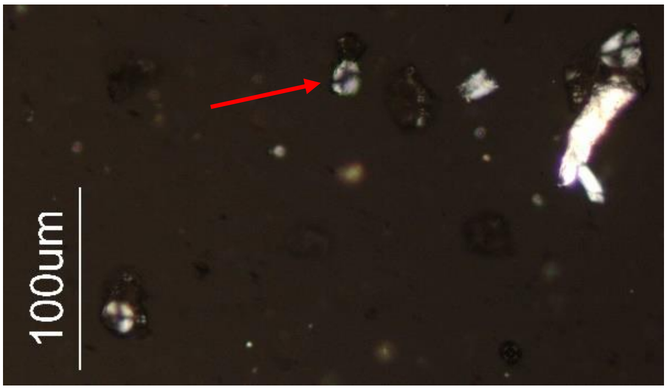


Figure IV.18 – Observation of a dispersed sample of the lining adhesive with PLM (Polarized Light Microscopy). The arrow indicates one of the starch grains.

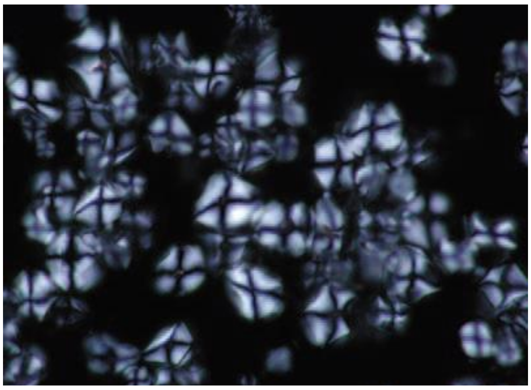


Figure IV.19 – Reference image for Maize starch under crossed polars. Image from the *Pigment Compendium* [47].

- **Varnish**

The varnish was identified as a natural resin. Strong C-H bending bands are seen in the spectra (Figure IV.20) at 2939 and 2870cm^{-1}. The C=O stretching at 1705cm^{-1} is a distinguishing band that all tree resins contain [45]. Another distinguishing feature of resins is the weak and broad band at 2700-2500 cm^{-1} which corresponds to the O-H vibrations of a dimerized carboxyl group. The band at 3420cm^{-1} is attributed to the O-H stretching while bands at 1450 and 1380cm^{-1} correspond to the C-H bending. Bands between 1300 and 900cm^{-1} correspond to C-O stretching [45].

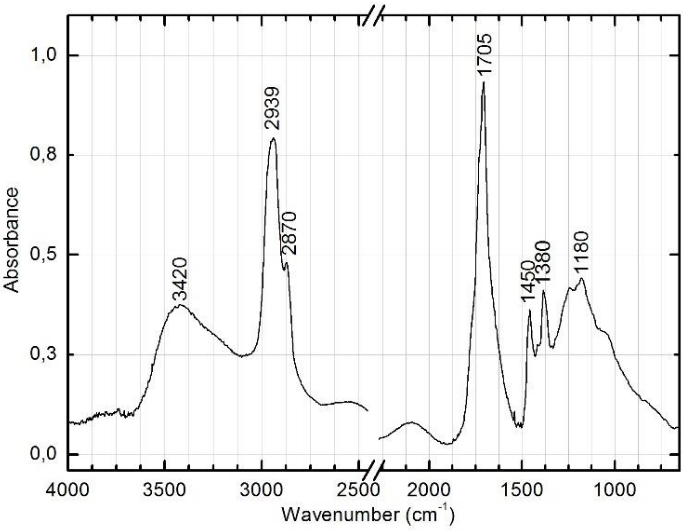


Figure IV.20 – Infrared spectra of the varnish.

APPENDIX V – During Treatment Photographs

Figure V.1 – Adhesive introduced in the cracks and losses with a thin brush to consolidate unstable areas.

Figure V.2 – Wood planks placed around the painting. Both the wood planks and the painting have the same height.

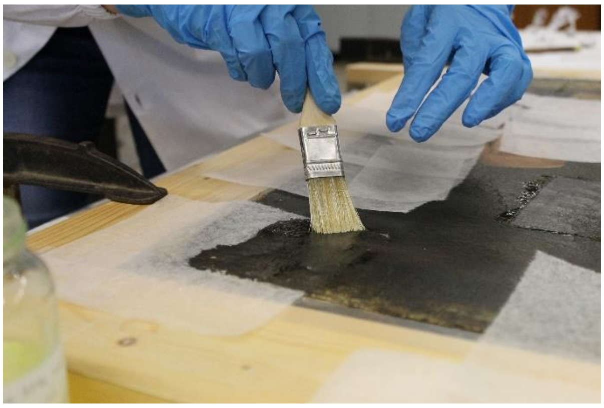


Figure V.3 – Adhesive (BEVA® 371b) being applied on top of the Japanese tissue during the facing step. Note the overlap of the tissue with the wood planks.

Figure V.4 – Note the conformation of the facing to the surface.

Figure V.5 – Painting's surface after the facing dried. The edges of the Japanese tissue overlapped slightly in order to avoid insecure areas.

Figure V.6 – Taking margins of the lining canvas being pulled away from the stretcher.

Figure V.7 – Bottom of the lining canvas exhibiting severe disintegration of the material and extensive mould growth.

Figure V.8 – Lining canvas being cleaned by brushing debris into the nozzle of the vacuum cleaner.

Figure V.9 – Lining canvas was peeled away from the back of the painting at a very low angle.

Figure V.10 – Lining strips with BEVA® 371 film being attached to the painting's margins with heat.

