Treatment of a nineteenth century male portrait in oil including the characterisation of materials, technique and a study of the lead soap aggregation in the paint composite

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Resumo

Este projecto envolveu o tratamento de um retrato a óleo do século XIX do Ecomuseu do Seixal (Portugal). A pintura de "João Luiz Lourenço" encontrava-se em muito mau estado de conservação. Devido à variedade e gravidade dos problemas apresentados, esta ofereceu uma oportunidade de explorar aspectos importantes na área da conservação de pintura. A abordagem ao tratamento da pintura exigiu uma investigação empírica de um número de materiais e técnicas utilizadas no campo da conservação/restauro. De interesse adicional, a pintura apresentava evidências da presença de agregados de sabões metálicos (carboxilatos de chumbo). Os materiais da pintura e os referidos agregados foram estudados e caracterizados por diferentes técnicas analíticas: μ-EDXRF (Micro-espectroscopia de Fluorescência de Raios X Dispersiva de Energias), μ-Raman (Micro-espectroscopia de Raman), μ-FTIR (Micro-espectroscopia de Infravermelho com Transformada de Fourier) e SEM-EDX (Microscopia Electrónica de Varrimento com Espectroscopia de Raios X Dispersiva de Energias).

Parte 1: descreve o estudo dos materiais e da técnica da pintura e dos agregados de sabão metálicos presentes na camada de preparação.

A observação de cortes transversais da pintura com o Microscópio Óptico e com SEM-EDX revelou a presença de dois agregados de chumbo visualmente distintos: uns completamente brancos, outros com um centro branco rodeado por distintas partículas vermelhas identificadas como vermelho de chumbo (minium: Pb_3O_4) por μ-Raman. A presença destes dois tipos de agregados metálicos levanta questões relacionadas com os materiais de origem destes e com o mecanismo de formação/evolução dos mesmos.

Parte 2: descreve o projecto e implementação do tratamento de conservação/restauro.

O tratamento da pintura levantou diversos desafios e envolveu a exploração de métodos não-tradicionais. Durante o tratamento, as consequências de cada passo da intervenção foram cuidadosamente consideradas em relação às etapas subsequentes. Todas as decisões foram tomadas de acordo com os problemas de conservação intrínsecos da pintura, com os materiais desta e em relação ao futuro meio ambiente da pintura.

Palavras-chave: retrato a óleo do século XIX, materiais e técnica; agregados de sabões metálicos (carboxilato de chumbo); tratamento de conservação / restauro.

Abstract

This project involved the conservation of a 19th century portrait in oils from the Ecomuseu do Seixal (Portugal). The painting of “*João Luiz Lourenço*” was in very poor condition. Because of the range and severity of the problems presented, it offered an opportunity to explore important aspects of painting conservation in-depth. The approach to its treatment required an empirical investigation of a number of materials and techniques used in the field of conservation/restoration. Of additional interest, the painting exhibits widespread evidence of metal soap (lead carboxylate) aggregates protruding through the paint from the ground layer. The painting’s materials and the metal soaps aggregates were studied and characterised with different analytical techniques: µ-EDXRF (*Energy Dispersive X-ray Fluorescence*), µ-Raman Spectroscopy, µ-FTIR (*Fourier Transform Infrared Spectroscopy*) and SEM-EDX (*Electron Scanning Microscopy with Energy Dispersive X-ray Spectroscopy*).

Part 1: describes the study of the materials and the technique of the painting, and of the metal-soap aggregation within the painting’s ground layer.

Observation with the Optical Microscope and with SEM-EDX of paint/ground cross-sections reveals the presence of two visually distinct lead carboxylate aggregates: one, completely white, and the other with a white centre surrounded by distinct red particles identified as red lead (minium: Pb_3O_4) by µ-Raman. The presence of these two types raises questions about whether there are different starting materials for the aggregates or whether they could be in different states of evolution.

Part 2: describes the design and implementation of the conservation/restoration treatment.

The treatment of the painting raised challenges and at various stages involved the exploration of non-traditional methods. At every stage during the treatment the consequences of an intervention was carefully considered in relation to the subsequent steps. All decisions were taken according to the painting’s intrinsic conservation problems and materials and with regard to the future environment of the painting.

Keywords: 19th century portrait in oils; materials and the technique; metal soap aggregates (lead carboxylate); conservation/restoration treatment.

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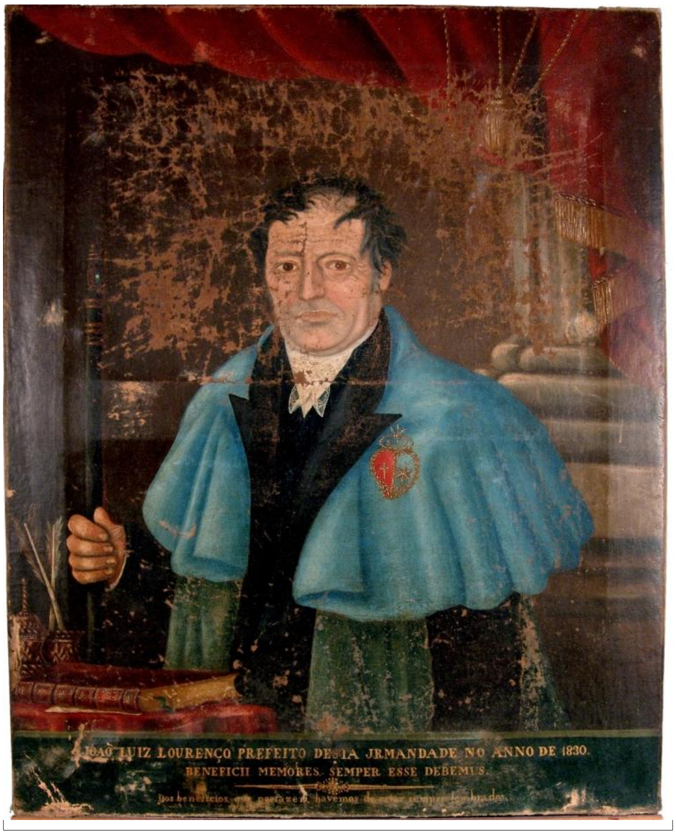
Chapter 1: Introduction and description of the painting

The painting is a nineteenth century portrait on canvas (see appendix I).

The figure is presented in a formal position against a brown background with a red curtain, behind a table with a book and writing objects on top. The man represented has an insignia on his coat – a heart divided in half with two symbols, a star and a cross, with the letters S.J.V - referring to the brotherhood to which he belonged and where he probably exercised management functions (according to information provided by the Ecomuseu Municipal do Seixal). At the bottom of the painting, there is a dark green bar with gold letters with the inscription: *"João Luiz Lourenço Prefeito desta irmandade no anno de 1830. BENEFICII MEMORES SEMPER ESSE DEBEMUS. Dos benefícios que nosrazen, havemos de estar sempre lembrados".*


JOÃO LUIZ LOURENÇO PREFEITO DESTA JRMANDADE NO ANNO DE 1830.
BENEFICII MEMORES SEMPER ESSE DEBEMUS.

Normal light before treatment photograph of front of João Luiz Lourenço: belonging to ECOMUSEU Municipal do Seixal, Portugal). Artist: unknown.

The paint surface ranges from areas with a very smooth application to areas with a pronounced impasto and visible brushstrokes. The image has been created in a naive manner with little visual evidence of paint layering or glazes.

Little is known about the provenance of the painting, except that it was incorporated in the Ecomuseu collection through a donation on the 29th September, 2009. According to the donor, this painting was in the possession of the Lourenço family for several generations. João Luiz Lourenço was connected to the Tide Mill in Corroios. The following text was taken from a document about the Mill: *"Tide Mill in Corroios: D. Nuno Álvares Pereira, owner of many lands near Tejo river, built the tide mill in 1403 in a district where there was intense mill activity for many centuries. (…) Later, it was donated to the Convento do Carmo, remained in their ownership until 1834. On this date, due to the extinction of religious orders in Portugal, it was incorporated (…) in the National Treasury. In 1836, it was bought by* ***João Luiz Lourenço****"* [1].

It is also known that the Lourenço family has connections to England. The painting has a label on the stretcher referring to a British removal firm (Woodbridge & Co. Ld), indicating that it was in the UK at one point (see Figure 7, appendix II.2).

The painting was lined in the past and later suffered water damage (likely due to being in a wet condition for a period of time).

Chapter 2: Examination: condition, materials and technique

The techniques for all instrumental analyses are described in full in Appendix VIII. Here they are listed with their acronyms: OM (Optical Microscope), μ-EDXRF (*Energy Dispersive X-ray Fluorescence*), μ-Raman, μ-FTIR (*Fourier Transform Infrared Spectroscopy*) and SEM-EDX (*Electron Scanning Microscopy with Energy Dispersive X-ray Spectroscopy*).

2.1 Examination and Condition Summary

The portrait of *João Luiz Lourenço* was executed in oil (see: Paint layering section, 2.5). The simple paint application, in almost all areas consisting of a single thin layer, was confirmed in the paint cross-sections (appendix VIII.4). There was no visible evidence of underdrawing using infra-red photography. However, this technique will only reveal the presence of a carbon containing materials (appendix I) [2], and it is not a particularly sensitive technique. Infra-red reflectography could reveal more information.

The major problem that this painting presented was the severe distortions in the canvas and the extensive paint/ground losses associated with these distortions (appendix I&IV). Because the losses were particularly concentrated in areas of the greatest deformation in the canvas, this suggested that the severe distortions in the support (see below: Previous treatment) led to paint/ground losses as these more rigid layers were unable to conform to the upheaval in the fabric. It is likely that water and high humidity conditions led to mismatched movements of the materials presented.

2.2 Previous treatment: lining

The painting had been lined in the past, and appears to have been partially cleaned, with associated areas of severe abrasion, particularly in the face (Fig.14, appendix II.5). The lining had been performed before the painting was in direct contact with water since both canvases were separated along the bottom edge (this area no longer had lining adhesive), and there was a dark tide line presumably due to water exposure on the back of the lining canvas (Fig.1, appendix II.1).

The lining canvas consisted of a single piece of fabric with a plain (tabby) weave and finer threads than the original canvas. The identification of the fibre of the lining canvas was made through observation under polarized light in the OM. The fibre showed characteristics similar to Bast fibres. It presents dislocations on the cell wall along the fibre, usually attributed to flax (*Linum usitatissimum)* or hemp fibres (*Cannabis sativa*) (Fig.23, appendix V) [3].

The lining canvas generally appeared to be strong, but a small tear (4cm long) is clearly evident (Fig.2, appendix II.5). This was presumably caused by a blow to the front of the painting, which tore both the original and the lining canvas. On the back, the lining canvas exhibited significant spotting with dark and light areas likely due to the existence of fungi (Figure 1&2, appendix II.1). The fixtures were tacks in a poor condition (rusted) (Fig.3, appendix II.1). There was evidence of 63 metal tacks being present originally, but some were missing. This resulted in a lack of tension in the painting. The tacking margins of the lining fabric were deteriorated (brittle), extremely dirty, with poor attachment to the stretcher, in part due to the condition of the tacks.

The adhesion between the lining and the original canvas was very poor. Separation had occurred in many of the most extreme deformations (Fig.5, appendix II.1).

The lining adhesive was analysed by µ-FTIR. By observing the spectra obtained it was possible to identify characteristic bands related to animal glue and starch (Fig.1), a common mixture for lining adhesives used in the past.

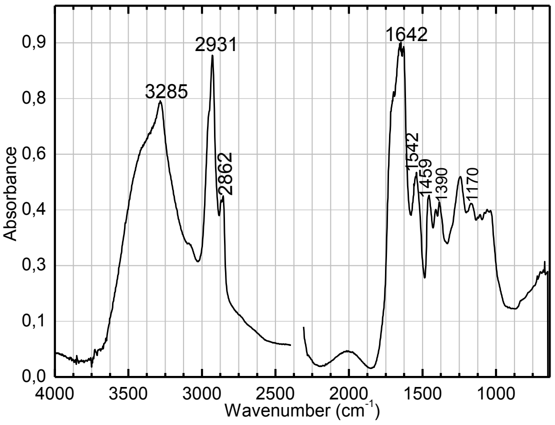


Figure 1: µ-FTIR spectrum of the lining adhesive.

The infrared spectra for proteins exhibit absorption bands associated with their characteristic amide group [4]. Animal glue is protein based and therefore can be identified by its amide group (-CONH-). It is possible to observe its characteristic peaks at: 3285 cm^{-1} (N-H stretch[1]); 1642 cm^{-1}(amide I); 1542cm^{-1} (amide II: combination of C-N and N-H vibrations) and 1459 cm^{-1} (amide III: C-H bending vibration) in stair-step-type intensities [5]. The presence of starch was detected trough the peaks at: 1459, 1390 and 1170 cm^{-1} and confirmed with an Iodine test[2] performed on a glue-lining sample with and with PLM[3] (see appendix VI).

The significant disadvantages associated with glue linings are related to the lining process itself, but also with the consequences of this treatment. This painting offers a good illustration of these side effects. A glue lining involves high temperature, pressure and moisture, which can result in damage to the paint composite [6]. The painting *João Luiz Lourenço* does not have many obvious and pronounced brushstrokes and impastos however flattening and loss of texture thought to be associated with the lining can be seen (Fig.6, appendix II.1). In addition, animal glues are very susceptible to attack by molds and insects [7], which is clearly evident in this painting. After removing the lining canvas, it was possible to see that the adhesive had been severely affected by microorganisms (Fig.4, appendix II.1). Another great disadvantage of an animal glue-based adhesive is its ability to response to relative humidity (RH) changes, by contracting and expanding (swelling) [8,9]. These movements can be transferred to the paint composite in the form of stresses, which can create cracks, cupping and flaking [8]. The other adhesive ingredient found, starch, is a carbohydrate. Carbohydrates are polysaccharides composed of various proportions of several monosaccharide units [5]. Starch retains some water solubility [5]. The solubility the adhesive and the particular swelling of the glue help to explain how the extreme deformations of the original support had formed (see: Original support: Fabric, 2.4).