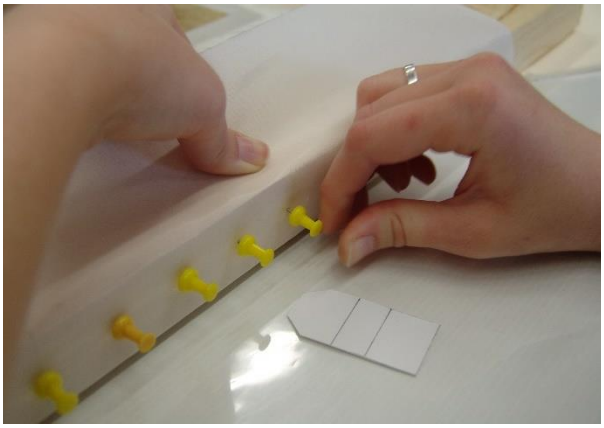


Figure V.11 – Pushpins attaching the lining strips to the loom. The ruled card was used to achieve even spacing of the pushpins.

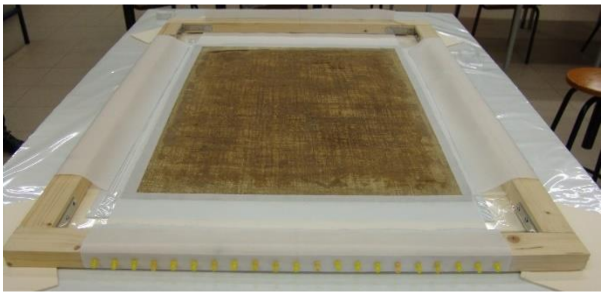


Figure V.12 – Painting with the strip lining attached to the loom. The painting was ready to be worked on from the back.

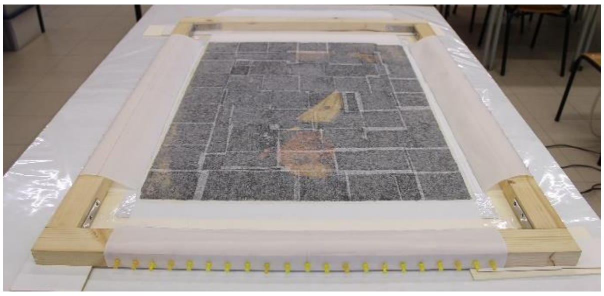


Figure V.13 – Painting after its orientation was changed in the loom. It was ready to be worked on from the front.

Figure V.14 – Lining adhesive with a melted appearance.

Figure V.15 – Cleaned area on the left (after the lining adhesive was scrapped off) contrasting with the still uncleaned area on the right side.

Figure V.16 – Concreted piece of adhesive lifted with the dentist tool.

Figure V.17 – Trials with the Dremel® tool. The stereomicroscope was used throughout the removal of the lining adhesive.

Figure V.18 – Back of the original canvas before the lining adhesive removal.

Figure V.19 – Back of the original canvas after lining adhesive removal (the painting's edges are covered by the strip lining).

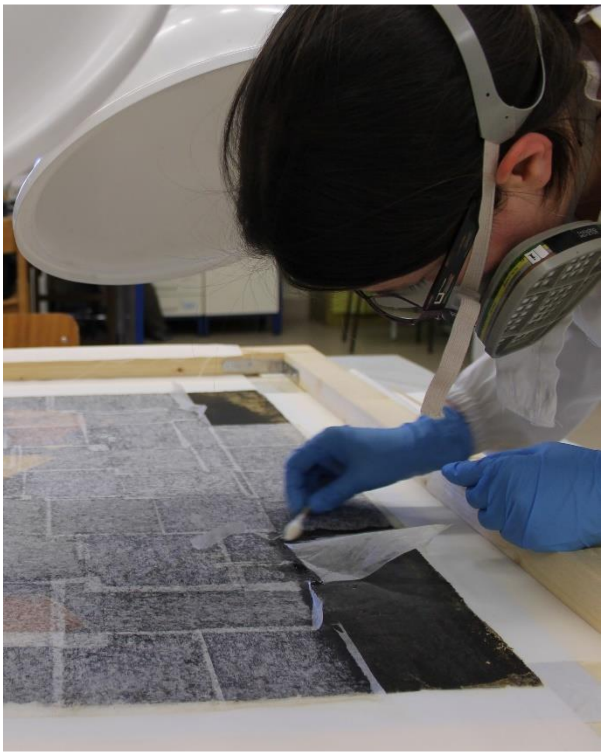


Figure V.20 – Removal of the facing tissue with a cotton swab with Shellsol® A100. The cotton swab was carefully rolled on top of the facing tissue until it started to loosen.

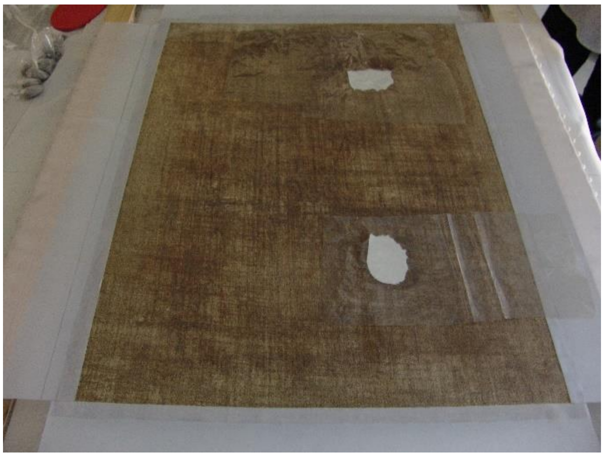


Figure V.21 – Blotting papers (slightly moistened with distilled water) placed on top of deformations, relaxing the canvas fibres. Melinex® covered the blotters to reduce evaporation of the moisture.

Figure V.22 – Flattening treatments underway. Area at the front with a moisture tent and area at the back with weights, after the materials were plasticized.