2.3 Auxiliary support: stretcher

In order to keep a painting canvas under tension, it is stretched onto a wooden frame (the stretcher or strainer) [6,10]. For larger paintings, the auxiliary support is usually reinforced by a cross-piece, as in the case of this painting [6] (appendix I). In this case, the auxiliary support is a replacement stretcher (likely soft wood) presumably supplied when the painting was lined. On the left side of the stretcher, there is a label of a British transport/removal company, which includes the name of the family that donated the painting (Newbery) to the current owner, Ecomuseu Municipal do Seixal (Fig. 7, appendix II.2). Although the wood is sound and the stretcher is stable, it is slightly warped. This factor could cause distortion in the painting. For this reason, a replacement stretcher will be made. Further details related to the stretcher' condition in appendix III.1.

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[1] N-H stretching vibrations occur near 3350 and 3180 cm^{-1}, but hydrogen bonding may expand the bands, giving the appearance of one band (sharper than O-H bands), as we can see in this spectrum [5].

[2] The Iodine test is used to detect the presence of starch, leading to the production of a dark purple colour. Iodine solution: iodine dissolved in an aqueous solution of potassium iodide [11].

[3] Polarized Light Microscopy [12].

2.4 Original support: Fabric

The original tacking margins have been removed, presumably when the painting was lined. The current dimensions of the original painting are 91.5 x 74cm approximate (see Fig.8, appendix II.3). The canvas is a single piece with a plain (tabby) weave. The original canvas has thicker threads compared to the lining canvas and few fabric imperfections. In relation to its condition, the fabric did not appear to be significantly degraded. The tear, at lower middle, left side, is a crescent-shape and judging by the lack of significant paint loss and the clean appearance of the fabric it appears to be relatively recent (Fig.9, appendix II.3). To support this assumption, in some other areas of damage where the original canvas is exposed the fabric is significantly darker with significant dust and dirt and in others the canvas is a light colour (Fig. 10, appendix II.3). The lighter areas suggest less oxidised fabric and that the loss occurred more recently than in the case of the darker areas. There are two circular concave depressions with paint loss due to abrasion on each side (more pronounced on the right) (Fig. 11, appendix II.3). These damages are likely associated with projecting hanging hardware (*e.g. screw-eyes*) from another painting which was stacked or leaned against this painting, possibly during transport. The original canvas was very slack, due to the lack of attachment to the stretcher of the lining canvas (for example only 4 of 12 nails at the bottom of the painting were attached causing a major depression along the stretcher bar at the bottom of the painting) (Fig.2, appendix II.3).

The major problem presented by this painting, which contributing to an unstable state, is the series of significant, overall out of plane distortions (Fig.2). The extreme deformations in *João Luiz Lourenço* are related to the different response to moisture/water of the different materials in the painting. Sized canvas reacts characteristically to RH changes: when the RH is high, the sized threads expand and the fabric contracts and becomes stiff [6]. In contrast, the animal glue present in lining adhesive swells, loses strength and

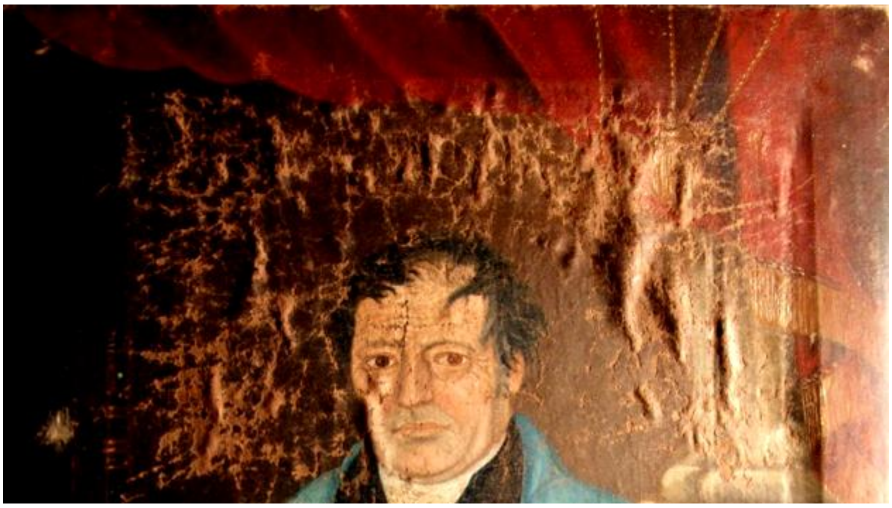

Figure 2: Before treatment, detail, raking light showing deformation on the original support associated with paint losses.

adhesive properties in very humid conditions [9]. Therefore, these deformations appear to result from the lack of adhesion between the painting and the lining support, due to the loss of strength of the lining adhesive.

The brittle aged paint/ground composite was unable to conform to the extreme distortions in the fabric. As well, its adhesion to the original canvas at the size layer compromised by high levels of moisture, thus the paint/ground separated and was lost. Further details in appendix III.2.

Fibre identification was made by observation through OM of one thread taken from the margin of the original canvas. Longitudinal and transverse view of a fibre provides detailed information related to the surface morphology of the fibre [13]. The longitudinal view verified the existence of x shaped joint-like cross markings (displacement points of the cell wall) along the fibre [3,10] (Fig. 24, appendix V). This is consistent with flax or hemp fibres described in the literature. In order to be able to distinguish between these fibres it was necessary to make the observation of the transverse view. With the transverse view, it was possible to verify the existence of polygonal shape of the wall of the cell [3] (Fig. 25, appendix V). The characteristics observed likely corresponds to flax.

2.5 Sizing and Preparation Layers

A size or water-based glue is applied on canvas to isolate it and to create a bond between the support and the ground layer [2]. In this painting, the sizing layer is not visible.

The ground or preparation layer[4] is a light warm beige colour. It covers the fabric evenly and reduces its texture (Fig.13, appendix II.4). Due to the lack of tacking margins it was not possible to evaluate its application to determine whether or not this layer was commercially applied. With the naked eye, is possible to see red and white particles in the ground. The ground appears to be lean and porous and in some areas it has crumbed. Where the painting is not damaged the adhesion of the ground to the support is good (appendix IV).

Observation of paint micro-samples under OM, indicate that the preparation is composed of two different formulations evident as visually different layers[5] (appendix VIII.4). The first ground layer (identified in the Fig. 3 with the number 1) is thicker and more orange than the second. The next layer is thinner and lighter (identified with the number 2 in Fig. 3). Using SEM-EDX, it was determined that both layers are rich in lead, and are heterogeneous with particles of different shapes and sizes. However, the second thinner preparation layer has a higher ratio of lead and a finer particle size distribution (Fig. 4).

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[4] The ground (or preparation layer) of a painting is applied to the support, covering the fabric providing a surface on which the paint is applied [6,10,17]. Grounds have physical but also aesthetic functions [2]. The main function is to preparing the canvas to hold the paint (physical function) and control the colour, luminosity and texture of the support (aesthetic) [2].

[5] Each layer could consist of several applications of the same materials, but would not show as different layers in cross section unless the formulation changes [18].

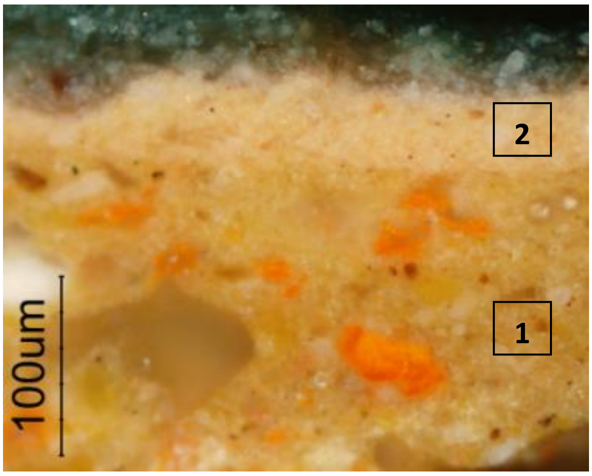

Figure 3: OM image of the X07 section: total magnification 200x, Vis-light - Polarized Light

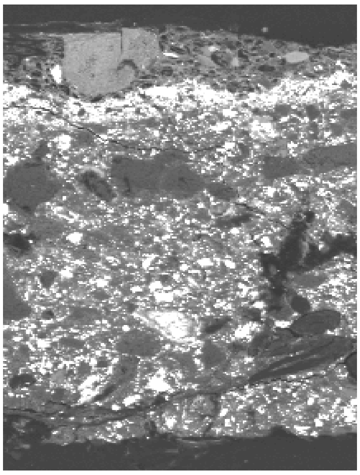

Figure 4: SEM BSE image of a cross-section (X15) showing heterogeneity of the particles and the differences in the ratio of lead in the two preparation layers.

Through µ-Raman it was concluded that the first preparation layer consists mainly of a mixture of lead white ($2PbCO_{3.}Pb(OH)_2$), red lead (minium - Pb_3CO_4), calcium carbonate ($CaCO_3$), quartz (SiO_2) and iron oxide, probably haematite (Iron(III) oxide)[6]. In the second layer the presence of lead white, quartz and iron oxide were detected. Further information see Appendix VIII 5.1.

A ground is usually classified according to the binding medium used [2]. This preparation layer contains oil as confirmed with µ-FTIR by the aliphatic vibrations around 3000 cm^{-1}, due to the presence of CH_2 and CH_3 groups (2926 and 2854 cm^{-1}, respectively) and in the carboxylic acid absorption at 1710 cm^{-1} [14] (Fig. 5). The µ-FTIR spectra exhibit peaks associated with metal carboxylates: asymmetric COO^- stretch vibration (1510cm^{-1}) and symmetric COO^- stretch vibration (1409cm^{-1}) of metal carboxylate [14-16,23,25,30].

The formation of carboxylic acids and the formation of metal carboxylates are generally associated with degradation of the oil [14]. It was not possible to distinguished the two ground layers using µ-FTIR.

However, the following components were identified in both layers: kaolin ($Al_2Si_2O_5(OH)_4$) (3697 and 3620 cm^{-1}, associated with hydroxyl ion bands and 917 cm^{-1} to Al–O–H band) [5,21]; quartz (797 cm^{-1}) [21]; lead white (1409, related to C-O stretch and 680 cm^{-1} to CO_3 inplane rocking) [22], calcium carbonate (1409 and 876 cm^{-1}) [5,21] and iron oxides (3401, 3202 cm^{-1}, 1029cm^{-1} and 797cm^{-1} [21]) in the ground layer.

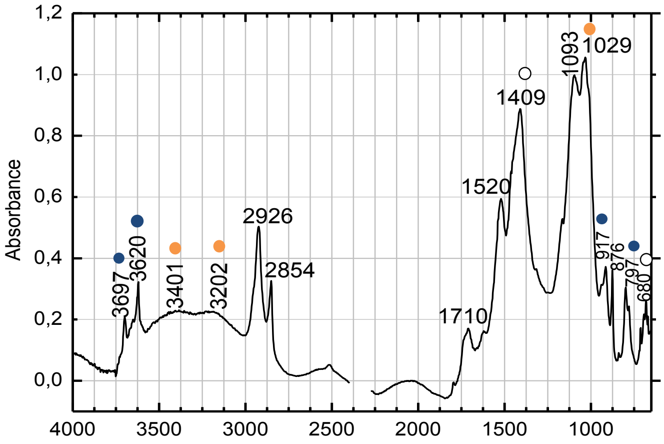

Figure 5. µ-FTIR spectrum of the sample F1 (see appendix X: sampling areas). Kaolin ● ; iron oxide ● ; lead white ○

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[6] The iron oxides and hydroxides are the base of many natural and synthetic pigments [19]. "Natural iron oxides are processed from several different ores, including haematite, limonite, siderite, and magnetite, providing a wide range of reds, yellows, purples, browns and blacks" (p.107) [20].

These results are consistent with elemental analysis performed with SEM-EDX and µ-EDXRF. With SEM-EDX analyses, in the first layer the following were detected: Mn, K, Ca, C, O, Al, Si, Fe and Pb and in the second layer: Ca, O, Si, Fe and Pb. µ-EDXRF analysis detected Mn, Ca, Fe and Pb. The presence of manganese may indicate the existence of a Sienna or Umber pigment, characterized by the presence of manganese dioxide [I]. In the FTIR spectrum the characteristic absorption band belonging to MnO_2 (1029 cm^{-1}) [21] is evident (Fig.5).

2.6 Paint layering

The presence of an oil binder was confirmed with µ-FTIR. The Infrared spectra of all paint samples analysed presented peaks associated with an aged drying oil: aliphatic vibrations around 3000 cm^{-1} (CH_2 and CH_3 groups), a carbonyl peak around 1740 cm^{-1}[14], carboxylic acids absorption at 1710 cm^{-1} [14] and peaks associated with metal carboxylates at 1400 and 1500 cm^{-1} (COO^-symmetric and asymmetric stretch, respectively) [14-16,23,30] (appendix VIII.6). The pigments were analysed using: µ-EDXRF, µ-Raman and µ-FTIR. The pigments were identified as follows: a carbon-based pigment, Prussian blue, lead white, iron oxide, chrome yellow and red lead. Through the results obtained, it was possible to conclude that all the materials identified are consistent with the materials available in the early 19th century. Pigment analyses are summarized in Appendix VIII.4 (see also appendices VIII.6 and VIII.7).

The major problem associated with the paint layer is overall losses (appendix IV). The small tear is also associated with paint losses and flaking (Fig. 6). There was some significant flaking at the interface of the paint/ground and the canvas, in the location of distortions, which appeared to be more recent. These areas presented a high risk of further losses to the pictorial layer (Fig. 7). There are also paint losses and abrasions due to mechanical damages as well as signs of surface abrasion (appendix I and IV).

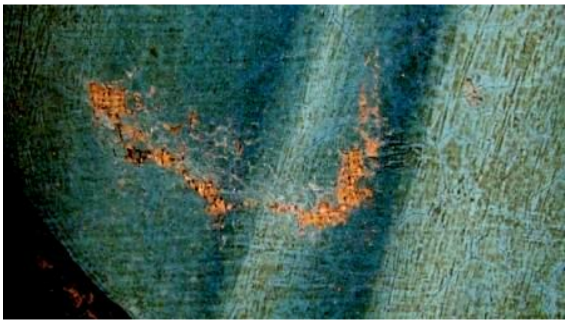

Figure 6: Before treatment detail of the tear located on blue jacket of the figure.

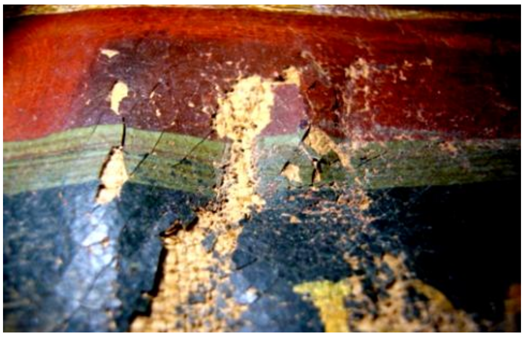

Figure 7: Before treatment detail photograph of flaking at the interface of the paint/ground and the canvas.

In unaffected areas, the paint cohesion appears to be good with a good layer adhesion, despite the overall mechanical cracking (associated with normal aging of an oil painting) (Figs. 14 and 15, appendix II.5).

2.7 Coatings: varnish

Traditionally the varnish was seen to have two functions: to protect the paint layer and to modify the appearance of a painting [2]. Traditional varnishes are commonly made from resins or insect secretions (more rare) [2].

There was visual evidence of a discoloured varnish. In normal light, varnish residue is most evident on the blue coat and the white scarf (Figs. 16 and 17, appendix II.6). It's overall appearance is patchy with a low-level satin lustre. In some places (Fig. 18, appendix II.6) there is significant blanching (associated with previous water damage). The varnish which remains is significantly yellowed and degraded.

Not all cross-sections showed evidence of the varnish layer. Where it could be seen, it was relatively thin, except in the sample X2 and X4 where the varnish layer appears darker and thicker (appendix VIII.3and VIII.4).

The varnish has the appearance of a natural-resin. This was supported by observation of the painting using Ultraviolet (UV) light where fluorescence typical of natural resins could be observed (appendix I) [2]. The fluorescence is lower in the face, scarf and central area of the figure, which likely indicates that it was partially removed in a previous cleaning.

µ-FTIR analysis confirmed the presence of a natural resin. Natural tree resins are composed by aliphatic three-ring structures [5]. The IR spectra of resins can be distinguished by: a weak and broad band due to the O-H vibrations of a dimerized carboxyl group and by the strong carbonyl (C=O) stretch band [5]. Bands in the "fingerprint" region are characteristic for each particular tree resin and may be used to distinguish [5].

It is very difficult to distinguish natural resins. The bands in the spectra acquired are similar to those attributed to Dammar and Mastic resins (in use as a painting varnish from the early nineteenth century [24]: 3409cm^{-1} (O-H stretching band); 2930 and 2858 cm^{-1} (C-H stretching bands); 1713 cm^{-1} (C=O stretching band); 1465-1385 cm^{-1} (C-H bending bands) and 1385-1037 cm^{-1} (C-O stretching band) [5] (Fig. 8).

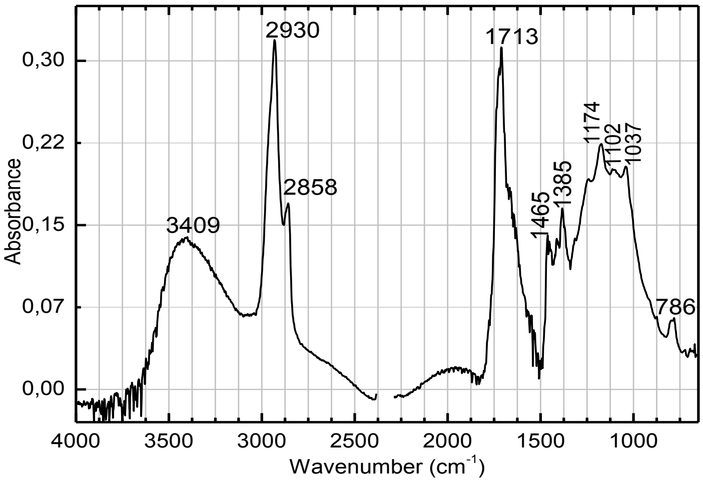

Figure 8: µ-FTIR spectrum of the varnish layer.

Chapter 3: Characterisation and documentation of lead soap aggregates

The painting exhibits widespread evidence of small white spots protruding through the paint layer, with associated round shaped paint losses. There is no obvious relation to coloured areas. These protrusions disturb the surface of the painting and create a textured effect (like paint plus sand), as it can be seen in the following images (Fig.9). The visual characteristics of the protrusions and losses observed on this painting correspond to characteristics attributed to metal soap aggregates in various publications [15, 23,25-28]. This is identified as an oil paint defect, and they can affect the stability of the paint layers [23,32].

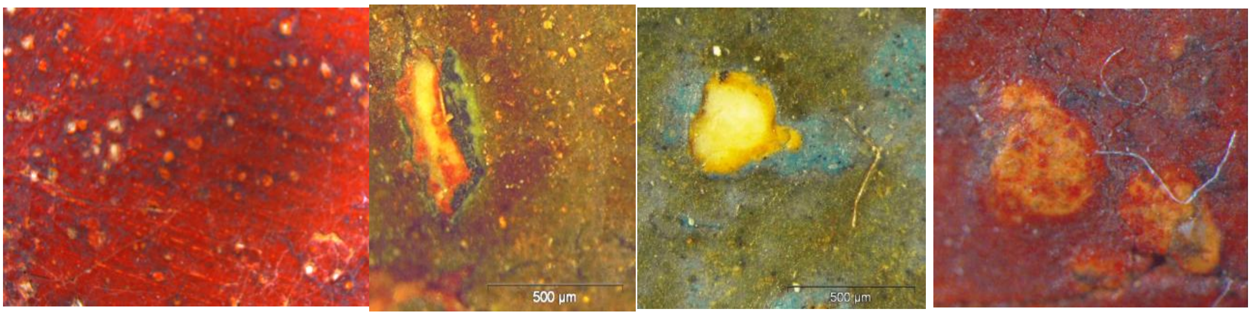

Figure 9: Before treatment details. The appearance of Lead soap aggregates at the paint surface.

A scheme has been suggested by J. Boon[7] (see appendix VII, Fig.28), which describes the development of lead soap aggregates in lead white-containing paint. In this scheme is proposed that the lead particles react with free fatty acids (from the oil) forming lead soaps (lead carboxylates). As the lead soaps aggregate and grow in volume, they can protrude the overlying layer. During and after aggregation, remineralisation is thought to take place inside the aggregate [14]. Further information on the phenomena of lead carboxylates is report in appendix VII.

Under the microscope, lead soap aggregates in cross-sections appear transparent to whitish-opaque under visible light while they strongly fluoresce under UV illumination [23]. By OM differences between the aggregates (marked with an arrow) were detected in this painting: some aggregates were transparent (Fig.10 and 11), others completely white and some with a white centre surrounded by red particles (Fig.12 and 13), all these phenomena were present in the same layer (1ºground layer). As already mentioned the ground is oil-based and is composed of two preparation layers. The main difference between the two ground layers is the absence of minium (red lead) in the second layer. Of several articles consulted [15,23,25,27,31,58], only one showed a paint sample with both types together in the same layer, in the same painting [29].

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[7] Boon, J. J., van der Weerd, J., Keune, K., Noble, P., Wadum, J., 2002, Mechanical and chemical changes in old master paintings: dissolution, metal soap formation and remineralization processes in lead pigmented ground/intermediate paint layers of 17th century paintings'. In *ICOM Committee for Conservation, 13th Triennial Meeting, Rio de Janeiro, Preprints,* ed. R. Vontobel, James and James: 401- 406.

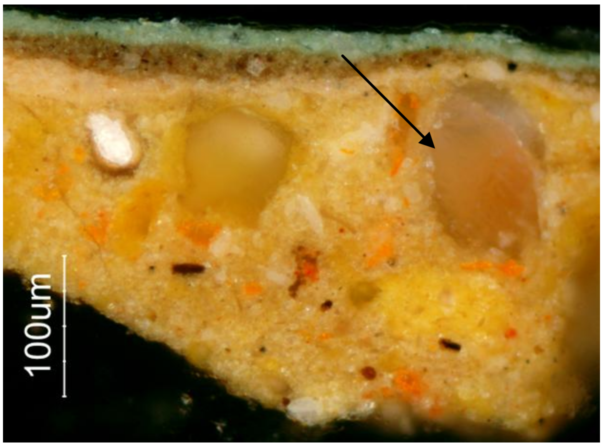

Figure 10: OM image of the sample X10: total magnification 200x, Vis. light - Polarized Light

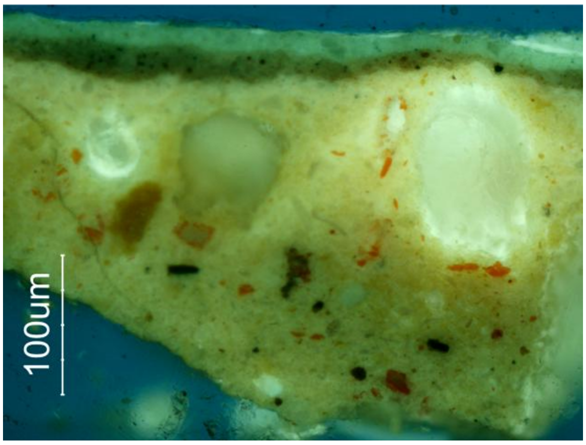

Figure 11: OM image of the sample X10: total magnification 200x, UV light-Filter set5

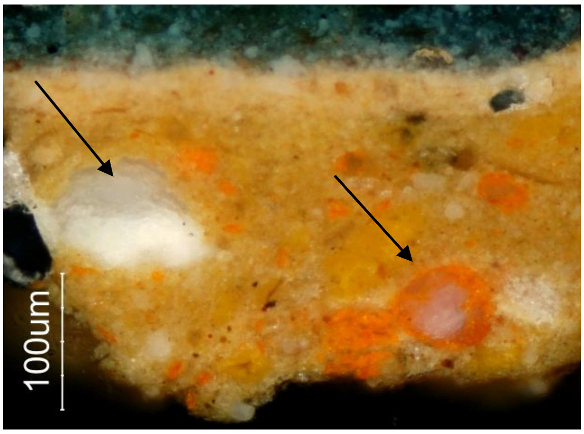

Figure 12: OM image of the sample X07: total magnification 200x, Vis. light - Polarized Light

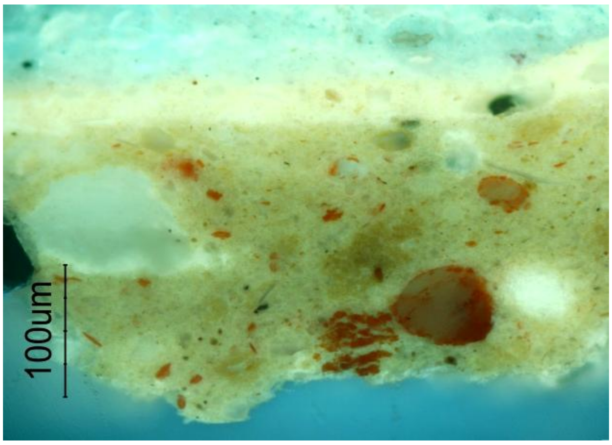

Figure 13: OM image of the sample X07: total magnification 200x, UV light- Filter set5

Aggregates from different colour areas were analysed by μ-FTIR (appendix VII.2). In all the samples, peaks associated with lead carboxylates and basic lead carbonate[8] were found.

As confirmed by μ-FTIR spectrum of a protrusion (Fig.14), the formation of a soap is related with the reduction of the band assigned to the O-H stretch and with the substitution of the bands attributed to the C=O and C-O stretch with the bands attributed to metal soaps [16]. Lead carboxylates are identified by the peaks around 1518 and 1406 cm^{-1}, associated to asymmetric and symmetric stretch vibrations, respectively, of the group COO^{-} in metal carboxylates [15,16,23,25,30]. The sharp bands corresponding to the C-H stretches (at 2924 and 2850 cm^{-1}) are due to the fatty acid carbon chain portion of the lead soaps [16, 25,26,30]. The small peaks in the 1350-1180cm^{-1} region correspond to the vibrations associated with the long hydrocarbon chains of the fatty acids [30]. The basic lead carbonate was identified by the characterics IR bands at: 3535 (O-H stretching band), 1406 (C-O stretch), 1048 (CO_3 symmetric stretch), 876 (CO_3 out of plane rocking) and 684 (CO_3 in plane rocking) [22].

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[8] The lead soaps were identified by comparison with the literature [15,16,23,25,26,30].

Through this analysis, it was possible to conclude that the protrusions on the surface are actually lead soap aggregates. The IR bands for lead carboxylates and lead carbonates overlap in the 1400 cm^{-1} region. The presence of lead carbonate is proved by the absorptions at 3535, 1050 and 680 cm^{-1}[30]. The presence of the O-H stretching band indicates that the lead carbonate is present in the hydrocerussite form (basic lead carbonate), $2PbCO_3.Pb(OH)_2$ [26,30]. The presence of free fatty acids was only detected in sample FL3 by the band at 1709cm^{-1} (Fig.14) (see appendix VII.2). Often, a heterogeneous structure with lamellar bands (enriched in lead) is seen in the centre of aggregates [23,31]. The striations are interpreted as precipitation bands of a new lead compound - lead carbonate [31]. It is assumed that the lead soaps formed react with atmospheric carbon dioxide (CO_2), the carbonate source [15,28]. The aggregates analysed with μ-FTIR were limited to those that protruded at the surface, perhaps indicating that they were already in an advanced stage of the mineralization [15,23,28,31,32]. This could be the reason why basic lead carbonate is detected in all spectra.

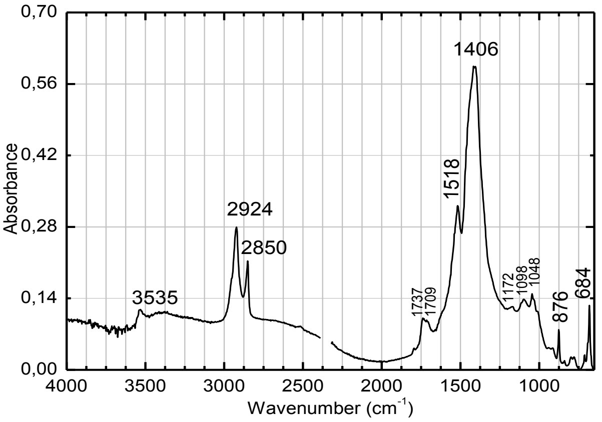
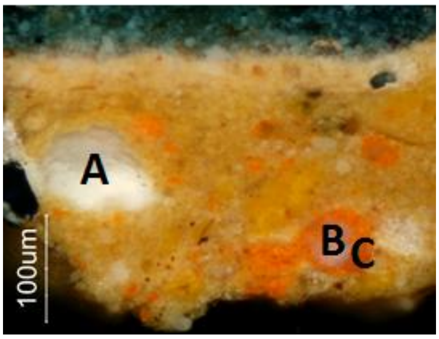


Figure 14: IR spectrum of a lead soap aggregate on a green area (sample FL3).