Figure V.23 – More difficult areas (such as overlapped and severely tented paint) were flattened by plasticizing the paint: first introducing BEVA® 371b (1:1 in White Spirits by volume), then with the use of heat and the remaining solvents from the adhesive. Once plasticized, the paint was kept flat with weights on top of a foam-core board with chamfered edges.

APPENDIX VI – Study of the Fungal Community

Appendix VI.1 – Fungi Identification

Introduction

As stated by Ciferri (1999), the organic components in paintings represent a rich nutrient source for a wide range of heterotrophic microorganisms. The support material (cellulosic) and the materials used to “size” the support and to prepare the ground layers (animal or plant glues), can be easily biodeteriorated. Other materials used in paintings, such as sugars, gums, linseed and other oils, waxes, etc., may also be used as nutrients for microorganisms [48]. Apart from the materials used to make the painting, materials introduced during a restoration procedure, like the glue-pastes used in a lining, may provide further sources for microbial growth [49].

The microbial attack of paintings can result both in aesthetical and structural damage, the two being strongly associated [48]. Problems like pigmentation/ staining, degradation of compounds and hydration or penetration of microorganisms into the painting’s materials can occur [50]. Microorganisms can grow within or below varnishes, paint layers, binding media, adhesives and in the canvas and lining fabric. This can result not only on painting’s material deterioration but also in loss of cohesion in and between the infested layers [51]. Since natural and synthetic polymers, which are used as painting materials, cannot be used by microorganisms as carbon sources without breakdown into oligomers or monomer molecules, exo-enzymes play an important role [51]. These are produced by the microorganism and released outside the cell in order to digest the polymer, which in a prolonged attack to a painting, can result in the complete loss of material [50, 51].

Microorganisms can grow either in the front or at the back of an oil painting on canvas. Usually, the microbial attack starts in the back due to the canvas polymers and its size layer [52, 53] but cases where the microbial growth is dominant in the front can occur [54]. As stated by Caneva et al. (1991), the biological attack on the paint layer also depends on the nature of the pigments. Pigments composed of earth sienna, umber and boles are particularly liable while pigments containing heavy metals, such as lead white or zinc oxide are more resistant to microbial attack [55].

For an oil painting to suffer from microbial attack by fungi and bacteria conditions such as water damage or exposure to high relative humidity and temperature (RH > 65% and T > 20ºC) must have occurred [20].

The microbial growth in the portrait of *Domingos Affonso* can be easily understood by its exposure to water, which conferred a favourable environment for microbial growth, and for the presence of lining materials (the glue-paste adhesive) that conferred an extra source of nutrients for microorganisms.

Materials and Methods

Sampling and inoculation

Samples were taken from the painting in areas where there were visual signs of possible microorganisms’ activity. Three samples were taken from the front, from areas that showed the presence of small white dots (F1 to F3) (Figure VI.4) and one was taken from an area with no sign of biodeterioration, as a control (FC) (see map of sampling Figure VI.1). As for the back of the painting six samples were taken from areas that showed possible signs of biodeterioration (B1 to B6). Since not all of the visual phenomenon at the surface of the paint and canvas offered clear evidence of biological activity, samples were taken to see if they could be related to the action of microorganisms. These areas consisted of black dots, whitish stains and areas with a brownish or white UV fluorescence (Figures VI.5 to VI.9). One sample was taken as control from an area were the canvas did not seem to have signs of biodeterioration (BC) (see map of sampling Figure VI.2). After the removal of the lining canvas it was seen that the original canvas also exhibited mould growth (Figures VI.8, VI.9), therefore new samples were taken (OBC and OB1 to OB3) (see map of sampling Figure VI.3).

The samples were taken using a non-invasive sampling procedure: rubbing a cotton swab slightly moistened with distilled water in the areas mentioned above. All the materials used in the sampling procedure were previously sterilized. Petri dishes with Potato Dextrose Agar (PDA), an organic medium appropriated for the growth of filamentous fungi, were inoculated with the cotton swabs. The medium was prepared in advance with 39g of PDA to 1000ml of distilled water.

Incubation and identification methodology

After one or more weeks, depending on the specie, fungi growth was observed on the incubated petri dishes. Whenever more than one microorganism grew on one petri dish, each microorganism was isolated to new petri dishes with PDA. In some cases fungi grew without giving spores. In these cases fungi were further inoculated in diluted PDA media (20ml PDA to 10ml of Agar in 1000ml of distilled water). The reason for this procedure is that sporulation is induced when conditions are less than optimal for growth, for example, when there is exhaustion of a key nutrient [56, 58], therefore the amount of nutrients in the medium (provided by the PDA), were reduced and more Agar (with no nutritional value) was added.

Resulting microorganisms were observed in the OM (an Axiostar plus from Zeiss) and their identification was performed based on a dichotomous key with reference images from an unpublished work of the mycologist Dr. Alan J.L. Phillips [56]. Although current practice combines both cultivation and molecular identification [50], in this work only the cultivation method was used. This method has the advantage of identifying only the fungi that are able to grow, while molecular biology methods also gives the result of dead fungi. Since the main focus of this work was to investigate if the fungal community inhabiting the painting was active, the cultivation method was the most adequate for this work.

Results and Discussion

Samples taken from the front of the painting, including the control sample, exhibited growth of microorganisms (fungi, yeasts and bacteria) but fungi only grew on cultures from samples F2 and F3 (Table VI.1). A fungus from the genus *Humicola* was identified in F2. The identification of the fungus in sample F3 was not conclusive but it was seen that it had features of the *Erysiphe graminis* (a fungus that infects wheat and barley's leaves) [56, 57]. Although having some similarities with *Cladosporium*, such as the growth of spores in chains and the presence of a transverse septa in the spores, the morphology and appearance of the colony in the PDA culture is significantly different. The fungus isolated from F3 had a grey to brown mycelium and grows in height as well as into the PDA (depth), while cultures of the genus *Cladosporium* are always olive-green [56].