The main important Raman signals to identify lead soap are: 1090 (√ C-C ; δ C-C-C); 1064 (√ C-C ; δ C-C-C); 1130 (√ C-C ; δ C-C-C); 1300 (δCH_2); 1422 and 1440 (δCH_2) cm^{-1} [16]. In all the spectra acquired, it was possible to verify the existence of the main peaks of lead soaps and the presence of lead carbonate (except on transparent aggregate) [33]. The main difference between soaps with and without orange particles is the presence of minium for those which have orange particles, in the particle itself and in the centre (Fig.15-17). The minium' spectrum is more define in the case of which acquired on an orange particle (Fig.17). In the transparent aggregate only peaks associate to lead soaps were detected – without signs of lead carbonate (Fig.18). As already referred, carbonate is seen as a product of mineralization formed only at a later stage. Therefore, it can be suppose that the transparent aggregate is not yet in this stage.



OM X section X07: 200x mag. Vis. light - Polarized Light

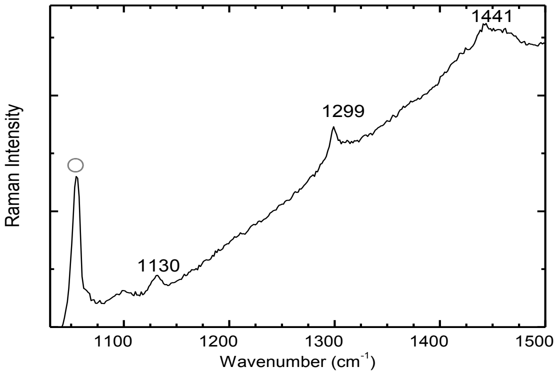


Figure 15: μ-Raman spectra point A

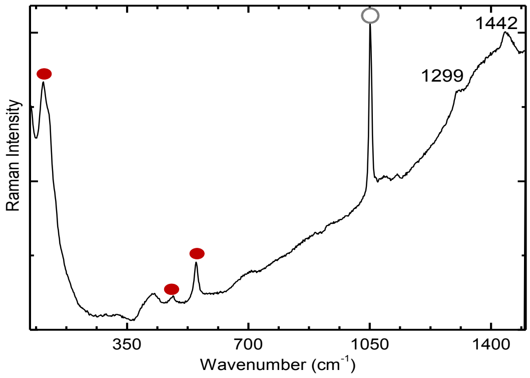


Figure16: µ-Raman spectra point B

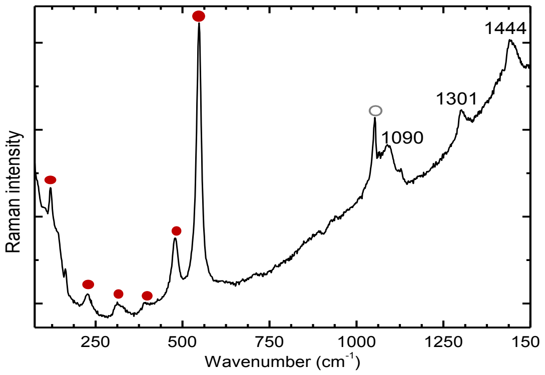
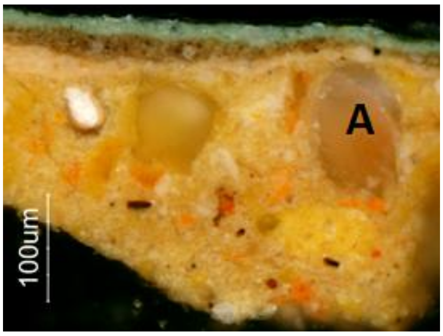


Figure17: µ-Raman spectra point C



OM section X10: 200x mag. Vis. light - Polarized Light

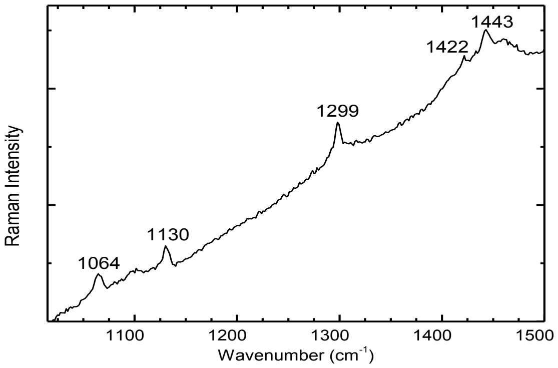


Figure 18. µ-Raman spectra of point A.

Legend: ○ **lead carbonate** ● **red lead**

To better understand the nature of these aggregates, SEM-EDX analysis was performed. As it can be seen in the following SEM back scattered electron images (BSE images), the aggregates exhibit quite different morphology (Figure 19 - 22).

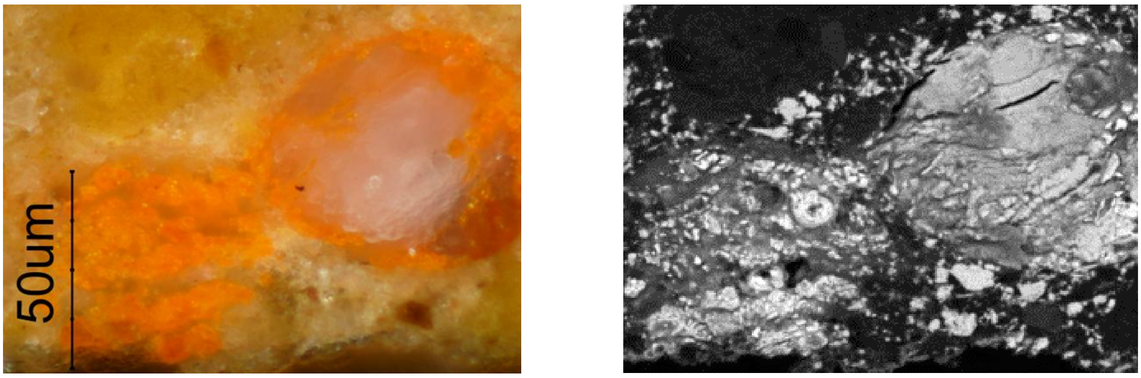


Figure 19: OM image: 500x mag. Polarized Light (right) and BSE image (left) of the sample X7

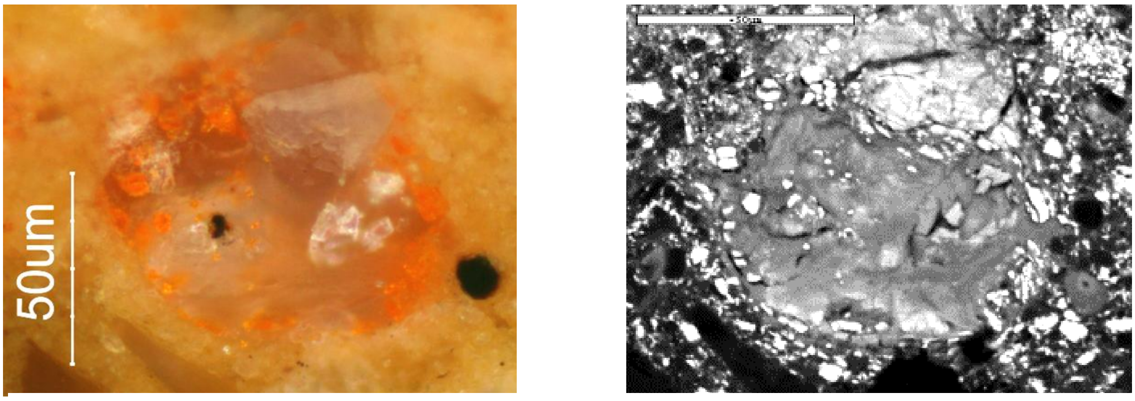


Figure 20: OM image: 500x mag. Polarized Light (right) and BSE image of the sample X13

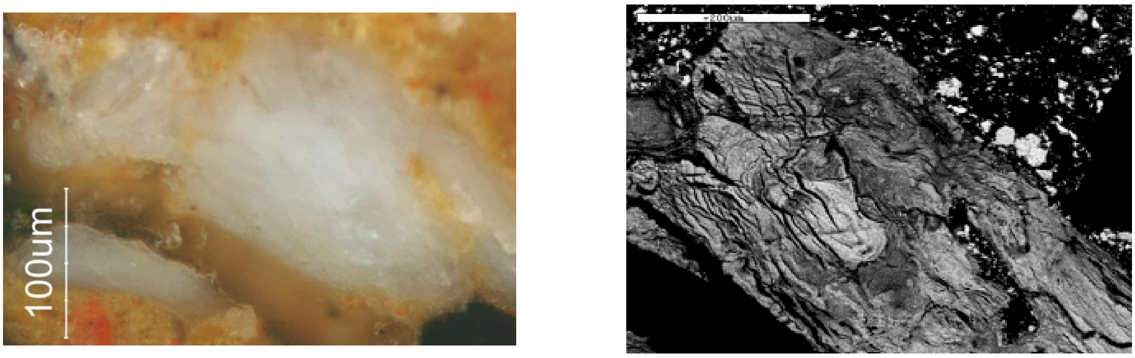


Figure 21: OM image: 200x mag. Polarized Light (right) and BSE image of the sample X13

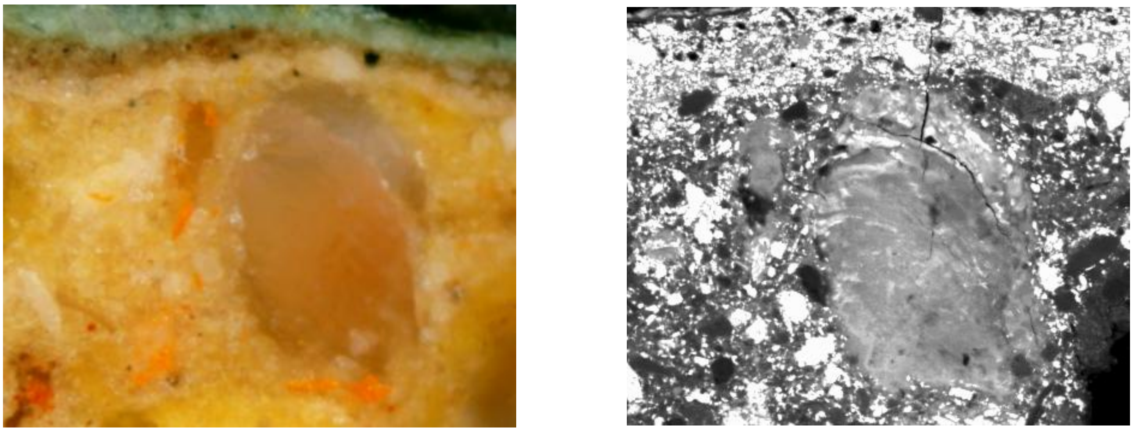


Figure 22: OM image: 200x mag. Polarized Light (right) and BSE image of the sample X10

In the BSE images of the orange aggregates (Fig. 19 and 20), it is possible to observe that these are a light-greyish large mass with dark-grey cracks. The bright and strongly scattering particles inside and around the aggregates correspond to the orange particles (red lead) seen in the visible light image. Tiny highly scattering particles around the soap mass on the Figure 20 seems to indicate the occurrence of dissolution of the pigment.

The white aggregate (Fig. 21) presents a lamellar structure: it has cracks, and it seems to have a high degree of remineralisation. The areas that strongly scattering indicates a higher lead density, which can indicate the presence of lead carbonate (precipitation bands) rather than lead carboxylates [30,31].

The transparent aggregate does not have an evident well-defined structure like the others aggregates (Fig. 22). According to Boon et all., saponified areas appear darker in the backscatter image than intact leads white due to their higher organic content and minor mineral fraction [31]. Therefore, it can be concluded that the grey amorphous area visible on the BSE image (Fig.22) is a lead soap with a lower lead carbonate content. This information is in accordance with the µ-Raman analysis of this sample, where only peaks associated with lead and none for carbonate were detected (Fig.18).

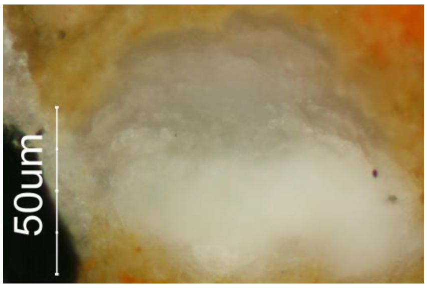


Figure 23: OM image: 500x mag. Vis-light - Polarized Light (right) of the sample X7

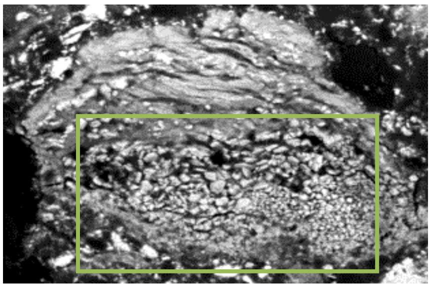


Figure 24: BSE image of the sample X7

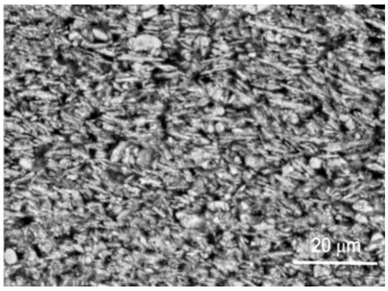


Figure 25. Image from: Keune,K., Van Loon, A. & Boon, J. 2011 [O]. BSE oil paint reconstruction with lead white

The BSE image of the white aggregate in Figure 24, shows rounded particles in the aggregate. By comparison with BSE images of intact white lead (not saponified) in the literature (Fig.25) [O], it is possible to see that the images are similar. Therefore, it is supposed that these particles are intact white lead which have not reacted with free fatty acids to form a soap. In other words, only a partial reaction has occurred.

Through the SEM-EDX mapping it was possible to conclude that lead is in fact the only metal inside the aggregate, and that the amount of lead is higher in the aggregate than the areas around (see appendix VII.2, Fig.29 and 30).