Table VI.1 - Table identifying the microorganisms.

	Sample name	Description of the sampling location	Fungi identification		
			Yeast	Bacteria	Fungi
Front	**FC**	Control	pink yeast	**-**	**-**
	F1	White dots on the paint surface	**-**	yellow bacteria	-
	F2	White dots on the paint surface	beige yeast	**-**	*Humicola*
	F3	White dots in a crack line	beige yeast	**-**	*Erysiphe graminis* ?
Back (lining canvas)	**BC**	Control	-	-	-
	B1	Dark stain in visible light	-	-	-
	B2	White stain in UV light	-	-	*Cladosporium*
	B3	Whitish stain in visible light	-	-	-
	B4	Brownish stain in UV light	-	-	-
	B5	Mould in the lining canvas	-	-	-
	B6	Black dots in the lining canvas	-	-	*Cladosporium* and a fungus that did not give spores
Back (original canvas)	**OBC**	Control	-	-	-
	OB1	Pink stain	-	-	-
	OB2	Dark stain in the original canvas	Orange yeast	-	*Cladosporium* (two species)
	OB3	Dark stain in the original canvas	Orange yeast	-	*Cladosporium* (two species) and a fungus that did not give spores

Among the samples taken from the back of the lining canvas only B2 and B6 showed fungal growth (no yeasts or bacteria were observed). Both fungi identified belong to the genus *Cladosporium*. Sporulation was not possible to obtain in one of the fungi from sample B6 (Table VI.1). Fungi that did not give spores in the PDA formulation described above were cultivated in the diluted medium. Even in these conditions some samples did not sporulated. Since the identification of fungi is mainly based on the morphology of spore-bearing structures, the way in which the spores are produced and on the spores themselves, the fungi that did not give spores could not be identified [56].

Samples OB2 and OB3 taken from the back of the original canvas exhibited the presence of two yeasts and fungi of the genera *Cladosporium* (possibly two different species were identified in each sample due to the different features, such as colour of the colony, observed among them). Sporulation did not occur in one of the fungi from sample OB3 (Table VI.1).

From all the genus identified in the present work, only *Cladosporium* was found in the literature as being present in easel paintings [59]. As far as the author could ascertain, no mention was found regarding the presence of the genus *Humicola* and *Erysiphe graminis* in such substrates [48 - 50, 54, 59], therefore our results are new.

It is also interesting that the mould in the form of small white dots at the front of the painting was restricted to certain colours, as predicted by Caneva et al. (1991). As expected, they appeared mainly in the black colour of the figure's jacket and hair and also in the background, although to a lesser extent. In these colours, a higher amount of carbon black and earth pigments (ochres) is present, and fewer pigments with heavy metals.

In conclusion, results from the cultivation essays confirm the presence of active microorganisms on the painting and emphasize the need for caution in selecting treatment options. It is also advisable to constantly monitor this painting after the conservation treatment because even though the painting was cleaned, spores may still be present because their complete elimination is difficult. Consequently, the painting should be kept in an environment with the temperature below 20ºC and RH below 65%.

It is important to underline that although some samples of microorganisms did not grow, this does not mean that they were not active in the past. A clear example for this is the sample B5 that was taken from the visible mould on the lining canvas where nothing grew in the culture. In future work of this kind, more focused on the identification of the microorganisms, the samples should be inoculated in more than only one culture media since some fungi may not grow or sporulate in PDA.

Appendix VI.2 – Map of Sampling

Figure VI.1 – Map of the fungal sampling areas from the front of the painting.

Figure VI.2 – Map of the fungal sampling areas from the lining canvas.

Figure VI.3 – Map of the fungal sampling areas from the original canvas.

Appendix VI.3 – Photographs of areas with signs of biodeterioration

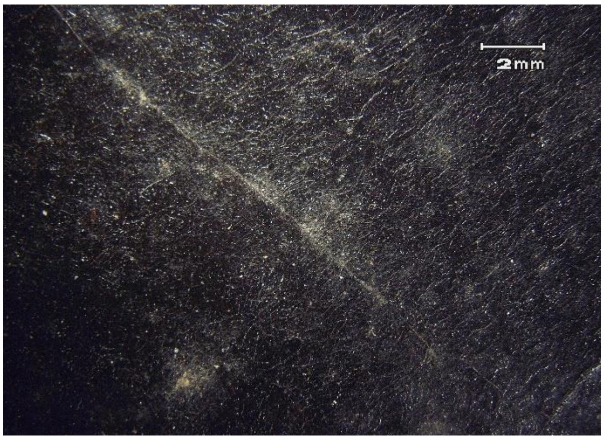


Figure VI.4 – Stereomicroscopic image of the small white dots on the surface of the black paint and between cracks.

Figure VI.5 – Mould growth between the stretcher and the lining canvas.

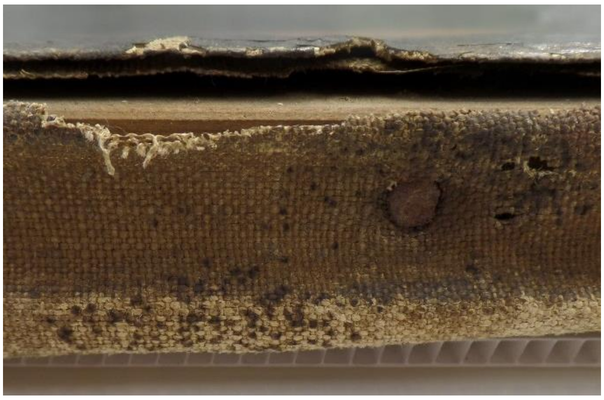


Figure VI.6 – Black dots from mould growth on the lining canvas.