To summarise: it was not possible to determine the source of lead compounds in the aggregates since the layer where they originate has both white and red lead presented. However, the aggregates are always in the first layer of ground, and this is the only layer with minium present. However, it should be noted that other paintings exhibit lead soap aggregates in layers with lead white only, so minimum is unlikely to be the only factor in their formation in this painting. What remains to be seen is the difference in amount of oil binder in the two layers, since aggregation may be influenced by a higher binder to pigment ratio. Another factor to consider, is the possibility that paint layering plays a role, and that fatty acids were introduced to the bottom layer when the top layer was applied-feeding the system to create lead soap aggregates in the bottom layer. According to Keune, the concentrations of the reactive components could play a very important role: in a layer with excess of metal and lack of fatty acids the paint is not affected, while with a medium rich layer (excess of reactive monocarboxylic acids) a metal soap aggregate system can develop [15].

Red particles (minium) are often observed and identified in lead soap aggregates [15,23,32]. The presence of the minium crystal inside the soap mass raises discussion and questions. It has been suggested that minium inside or around lead soap aggregates is original mineral matter present as drier or pigment, or, alternatively, it is formed as part of the lead soap formation process [15]. In the case of *João Luiz Lourenço* the minium seems to be original matter, since unreacted red lead particles remain distributed through the ground.

The phenomenon of aggregation of metal carboxylates, despite being intensively studied by other researchers, is still not fully understood. Therefore, despite all the studies performed and the careful characterization done, many questions are left unanswered. In this painting the aggregates are visually different, but no explanation of the reasons for this difference is currently available.

The main questions focus on the mechanism of formation of the aggregates that are present in this painting:

1) Are we seeing two distinct mechanisms of aggregate formation? Is red lead the source of lead in the case of white aggregates with minium surrounding, and white lead pigment the source of lead in the case of the white aggregates?

2) Or are we seeing two different states of evolution of a single type of aggregate? At first minium reacts with fatty acids, dissolution occurs, and then it starts to form the aggregate (resulting in aggregates with orange particles around and white inside). At a later stage, the minium is all dissolved and what results is the larger white aggregate where remineralisation inside the aggregate from lead soap into lead carbonate takes place.

Dr Jaap Boon and Dr Katrien Keune[9] were consulted regarding these questions, and kindly responded with detailed information on the phenomena observed. Dr Keune suggested that the latter proposal might be more likely but both concurred that the mechanism for aggregate formation is still unclear.

During the painting's treatment, water/moisture was necessary to remove lining adhesive, and to apply and remove a facing, as well moisture treatments were required to relax the severe distortions. For future comparison and research, and to monitor the possible effects of moisture, a section of the painting was photographed through the microscope with a Dino-eye (Microscope Eye-Piece Camera) and a micro-scale (see Fig. 31, appendix VII.3).

In addition, a new development for future investigations of lead soap aggregates was explored using a very high resolution digital camera and Photoshop (appendix VIII.1), in an attempt to document (mapping) the distribution of the protrusions at the surface of the painting. Should a correlation between colour areas and the quantity of protrusions be made, this could point to a relationship between the oil content of the upper layers of paint and protrusions, demonstrating a possible source of fatty acids for the formation of aggregates. Alternatively, to test the hypothesis that moisture/water is a contributing factor, the distribution could show correlation to known areas of water damage/exposure. Although promising, the initial results demonstrated that imaging the protrusions is a complex process, beyond the scope of this thesis (see appendix VII, Fig.32-34).

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[9] Dr Boon and Dr Keune are both involved in the Science4Arts Programme (NWO: Netherlands Organisation for Scientific Research), in a project to research metal soap aggregation in oil paintings, their input is very much appreciated.

Chapter 4: Treatment Options: evaluating conservation materials and methods

4.1 Treatment options

All conservation treatments must be designed and developed according to the characteristics of the painting, the materials present, its particular conservation problems and the environment the painting will be exposed to after treatment. No treatment should be applied without a methodical examination of the artwork and a detailed and appropriate treatment plan. After a careful examination and characterization of *João Luiz Lourenço,* a treatment procedure was designed incorporating the following: consolidation of loose paint; facing; removal of the stretcher and the lining canvas; strip-lining and looming; removal of the lining adhesive; removal of the facing and facing adhesive; treatment of deformations; tear repair; lining; varnishing (isolation layer); infilling; varnish removal; and final varnishing. The painting presented conservation problems whose treatment involved some non-traditional approaches. For example: several researchers involved on the study of lead soap aggregates in oil paintings speculate that temperature and moisture can influence their occurrence and/or development. Therefore, both factors were avoided where possible or were minimized and controlled during treatment. In addition, an exploration of facing adhesives, including a non-traditional non-aqueous material was instituted, and great care was taken to establish the most suitable de-lining and re-lining methods. Future environmental exposure was considered[10] in the choice of both lining adhesive and infilling material for the extensive losses. The following details the steps taken to explore treatment options in each step.

4.2 Facing adhesives and facing tissues

Loose or fragile paint can be protected with a facing to hold the paint/ground composite in place during treatment, storage or transport [35]. Facing involves adhering a thin flexible tissue (e.g. Japanese tissue paper) to the surface [9]. A facing adhesive should ensure a good adhesion between the paper and the painting, but at the same be compatible with the painting and be easily removed. It is not necessarily the same adhesive used for paint consolidation [35].

The following facing adhesives were explored: cyclododecane, sodium carboxymethyl cellulose (CMC), and cellulose, 2-hydroxypropyl ether (Klucel E).

Whereas the two cellulose derivatives are well characterised [36], the newest material is cyclododecane (CDD). It is a saturated cyclic alkane - $C_{12}H_{24}$ [37-39], which was synthesised in Zurich in 1926 by Leopold Ruzicka [37]. Its introduction in the conservation field occurred around 1995 [38]. Since then, CDD has been increasingly used in conservation as a temporary consolidant, binding medium, adhesive or support material [38,39]. CDD is a white crystalline solid with a slight odour, which has a melting point of 58° to 61°C [37,39]. When heated the molten CDD conforms to any surface and solidifies at room temperature in a hard crystalline layer [38]. With exposition to air, CCD will completely sublime and disappears [38]. As a non-aqueous reversible facing for short-term use, this material seemed promising [37, 38]. The sublimation time depends on the room temperature, the thickness of the CDD layer and its access to air [38]. CDD can be applied by spraying, melting and as a solution[11](dissolved in non-polar aromatic solvents). All three application methods were explored over oil paint surfaces, plain canvas and on glass slides (the later to evaluate any possible residue left after sublimation). Observations were also supported with OM. Molten CDD was extremely difficult to apply with a brush because it hardens extremely quickly and it was impossible to obtain an even film. CDD in solvent solution was slightly easier to manage, but still presented difficulties. These observations are also reported in the literature: CDD does not form a homogeneous film; rather it coalesces into needle-like crystals [39]. In contrast, CDD as a spray (commercially supplied) was very easy to apply in a homogenous film. Experiences with the CDD are further detailed in Appendix X.1.1. In summary, although the CDD offered good surface conformation and possibly ample time before sublimation, the films formed were extremely brittle. It was feared that this material would not therefore protect the paint/ground composite during the anticipated action of scraping lining adhesive off the back of the canvas, since it could detach the paint surface as pressure was applied.

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[10] The future environment of the painting is not controlled, then this will be subject to RH and temperature fluctuations (see Appendix IX).

A 3cm x 4cm squares of Klucel E and CMC (3 and 5% solution) were applied through facing paper on the margin of the painting, 24 hours later the adhesive strength was tested by attempting to peel the dry tissue off the paint to evaluate resistance. Then removability was tested using a cotton swab moistened with water. Both tests gave reasonable results, however in application Klucel E adhesive was very runny (with low surface tension), indicating that it could easily introduce too much moisture in the paint/ground of canvas during in application. Both CMC solutions in water form a gel (limiting penetration into the painting) and both provided good adhesion (peel strength) [36]. CMC produces a reasonably strong bond; it has a neutral pH and good reversibility even on aging [40]. The paint surface was visibly unaffected by application and removal. For removal the 3% gel required less water and was therefore chosen for the facing.

Two facing papers were considered, one thin[12] and one thicker[13]. Rectangles (3cm x 4cm) of each tissue were applied with the 3% CMC solution (Fig.37, appendix X.1.2) and allowed to fully dry. The thicker tissue was chosen since the thinner tissue left more fibres on the surface after removal than the thicker one. The thick tissue still provided good conformation to all deformations (Fig.38, Appendix X).

4.3 Methods to remove the lining adhesive

Because of the extreme distortions in the surface of the painting, the removal of the lining adhesive was challenging. Lining adhesives are generally removed mechanically using dry or moist methods. However, in both cases the application of some pressure is required. Support for an aged embrittled paint/ground composite is usually supplied by placing the painting face-down on a solid surface. The rigid deformations (some projecting between 2-3 cm from plane) kept the paint composite from being evenly supported. The ideal solution would be to reduce the deformations (to obtain a flat surface) before the lining adhesive removal. Unfortunately, the use of moisture, required for flattening the canvas, would reactivate the lining adhesive likely making it even more difficult to remove, and the presence of the lining canvas and adhesive was likely to severely restrict the movement of the painting making it impossible to restore it to plane. Thus, treatment options were explored involving the creation of a solid support moulded to the profile of the distortions. This would allow sufficient pressure to remove the adhesive from the original canvas without risk to the painting (see Fig. 26).

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[11] See suppliers (appendix XII)

[12] Tengucho 5 gram Japanese Kozo spider tissue from Pel. made from long Kozo fibres which are both light and strong

[13] Filmoplast J; NESCHEN Documents; 8.5 g/m2 thin, transparent technical Japanese paper; raw fibre: 100% Manila fibre

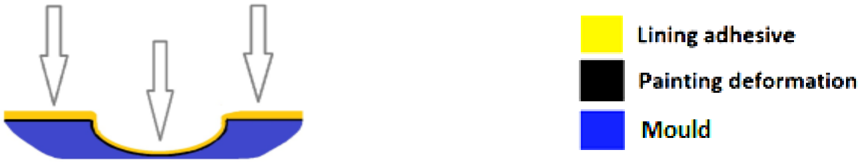

Figure 26: Diagram illustrating the concept of the system developed to remove the lining adhesive involving the creation of a solid mould to allow pressure needed during this procedure.

A range of materials were tested to create the mould: various types of paper with CMC (carboxymethyl cellulose); two types of plaster of Paris strips; silicone moulding material, “Pate A Bois” (paper maché), plasticine; agar (acid alginate) and powdered eraser. After extensive explorations, attempts to form a complete mould of the painting were eventually abandoned as impractical, and a system to support distortions locally during lining adhesive removal was adopted. Powdered eraser (appendix XII) covered with a flexible plastic film (kitchen wrap or “cling film”) formed the best confirmation and support and could be adjusted to the different sizes and shapes of the deformations.

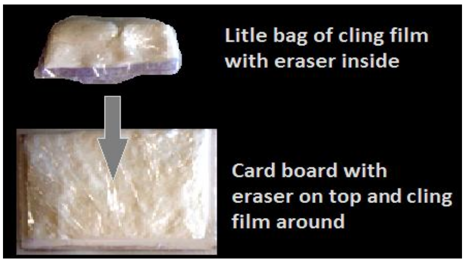
Litle bag of cling film with eraser inside
Card board with eraser on top and cling film around

Figure 27: two systems developed for moulds. The lower one is a card with powder eraser inside wrapped in clingfilm. The top is powder eraser wrapped in clingfilm and is more flexible than the previous one. These two moulds were used in combination to create a support with a shape well adapted to the deformation.

Two methods were chosen to remove the lining adhesive. In areas where the glue had been attacked by insects and mould and did not form a continuous film, it was possible to scrape the glue particles off using a small dental spatula followed by brushing the powdered glue into a vacuum cleaner nozzle held above the surface. In other areas, where the adhesive had been wet, it had formed a tough concreted mass. Scraping was very slow and involved too much pressure. Therefore, an exploration was carried out of various methods (appendix X.2) to introduce moisture to swell and soften the animal glue and starch-based adhesive to allow it to be removed by gentle scraping. Starch and the animal glue swell (without dissolving) when in contact with water [10]. Dissolution of the adhesive was not desirable as it could drive the adhesive further into the original canvas threads[14] and risk further water damage and paint loss. The preferred method was to use a system of moistened blotters (detailed in the Appendix X.2).

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[14] The removal of the lining adhesive with hot water was tested on a portion of the lining canvas after removal, but appeared to result in saturating the fabric as anticipated.

4.4 Choosing an appropriate infill material

Missing areas of paint and ground require “infilling” prior to reintegrating the losses with colour matched to the surrounding paint, to provide stability to the whole system. Infilling with a bulky material (e.g. putty) supplies a replacement to missing underlayers of paint and ground and brings the lacuna in plane with the picture as well as matching the painting’s surface texture. The choice of materials must be made carefully, based on the most appropriate material for each painting (appendix X.4). The final appearance of the painting, including the success of the retouching, will depend on this step. Fillers consist of an inert material and a binder. The binder may be a natural or synthetic material. There are also ready-made commercial fillers in use that were not tested in this thesis since their exact chemical composition and aging characteristics is unknown. According to Scheneider (1981), the materials used as a putty should match the physical and chemical characteristics of the ground layer and be sympathetic to the movement within the support [41]. The most common inert materials used as fillers are: chalk (calcium carbonate, $CaCO_3$) and gypsum (calcium sulphate, $CaSO_4.2H_2O$). Since the ground layer in *João Luiz Lourenço* contains chalk, calcium carbonate was chosen for the filler tests. Laura Lopez, notes that calcium carbonate has greater fineness and uniformity of grain (size and shape) than calcium sulphate [42]. Two qualities of chalk were explored (nº1&2) (see appendix XII). The chalk was added to the binders until reaching the desired consistency.

The recipes, details about the materials chosen (table nº2, appendix X.3) and a table of results (nº1, appendix X.3). Suppliers are in appendix XII.

Concerning the binder, a literature research was performed and two groups were studied:

- animal based: gelatine, isinglass and rabbit skin glue (RSG)
- synthetic resin: Mowiol 4-88 (polyvinyl alcohol - PVAL)

The recipe for a gelatine/chalk filler was from the Hamilton Kerr Institute (University of Cambridge, England[15]). Two private conservators provided isinglass’ recipes after a question has been placed on Conservation DistList: an interdisciplinary forum for conservators[16].

The fillers were applied on both linen fabric and Polyester film (Melinex). Since the majority of the losses in *João Luiz Lourenço* include both paint and ground, leaving bare fabric exposed, it was important to test the behaviour of the different materials in direct contact with canvas. Both supports were also used to observe the formation of cracks or shrinkage after the filler dried (see Figs. 28 and 29). The fillers were also applied to losses created in a "model painting" (supplied by Dr. Carlyle).

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[15] provided to Dr. Leslie Carlyle, personal communication Mary Kempski, and Renate Woodhuysen-Keller.

[16] http://cool.conservation-us.org/byform/mailing-lists/cdl/

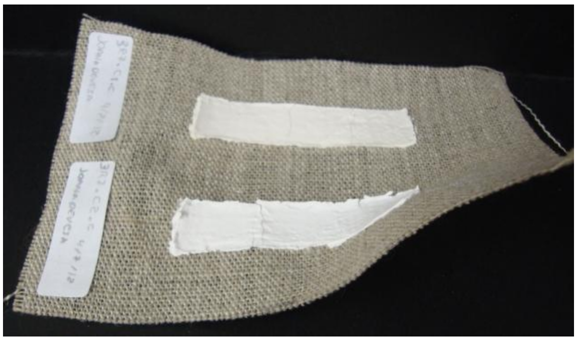

Figure 28: Rabbit ski glue filler on canvas. This was the filler that presented the greatest deformation upon drying.

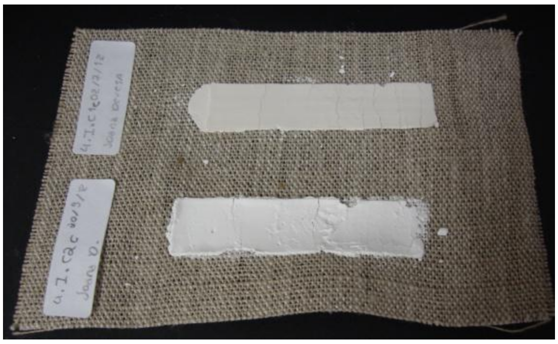

Figure 29: Isinglass filler. The largest deformation is associated with chalk nº2. The side of the canvas where chalk nº1 was applied was not deformed.

Results and discussion of filler evaluation

Concerning the binders, isinglass (10%), gelatine (nº2) and Mowiol (PVAL) (see table nº2, appendix X.3) were the best to work with and they presented less problems than the RSG after drying (Fig.28) i.e, fewer cracks, and a less shrinkage (judged by the degree of deformation in the Melinex sheet and the canvas support). Their characteristics also seem to be the most suitable for the thin fills required for this painting. However, all have advantages and disadvantages. Traditional glue-based fillers have compatibility with the original painting's materials and according to Laura Lopez they have "optimal elasticity and strength, good adhesion and proper cohesion" [42]. They are also easily reversible. Their drawbacks are well known: animal glues are easily attacked by fungi, bacteria and insects and their properties change with changes in relative humidity (RH) [7]. Beyond this, as observed during the tests, glue-based fillers have short working times and the viscosity increases during cooling, making them difficult to handle without significant experience. In comparison: gelatine showed some deformation due to contraction upon drying, but like isinglass, it was easy to apply and control. Isinglass was more flexible, exhibited less deformation due to shrinkage and is reported to be less reactive to changes in RH[17] compared with gelatine, however it is very expensive (fig.29).

Mowiol, the trademark of a polyvinyl alcohol emulsion (PVAL) is, according to Horrie, very stable to ultraviolet/oxygen ageing as chain scission occurs very slowly [36]. However, it may become insoluble, by the formation of ether cross-links, on light ageing or heating [36]. PVAL cross links with many metallic salts, some of which are used as pigments [36]. Also in slightly acid or alkaline conditions the chains will cross-link and become insoluble [36]. Another drawback is that PVAL is hygroscopic and will absorb water vapour, above 75% relative humidity [36]. Horrie assumes that treatments with Mowiol are irreversible. However, the irreversibility of this binder is not a concern nor a determining factor in the case of fillers for paintings since do not cover original paint and can be removed from lacunae mechanically, thus their irreversibility with solvents need not be an issue.

After this exploration, 10% isinglass in water appeared to be the most appropriate binder for the fills required by this particular painting as it is very good to work with, easy to apply and control. The working time is shorter than the Mowiol but still reasonable and longer than gelatine and RSG. In addition it is not necessary to keep the solution warm during use. Fillers with 10% isinglass did not contract significantly or form obvious drying cracks (like the RSG fillers) and as noted above it is reported to be more stable to HR fluctuations. Of the two types of calcium carbonate used, chalk nº1 seemed to be more suitable for filling on *João Luiz Lourenço*. In general, it presented less problems after drying.

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[17] Information given by one of the private conservators that provided one of the isinglass recipes.

4.5 Investigating and choosing the re-lining technique

Lining is a process where a secondary canvas support is attached to the original. Nowadays, lining is avoided and alternatives to this treatment tend to be chosen. However, this painting had been severely distorted and after local flattening treatments the distortions exhibited a tendency to return. Since it had already been lined in the past, a new lining, in an effort to stabilise this behaviour, appeared to be the best alternative.

The most common adhesives used for lining in the past can be divided into two groups: water-based glues and wax/resin mixtures [43]. Both methods have advantages but also drawbacks such as: the use of high temperatures and pressure, also in the case of water-based glues, the introduction of excessive moisture and in the case of wax-resins, the irreversible impregnation of the lining adhesive in the paint composite.

Alternative lining systems utilising low pressure, no heat and synthetic glues have been developed and used. One example, developed by Mehra in 1970, is known as “cold lining”. It was further developed at Stichting Restauratie Atelier Limburg (SRAL) in Maastricht ,Netherlands by Jos van Och. This is called *Mist-Lining* [43,44]. The name *Mist-Lining* is associated with the spray application of the adhesive to the lining canvas.

The advantages of *Mist-Lining* are:

- Minimal use of adhesive to obtain the required bond and strength [44]. This technique does not require the impregnation of the adhesive but involves only a superficial attachment of the lining canvas to the original canvas [43].
- Elimination of moisture during the process [44]. The adhesive on the lining canvas is left to dry for 24 hours before lining and is reactivated using solvents. *Mist-Lining* requires only a small amount of solvent to reactivate the adhesive (it is crucial that the glue layer is sufficiently ‘open’ to be regenerated easily with solvent vapours) [43].
- Use of low pressure [44].

The *Mist-Lining* method involves the use of Plextol, an acrylic dispersion adhesive. It is an aqueous emulsion of a thermoplastic acrylic polymer [44]. Och uses a mixture of two dispersions: Plextol K360 and Plextol D540 to which is added another thermoplastic acrylic polymer dispersion, the thickener - Acrylic Rohagit SD 15. Plextol K360 is based on 2-Ethyl hexylacrylate in a concentration of approx. 60% [45]. Plextol D540 is based on methyl methacrylate and ethylacrylate with a concentration of approx. 50% [46]. The thickener Acrylic Rohagit SD 15, is based on methacrylic acid and ethylacrylate (concentration approx. 30%) [47]. Plextol K360 has a glass transition temperature (tg) around -31°C and Plextol D540 about 29°C [45,46]. Since tg is an accurate indication the polymer’s softness [36]; Plextol K360 is soft and flexible whereas Plextol D540 is a harder material.

Plextol films are reported to be chemically stable and non-responsive to fluctuations in relative humidity [44]. They have a high surface tension and therefore penetration into the lining canvas during application is minimal, and spray application ensures virtually no penetration [44]. This property enhances removal of the lining canvas, by peeling or by regenerating the adhesive with solvents [44].

Mist-Lining can be adapted to each painting, because there are many variables that can be adjusted according to requirements, as for example: the use of different types of lining canvas and different adhesive mixtures (different ratios of the two dispersions) and the conditions for regenerating the adhesive (e.g. solvent type and amount) [43].

Because it does not require moisture and heat, and due to its stability and easy reversibility (because the adhesive does not impregnate the original materials), this method was identified as the best choice for relining *João Luiz Lourenço*. Thus, *Mist lining* process was tested with three variations using an untreated lined canvas with similar characteristics to the original. The aim of the tests were to find the best procedure and to evaluate the following properties: Details of the tests are found in Appendix X.4.

- the adhesive strength and flexibility based on peel strength by hand and comparative flexibility: two glue formulations were prepared using different ratios of Plextol K360 and Plextol D540;
- the different behaviour of the method using a single layer application or two glue layers;
- the ease of execution of this lining method;
- the role of an interleaf[18]: Two different types were tested: white polyester canvas and Reemay sheet (appendix XII);
- the solvent needed to regenerate the adhesive and the quantity.

Observations and Results:

After the experiments some preliminary conclusions were taken:

- Without an interleaf the lined canvas was flatter and it was possible to get a stronger bond. In contrast the interleaf maintained more of the original texture and deformations.
- Two different formulations were tested: Plextol K360/Plextol D540 (70%/30%) and Plextol K360/Plextol D540 (60%/40%): The higher amount of Plextol D540 (the harder material) made it possible to achieve a stiffer and less flexible adhesive, which provided stronger peel strength /peel resistance (most evident where there was no interleaf).
- The interleaf adhered better to the polyester lining canvas in comparison to the lined canvas. The reactivation of the adhesive is made through the back of the lining canvas, and perhaps not all of the solvent reached the lined canvas. For some linings, this could be a good feature.

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[18] An interleaf is thought to improve lining stiffness. This option was considered for *João Luiz Lourenço* because it could resist the return of the persistent deformations [48]. The interleaf allows the transfer of tensile stress away from the painting [48].

In the case of *João Luiz Lourenço* the objective is to reduce the response of the painting when exposed to RH fluctuations and to restrict its ability to deform. For this reason, a strong lining adhesive is preferred, forming a strong bond between the original and the lining to hold the painting flat. Consequently, the formulation Plextol K360/Plextol D540 (60%/40%) and the exclusion an interleaf seems to be the most suitable choice for lining this particular painting.

Although the experiment has been performed successfully, more tests will be needed before lining the painting.

Chapter 5: Treatment Report

5.1 Consolidation

Consolidation is the strengthening of one material with another, usually with the use of a liquid, the consolidant, that infuses and sets to form a strong phase within a weak substrate [9].

As noted, *João Luiz Lourenço*, required consolidation to re-attach and secure flaking paint/ground primarily at the edges of the many previous losses. Because of its high tack and strength BEVA 371 was chosen. It is a synthetic resin mixture forming a thermoplastic adhesive[19] based on ethyl vinyl acetate developed by Gustave Berger [49]. It is non-aqueous, translucent to transparent, and is non-staining [8, 50]. It comes as a white opaque gel and can be further diluted by the following solvents: Naphtha, petroleum benzene, acetone, alcohol and toluene [42, 49]. According to Berger the main advantages of BEVA371 are: strength, elasticity/flexibility, relatively free of cold flow, activation after drying (it is applied cold and activated with a temperature between 65-70ºC) and reversibility (it is reversible with heat and/or solvent). It does not exhibit dimensional changes (expansion or contraction) [8,9,50].

A dilute solution of BEVA371 in white spirit (1:1) was used in areas where the original canvas was not adhered to the lining canvas (isolation of the two was achieved with silicone coated Melinex between). Where the two canvas were adhered a more viscous solution was used in to avoid penetration of the adhesive which could interfere with the de-lining later on. The operation was performed under a magnifying glass with a ring light (Fig.30). BEVA 371 diluted in white spirit was introduced under paint islands with a fine brush (Winsor & Netwon No.00). Silicone coated Melinex was placed over the consolidated areas, and heat was introduced with a hot spatula (about 60°C). During cooling light weights were positioned over the consolidated areas while the adhesive cooled and set.

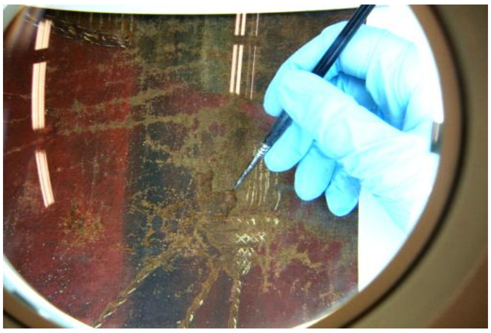

Figure 30: Consolidation being performed under a magnifying glass with a ring light.

5.2 Facing

The treatment of the painting involved the removal of the stretcher, lining canvas and its adhesive. To secure and protect the paint layer during this treatment the painting was faced with Carboxymethylcellulose (CMC, 3% in distilled water) which was applied with a brush through 15cmx15cm squares of tissue (see testing: 4.2).[20] Squares of tissue were applied such that they formed in a *bridge* between stable and less stable areas, and were alternated wet/dry to provide dry areas surrounding the wet to reduce deformations (Fig.31). At the edges, where the painting was no longer attached to the lining the facing tissue was adhered to wood planks to keep the edges stable as the facing dried[21] (Fig. 32 & 33).

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[19] The original formula includes: 60% toluene and Naphta, 40% of two Ethylene vinyl acetate copolymers (Elvax150 resin and Allied A-C Copolymer), and Cyclohexanone resin (BASF Laprapol K80), Phthalate ester of hidroabietyl alcohol (Hercules' Cellolyn 21) [51, 52].

[20] The gel used was 3% prepared with 300ml water to 9 grams of CMC.

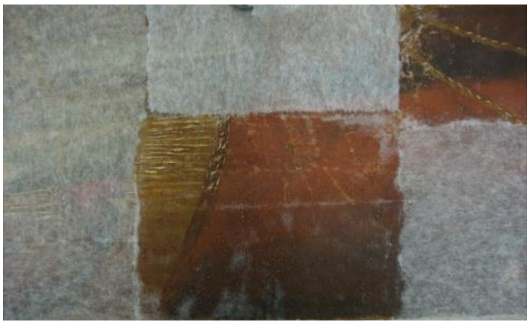

Figure 31: Squares of tissue were applied alternately wet/dry.

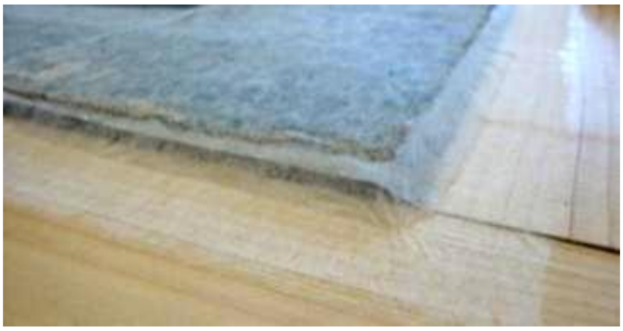

Figure 32: facing tissue was adhered to wood planks.