Figure VI.7 – The arrows point out the areas with brownish and white UV fluorescence thought to be associated with surface mould on the painting.

Figure VI.8 – Pink stain in the original canvas thought to be associated with mould.

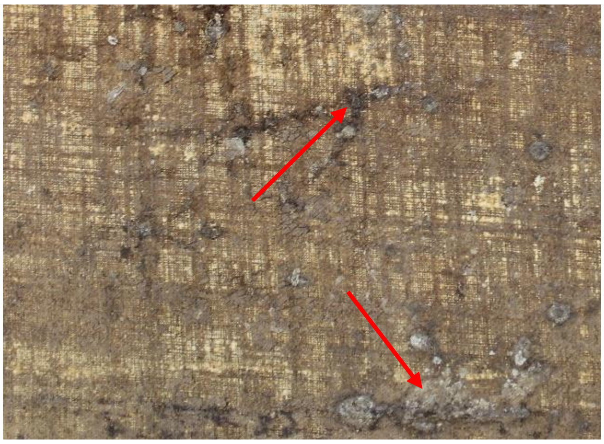


Figure VI.9 – Mould growth on the original canvas and in the lining adhesive. The arrows indicate two sampling areas.

APPENDIX VII – The Microclimate Frame Project

Appendix VII.1 – Instrument Description

Flatbed scanner:

The coupons were digitalized with an hp scanjet 8200 flatbed scanner and images were acquired with a resolution of 4800dpi.

Dataloggers:

Dataloggers are from Lascar Electronics, model EL-USB-2. Temperature, Humidity & Dew Point readings are in the range of -35 to +80ºC and 0 to 100% RH. They have a typical accuracy of ±0.5ºC and ±3% RH and maximum of ±2ºC and ±6% RH. Information from Lascar Electronics information sheet.

Custom Made Dataloggers:

Pieces for the dataloggers were bought separately and were assembled by the author with the assistance of Rui Cardoso[9]. Two dataloggers with four sensors each were made and each datalogger recorded data from one set of microclimate frames, one sensor being placed inside each frame. Digital temperature and humidity sensors type AM2302 DHT22 were used. The sensors enabled readings in the range of -40 to +80ºC and 0 to 100% RH, and have a typical accuracy of ±0.5ºC and ±2% RH according to the manufacturer. An Arduino Uno unit received and processed the data generated from the sensors. The Arduino Uno unit was combined with a module logging recorder shield V1.0 to enable the record of data onto a SD card. A HQ Universal AC/DC Adapter 1000mA supplied the energy to the Arduino.

Appendix VII.2 – Images of the Tests

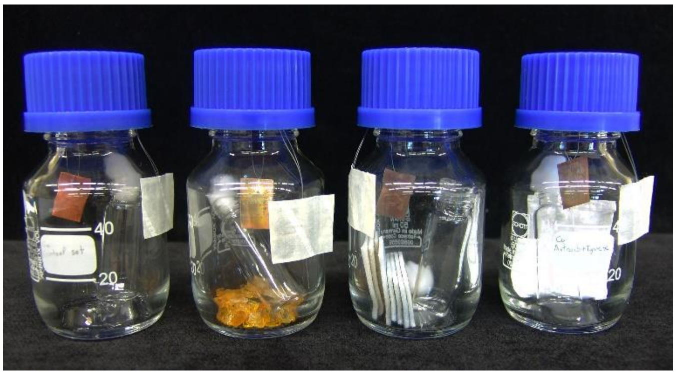


Figure VII.1 - Oddy test bottles of the copper coupons. From left to right: Control, Orange silica gel, Artsorb® and Tyvek® covered Artsorb®.

Figure VII.2 - Box for pre-conditioning the Artsorb® with the metal container to deliver water.

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[9] Rui Cardoso is a student of the Department of Electrical and Computer Engineering at the FCT-UNL.

Appendix VII.3 – Digitalized Images of the Test Coupons

Table VII.1 - Digitalized coupons from the first Oddy test (Test 1) acquired with the flatbed scanner.

	Control		**Silica gel with indicator**		**Artsorb**		**Artsorb + Tyvek**	
	Side 1	Side 2	Side 1	Side 2	Side 1	Side 2	Side 1	Side 2
Copper								
Silver								
Lead								

Table VII. 2 - Digitalized coupons from the second Oddy test (Test 2) acquired with the flatbed scanner.

	Control		**Silica gel**		**Artsorb**		**Artsorb + Tyvek**	
	Side 1	Side 2	Side 1	Side 2	Side 1	Side 2	Side 1	Side 2
Copper								
Silver								
Lead								

Table VII.3 - Digitalized copper coupons[10] from the Adapted test (Test 3) acquired with the flatbed scanner.

	60ºC (oven)		**Ambient Temperature (~25ºC)**	
	Side 1	Side 2	Side 1	Side 2
Control				
Artsorb + 2.5ml H_2O				
Artsorb + 6.5ml H_2O				