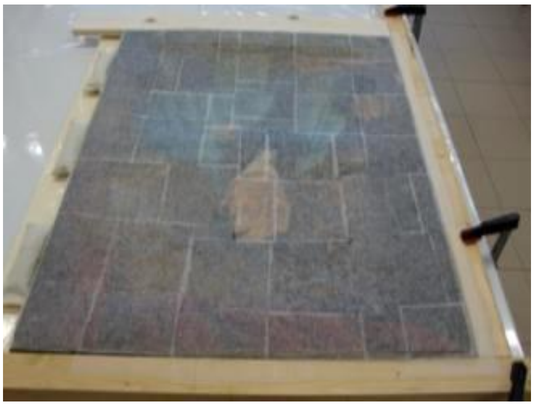

Figure 33: Painting with the facing.

5.3 Removal of stretcher and lining canvas

To remove the stretcher and the lining canvas the painting was laid face down on cushioning material to accommodate and provide some support to the severe out of plane distortions.[22] The lining canvas was gently pulled away from the stretcher along the tacking margins, and the stretcher lifted out (Fig.53-55, appendix XI.1). After removing the stretcher, a surface cleaning of the lining canvas with a soft brush and a vacuum cleaner was performed. The canvas was extremely dirty (Figs. 56 & 57, appendix XI.1).

To facilitate lining canvas' removal from the painting, this was cut off where it was no longer adhered to the original canvas along the outside edges. Then the lining canvas was gently peeled back off the original fabric (Fig. 58, appendix XI.1). In some areas, where the adhesion was still strong, the glue-starch adhesive strength was reduced by placing a slightly moist blotter paper over the lining canvas for 10 minutes before attempting removal. After the lining canvas was completely removed, dust, dirt and insect debris was brushed off the back into the nozzle of a vacuum cleaner.

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[21] Thanks to the suggestion of Diana Conde.

[22] Non-woven polyester used for quilting. A thin Melinex sheet was placed on top to isolate the painting from the fibres.

5.4 Strip-lining and looming

The next step prior to flattening treatments was to place the painting under tension by attaching it to a temporary loom (wooden frame). This was accomplished using a strip lining with polyester fabric strips adhered to the back of the original canvas with BEVA 371 film[23],[24] (appendix XII). These materials have been in use for strip linings for many decades [53].

Strip Lining procedure:

Strips of 3 cm wide BEVA film were applied to polyester fabric strips with a hot spatula (around 70ºC). The strips were then adhered to the back of the painting using a hot spatula (about 60ºC). Prior to this it was necessary to remove the lining adhesive in these areas. This operation was performed with moist blotters and scraping. Once in place the strips were attached with pushpins to the loom - a pine wood frame[25] with lap join corners. Pushpins were used because they are simple to remove thus the tension applied could be easy adjusted during the flattening treatment. The orientation of the fabric on the loom and thus the relationship of the face of the painting to the loom-bars was changed according to the stage in treatment (Figs. 59 and 60, appendix XI.2).

5.5 Removal of the lining adhesive

Removing an old glue lining involves risk to the painting due to the pressure applied and the possibility of any moisture used disrupting adhesion between the ground and the canvas (e.g. allowing the size layer to swell and detach), as well, it can be very time consuming. The methods used to remove the lining adhesive are detailed in appendix X.2 and as previously noted, depended on the state of the lining adhesive. This process did not allow a complete removal of the adhesive as part of the glue had penetrated between the threads in some places. However, this system did not damage the original canvas. Removal of the glue on areas with more extreme deformation is detailed in the chapter 4.4 and was achieved by supporting the distortions underneath locally such that pressure applied during adhesive removal did not damage the paint layer (Figs. 34 and 35).

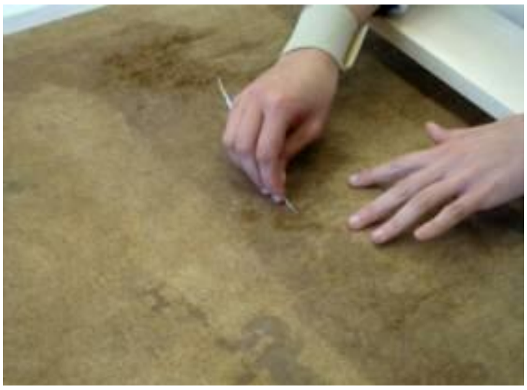
Figure 34: Removal of the glue-lining adhesive.

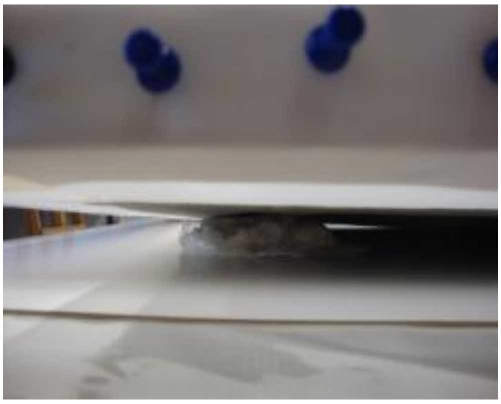
Figure 35: Mould supporting the distortions underneath.

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[23] Polyester Restoration Fabric. Polyester Restoration Fabric is a specialist fabric used for re-lining paintings. The un-dyed woven polyester is scoured and heat set and has unsurpassed dimensional stability. Information provided by: http://www.russellandchapple.co.uk

[24] BEVA 371 Film is made of pure BEVA 371 commercially prepared as a thin uniform film that can be heat activated.

[25] vertical bar: 120 x 5 x 3 cm; horizontal bar: 103 x 5 x 3 cm

5.6 Removal of facing and superficial cleaning

After the lining adhesive was removed, the facing was taken off using moistened cotton swabs (Fig.36). Excess water was rapidly absorbed with dry cotton. After removing the square tissue paper, the paint surface was cleaned with a moistened cotton swab.

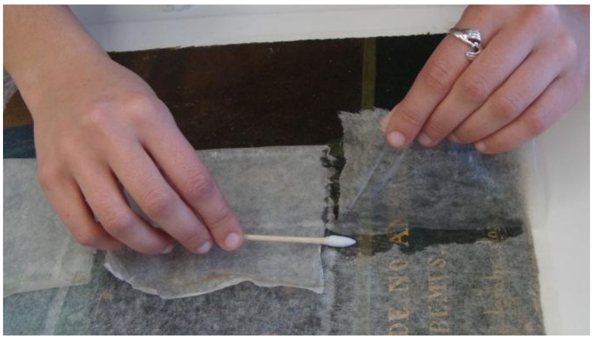

Figure 36: Removal of the facing with moistened cotton swab.

5.7 Treatment of deformations (flattening)

To restore the painting to plane, severe distortions in the original canvas were first treated locally with a system of moist blotters followed by weights. Flattening took place gradually. The moisture response of the painting had been explored during the facing application and removal and the removal of the lining adhesives, so the reactivity of the paint/ground/canvas was already well understood by this point.

The procedure was as follows (see Fig.37):

1. In order to have simultaneous access to the back and the front of the painting and to therefore treat more than one distortion at a time, the painting in its loom was lifted above the table by resting it on boxes (15 cm in high) placed at each corner. Three other lower boxes (13cm high) were covered with card and silicone-coated Melinex to provide a flat smooth surface. These were inserted underneath the painting to provide solid support during flattening.
2. Pre-conditioned[26] slightly moist blotting papers were torn[27] to size, slightly smaller than the deformation/distortion. They were attached to the top of the boxes and secured with tape, then the boxes were slid underneath the painting with the moist blotter immediately below the deformation. A piece of Melinex was placed over the paint surface to hold the moisture within the paint composite (Fig.61, appendix XIII.3).
3. The moist blotter was allowed to remain in contact with the painting until the distorted canvas or paint surface became flexible (monitored constantly with finger pressure), usually within 2-5 minutes (up to 10 minutes). Once plasticity was obtained, the blotter was removed and replace with a larger dry blotter, then mild pressure was applied over the Melinex covered distortion. Initially small lead weights were applied, followed by sand bags, and then after approximately an hour, those were replaced by large flat lead weights

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[26] Blotting paper was sprayed with distilled water then left wrapped in Melinex for 3 hours to 24 hours before use to allow complete equilibration of the moisture within each paper.

[27] The blotting paper was torn to create uneven soft edges as opposed to cutting which would result in sharp edges which could potentially transfer as lines in the painting

supported on a piece of foam-core[28] to distribute the weight. The foam-core and weights rested on top of the Melinex on top of the paint/canvas surface.

4. Where the deformations were very large, it was necessary to repeat this procedure more than once.

During this process while the painting was in a plastic state, pushpins were taken out of the loom and the strip-lining placed under additional tension. As the polyester fabric was gently pulled, it was possible to further flatten the fabric/paint tension. It was quickly established that distortions would return unless the painting was held under weights throughout this procedure.

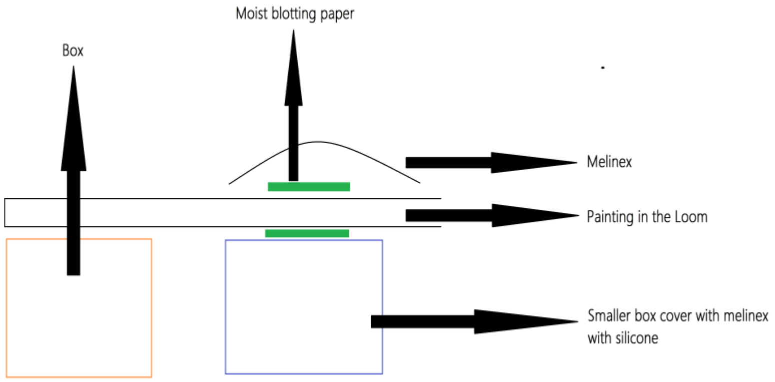

Figure 37: Diagram showing the systems used during the flattening.

After the main deformations were minimized with local flattening as above, an overall moisture treatment was performed. Two sheets of moistened blotters were placed under the painting with a Melinex sheet suspended over top (to create a moisture chamber). After two minutes the painting started to relax. The blotting papers were removed and new dry blotting papers were placed under the painting. On top (with a Melinex sheet protecting the paint surface), a series of small flat light-weight boards were placed on top and covered with weights (Fig.62, appendix XIII.3). Eventually, as the worst distortions flattened, it was possible to replace the smaller boards with three light-weight flat boards that covered the entire painting (these also had weights on top) (Fig.63, appendix XIII.3). Finally, when the deformations were reduced, a card-board (heavier than those used before) was placed on top of the painting. Above this, very uniform wooden board was used with weights on top in order to apply a heavy uniform pressure (Fig.63, appendix XIII.3). The painting was then left is under these boards and weights between flattening treatments.

After the overall treatment, some local flattening was repeated with the aim of minimizing small deformations that remained visible. However, particularly in areas with canvas only, some distinct deformations returned. Therefore another approach was needed. After discussion with Jos van Och in Maastricht[29], he suggested infusing (or resizing) the exposed canvas with a solution of isinglass in water. It was anticipated that due to a slight contraction of the isinglass in drying, the resized fabric will becomes flat and resistant to the return of the deformations.

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[28] When the heaviest weights were used, and they were place on top of a flat support (foam-core) the edges of the larger foam-core were chamfered to avoid sharp edges.

[29] Carlyle personal communication, S.R.A.L. Maastricht, Netherlands, June 2012

Two tests were performed with a 4% solution of isinglass: 0.125 g of isinglass to 5.5 ml of water[30]. The first, on piece of stretched linen canvas, the second: on the painting *João Luiz Lourenço*, in both it was applied by brush. On the linen canvas two strategies for flattening were explored: the first to apply weights while the isinglass was drying, the second using a vacuum table during the drying process. In both cases the canvas became flat and somewhat stiff, with the best results from the vacuum table. For the test on the painting the vacuum table was used. The isinglass was applied on a 2x2cm area of exposed fabric (Fig.38). To enhance air flow a sheet of non-woven fabric (Reemay) was placed immediately below the painting, with a sheet of blotting paper covering the perforated table top. The painting was covered with a thin flexible sheet of plastic (Fig.39 and appendix XII) to create the top of the vacuum system. To prevent this plastic from sticking, a sheet of silicon-coated Melinex was placed immediately above the paint surface. While under vacuum the Melinex did not conform perfectly to the surface, therefore, after approximately four hours when the fabric/isinglass was partially dry, the Melinex was removed so that the soft plastic sheet could follow the contours of the paintings surface and the areas of paint loss.

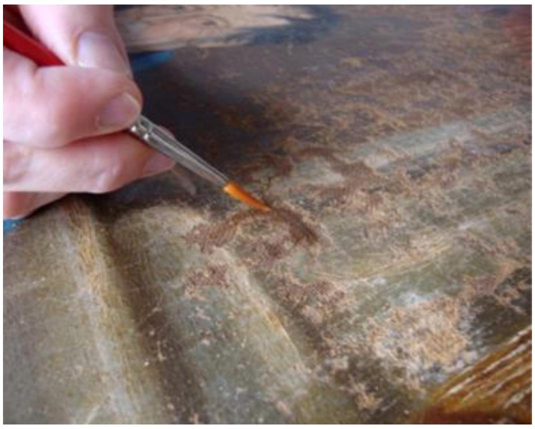

Figure 38: Isinglass being applied on canvas exposed.

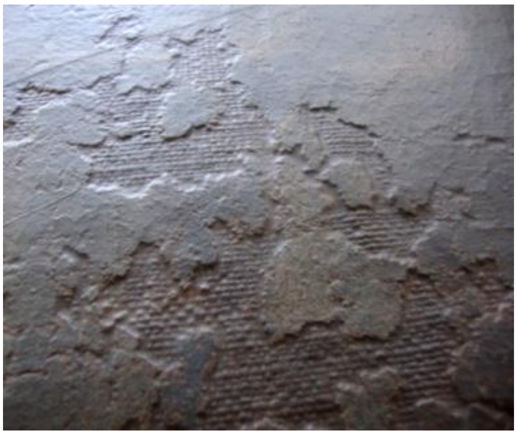

Figure 39: João Luiz Lourenço under vacuum after the isinglass has been applied with a soft plastic sheet on top.