Appendix VII.4 – Micrograph and spectra acquired with SEM-EDS

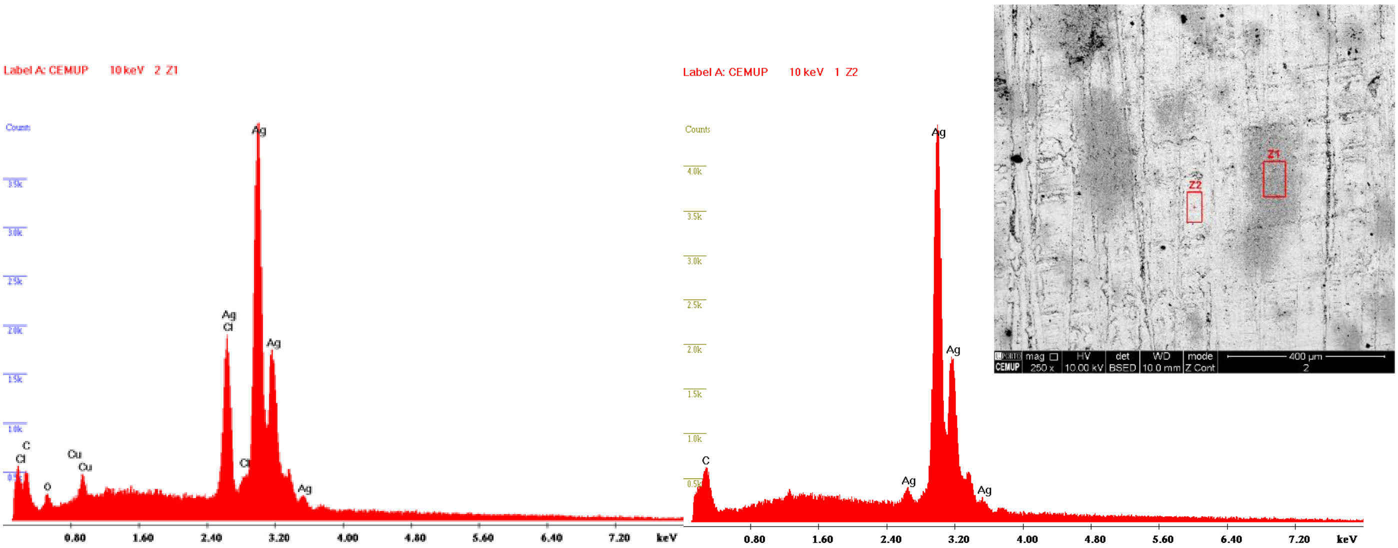

Figure VII.3 – EDS analysis on the coupon in the Artsorb® environment. **Left:** spectra from a dark stain associated with chloride corrosion products. **Right:** spectra from an area with no signs of corrosion. The red squares on the SEM-BSE micrograph indicate areas of analysis.

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[10] Only one coupon of each test is represented here since they were all very similar.

Appendix VII.5 – Construction and Installation of the Microclimate Frames

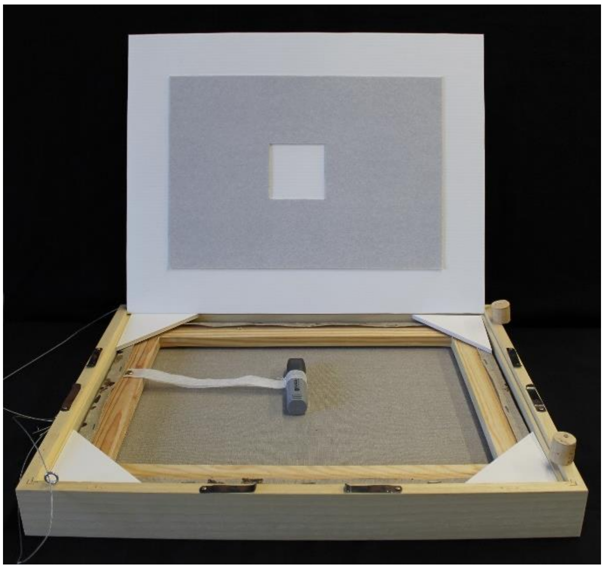

Figure VII.4 – Microclimate frame (open) with the Artsorb®.

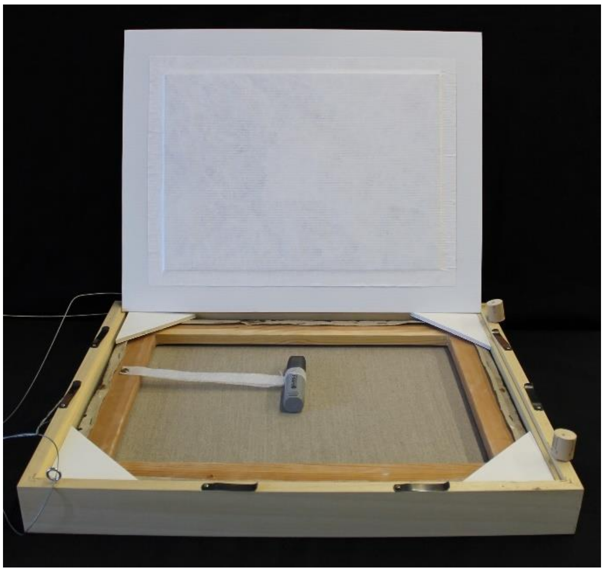

Figure VII.5 – Microclimate frame (open) with the Tyvek® covered Artsorb®.

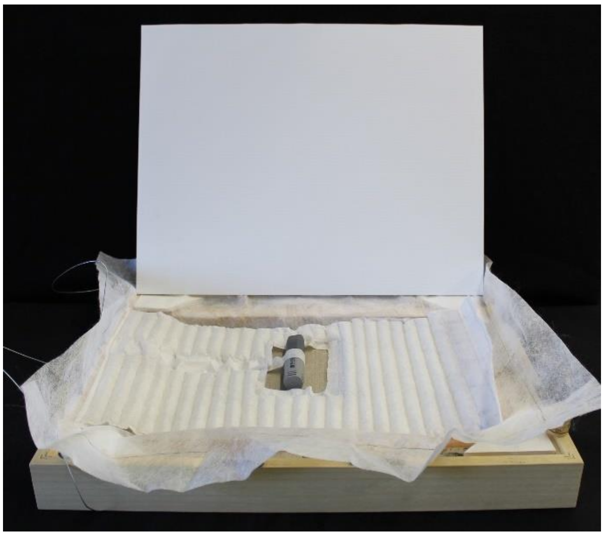

Figure VII.6 – Microclimate frame (open) with the silica gel in a hand woven Reemay® bag.

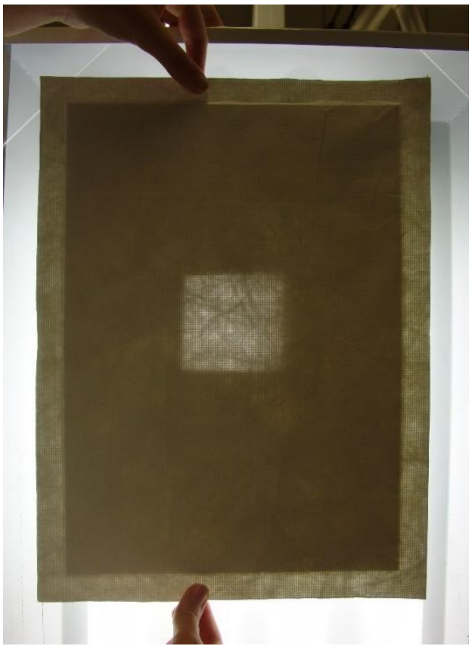

Figure VII.7 – Tyvek® covered Artsorb® in transmitted light to see the open square in the Artsorb®.

Figure VII.8 – The eight frames installed at the Tide Mill.

Figure VII.9 – Back of the microclimate frame with the silica gel. The Reemay® wraps around the backing board. The arrow points out the cork spacers in the bottom of the frame.

Appendix VII.6 – Relative Humidity and Temperature Measurements

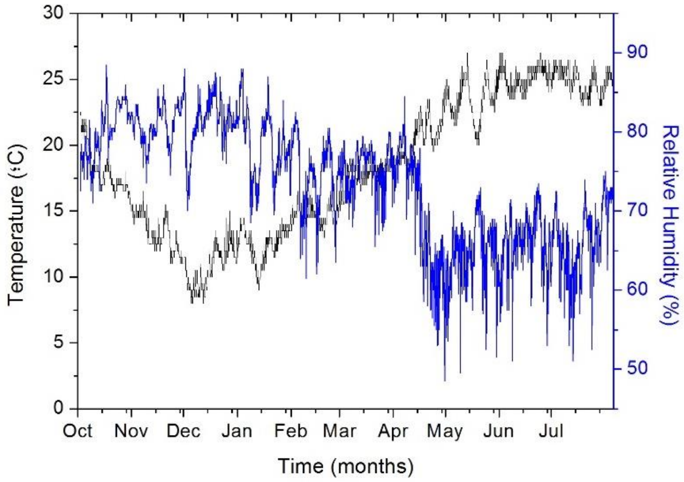

Figure VII.10 – Temperature and RH values of the exhibition room in the Tide Mill (one year readings).

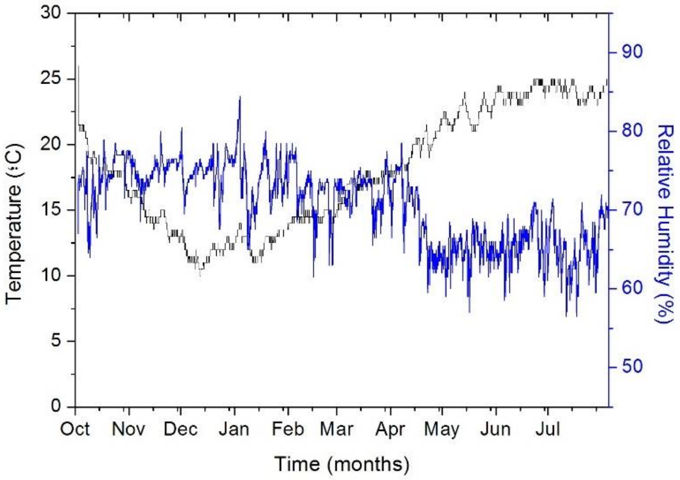

Figure VII.11 – Temperature and RH values of the storage room (one year readings).

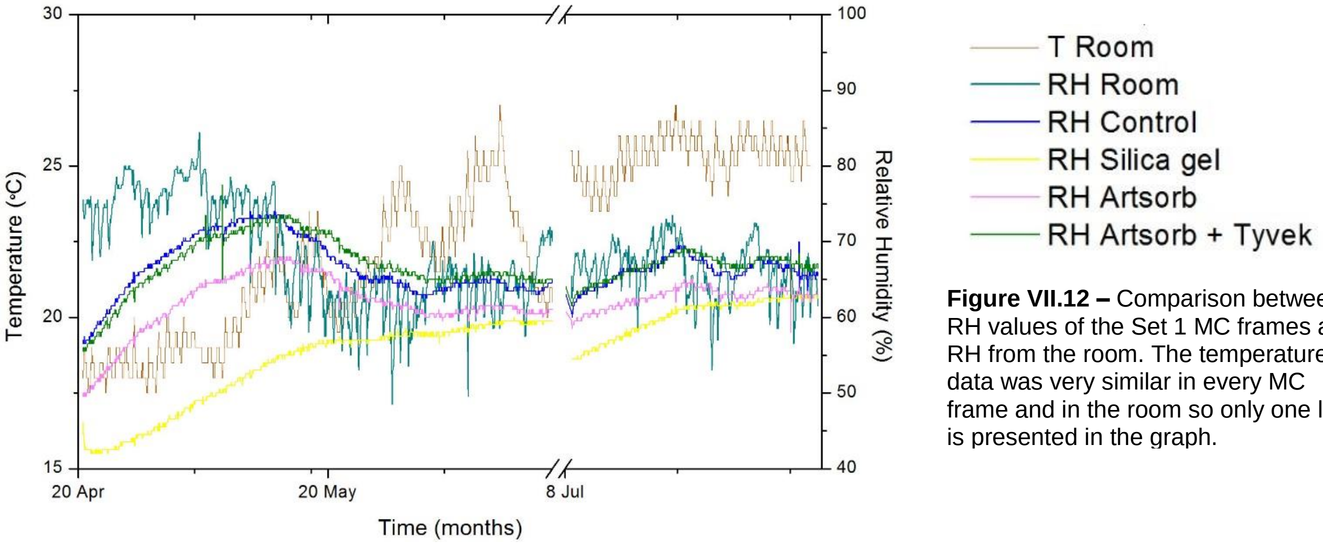

Figure VII.12 – Comparison between RH values of the Set 1 MC frames and RH from the room. The temperature data was very similar in every MC frame and in the room so only one line is presented in the graph.

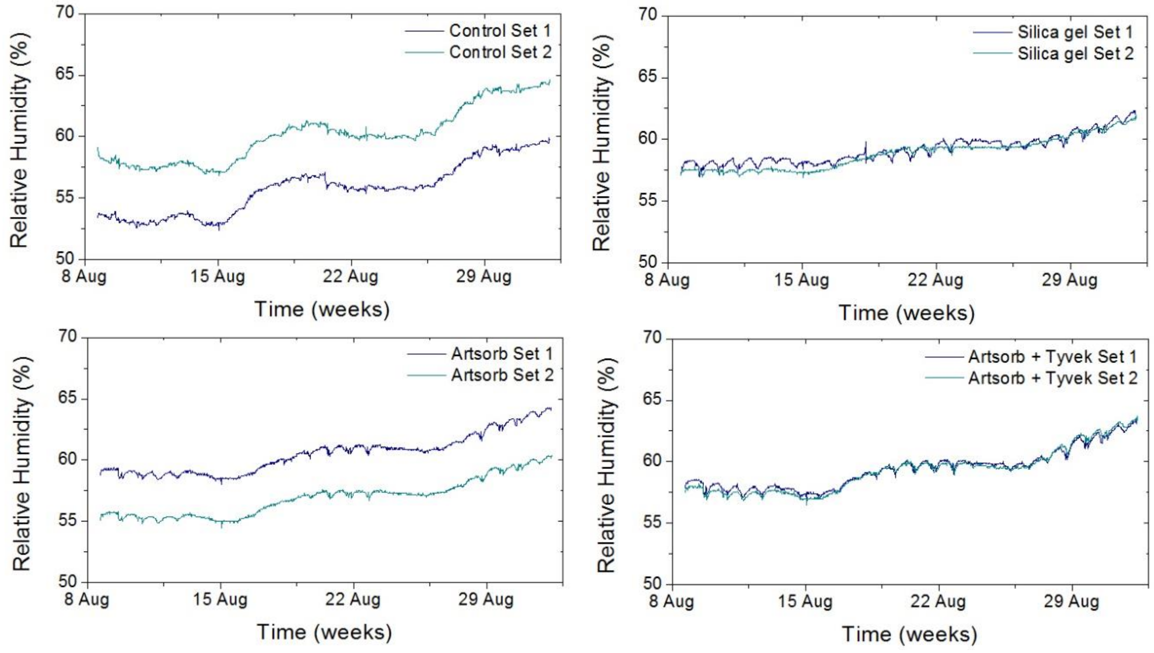

Figure VII.13 – Comparison between RH values originated by the custom-made dataloggers in Set 1 and 2 for the four MC frames.

APPENDIX VIII – Equipment and Suppliers

Appendix VIII.1 – Equipment

Heat spatula:

Heat spatula is from the Willards of Chichester, Sussex, England. Controller is a type "E". Serial No. 6171-479.

Oven:

The oven is from the Memmert GmbH + Co.KG. Memmert Oven is from type ULE 400 with 230 V- 6.1 A 50/60 Hz 1400W.

Appendix VIII.2 – Suppliers

Table VIII.1 - List of products and materials used and its suppliers.

Product	Supplier	Date of Receipt
BEVA® 371b	Kremer Pigmente GmbH & Co. KG kremer-pigmente.de	FCT-PNT Stock 2013
Facing tissue (Japanese Tissue): Filmoplast J 50 M x 31 CM K50 Serial No. 13906027498	NESCHEN Documents	FCT-PNT Stock
Strip lining BEVA® 371 film	Kremer Pigmente GmbH & Co. KG kremer-pigmente.de	FCT-PNT Stock 2011
Strip lining white polyester fabric, Polyester Restoration Fabric	Russel & Chaple UK www.randc.net	FCT-PNT Stock
Filter mask for organic vapours	3M http://www.3m.com.pt/	FCT-PNT Stock
Melinex®	PEL, preservation equipment www.preservationequipment.com	FCT-PNT Stock 2015
Cushioning foam	?	FCT-PNT Stock
EVA foam	Dollarama	Purchased 2015
Reemay®	PEL, preservation equipment www.preservationequipment.com	FCT-PNT Stock
Foam-core board	Nielsen & Bainbridge nielsenbainbridgegroup.com	FCT-PNT Stock
Artsorb®	PEL, preservation equipment www.preservationequipment.com	EMS Stock
Non-indicating silica gel	Brownell Limited http://brownell.co.uk/	Purchased 2015
Orange silica gel	Labchem www.labchem.com	FCT Scientific lab Stock
Tyvek®	NESCHEN Portugal	FCT-PNT Stock
Wooden frames and glazing	Leroy Merlin, Lisbon, Portugal www.leroymerin.pt	Purchased 2015
Polypropylene hollow sheets	Mitera, www.mitera.pt	FCT-PNT Stock 2014
Volara® Foam Rabbet Tape	PEL, preservation equipment www.preservationequipment.com	FCT-PNT Stock