After seven hours, the vacuum was turned off and the test area appeared completely flat; the day after it continued to remain flat. In view of this success, the same treatment was carried out on all exposed fabric in areas of loss, taking care to not to wet the area too much. The same treatment was carried out for the remaining deformations in painted areas, by applying the isinglass to the canvas on the back. In this case, a silicone-coated Melinex sheet was left over the painting during vacuum treatment to enhance flattening of the painted surfaces. Flattening was achieved after six hours of vacuum pressure (Figs. 40 and 41).

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[30] Isinglass consists of collagen derived from the swim bladder of a Russian Sturgeon [54,55]. It is easy to apply; it has low viscosity when warm enabling efficient penetration of the substrate, good cohesive forces and excellent adhesive properties; it causes no discolouration or sheen on the paint surface and it is stable to light and thermal aging and its pH is neutral [55].

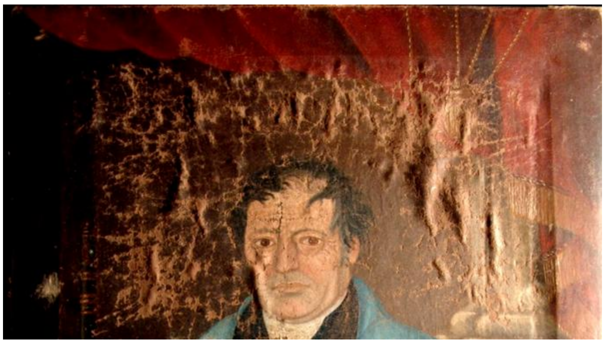

Figure 40: Before treatment, detail, raking light showing deformation.

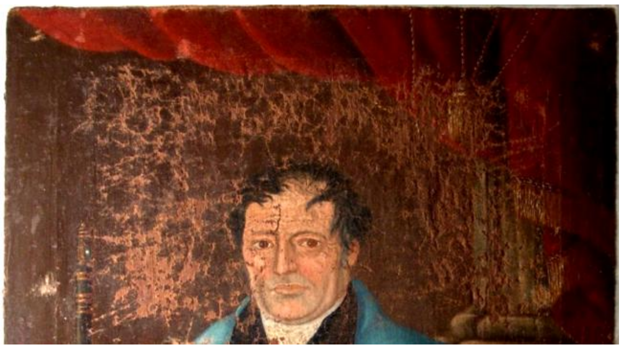

Figure 41: During treatment (after flattening), detail, raking light showing less evident deformation.

5.8 Treatment of the tear

Effective tear repairs for paintings on fabric involve ensuring that the torn threads are completely re-aligned, a delicate procedure since they are usually displaced and the edges of the tear can overlap. This was the case for the tear on *João Luiz Lourenço.* Realignment was achieved by first opening up the tear using a small raised lump of Melinex-covered plasticine placed underneath the painting immediately below the tear (Fig.42). As the painting was gently lowered over the mound of plasticine the tear opened, allowing access to the threads which, with the help of the 4% isinglass solution to increase their flexibility and to hold them in place, were successfully realigned (Fig.43). This operation was performed under a stereomicroscope.

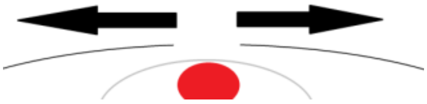

Figure 42: Diagram showing the system used to opening slightly the tear with plasticine underneath the painting.

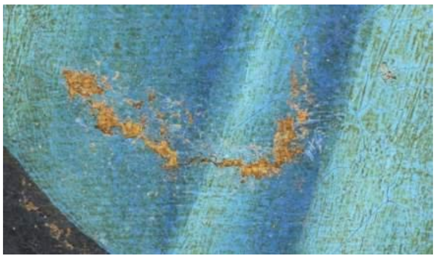

Figure 43: The tear after the realignment of the threads.

5.9 Discussion of further treatment

Given the complexity of the conservation problems presented by this painting, it was not possible to complete the treatment prior to the submission of this thesis. The remaining steps are:

To replace the current warped stretcher with a newly constructed stretcher

To re-line the painting (using the mist lining technique)
To apply an isolating varnish (likely Laropal A-81)
To fill paint/ground losses (using an isinglass/chalk mixture)
To carry out varnish removal
To apply a first coat of varnish (resin to be determined)
To inpaint losses (with Gamblin Colours).

To apply a final varnish (resin to be determined, likely Regalrez 1094[31])

To design and construct a packaging system for return of the unframed painting (such that the surface of the painting is not in contact with any wrapping material.

Conclusions

The painting presented several serious problems, and was in a very unstable state. The treatment was planned, developed and performed according to the specific characteristics of the painting, the materials present, and their state of conservation. An integrated approach was needed to relate the results of scientific investigations to the state of the painting in order to understand the causes of the deterioration and to plan an effective treatment. A further important aspect of this work, was the evaluation, using empirical investigations, of the methods and materials being considered for the treatment. In other words, the characterization of the painting's materials and the interpretation of their role in the painting's deterioration, helped to explain the conservation problems, which in turn established the order of the treatment, the methodology and the most appropriate treatment materials.

In view of this, all the treatment steps (already performed and to be performed) were designed based on:

- the significance and integrity of the painting
- the painting's original materials: the conservation and restoration materials chosen took in account compatibility with the original materials. This ensures similar behaviour under the same conditions, to avoid mismatched movements between materials within the composite, which could lead to further mechanical damage
- the degradation phenomena, for example the existence of lead carboxylates aggregates, which led to the minimization of parameters such as temperature and moisture;
- the future environment of the painting: this influenced the choice of filler and lining technique.

In the case of lead carboxylates aggregates, some moisture and heat could not be avoided as both were crucial in certain stages of the treatment. In this case, it is not known what influence and future impact these actions will have on this particular painting. For this reason, an area of the painting with aggregates protruding through the surface was documented for later comparison and research.

The severe problems this painting presented made it necessary to develop a broad understanding of treatment materials available for use in the field of conservation, and to confront the painting in a holistic way, since all actions taken and the materials used would be interdependent. It was important to always anticipate future steps while designing the treatment to avoid decisions that would compromise the next step (e.g. paint composite consolidation which could compromise de-lining). While many of the explorations undertaken during the treatment design were rejected for the final treatment, these experiences are valuable for a conservator´s overall career, as they expand their options and experience. For example, Cyclododecane (CDD) was one of the materials investigated that promised to meet specific requirements posed by the painting.

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[31] Regalrez 1094, a low molecular weight resin (LMW) has a gloss, saturation, and refractive index comparable with dammar and mastic varnishes but with added stability [56]. It consists of 100%hydrogenated oligomers of styrene and alpha-methyl styrene and is dissolved in aliphatic hydrocarbon solvents (no aromatic content) [57].

Although it proved to be too brittle for this case, it could be very useful in a future treatment, where experience with its special properties will be a great advantage. Investigations to solve the problem of removing adhesive residue from a distorted and unsupported fabric were also valuable as experience with a wide range of moulding materials was gained.

Concerning the lead soap aggregates phenomena, despite not reaching a clear understanding of the mechanism of their formation, the literature review and study of them in this painting has opened up new questions and the potential to document the phenomenon more closely. The effort to evaluate the distribution of the protrusions over the surface of the painting indicates that this is a very promising new approach which now remains to be developed.

The investigation and treatment of this painting offered the opportunity to explore new ideas and to form a better understanding of historic painting materials in context.

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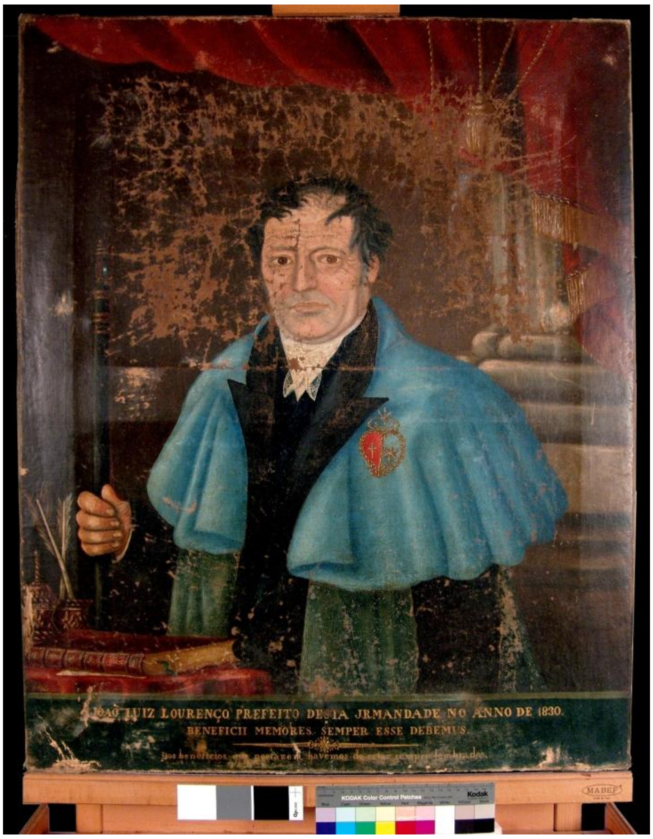
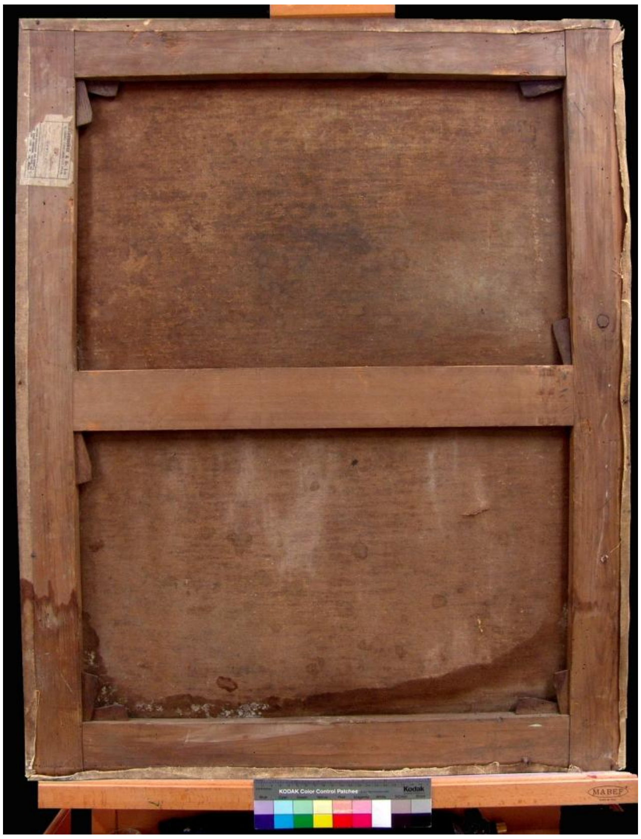
Appendices

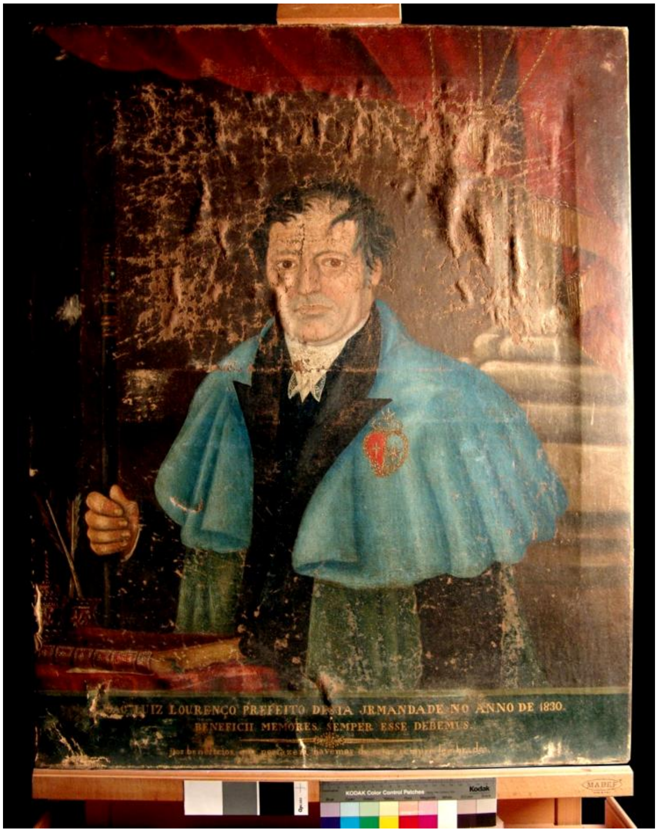
Appendix I – Before and During treatment photographs of *João Luiz Lourenço*



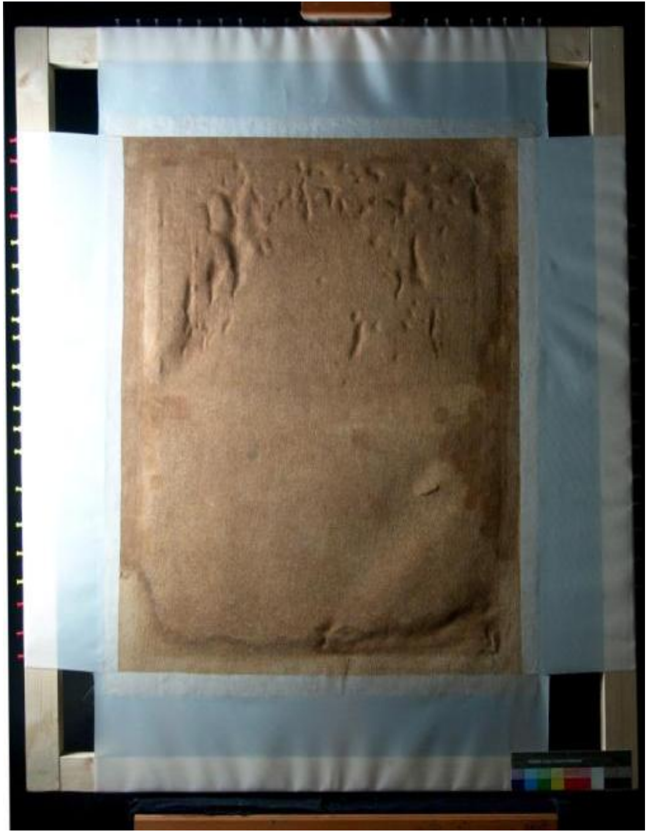
Before Treatment: Normal light, João Luiz Lourenço.



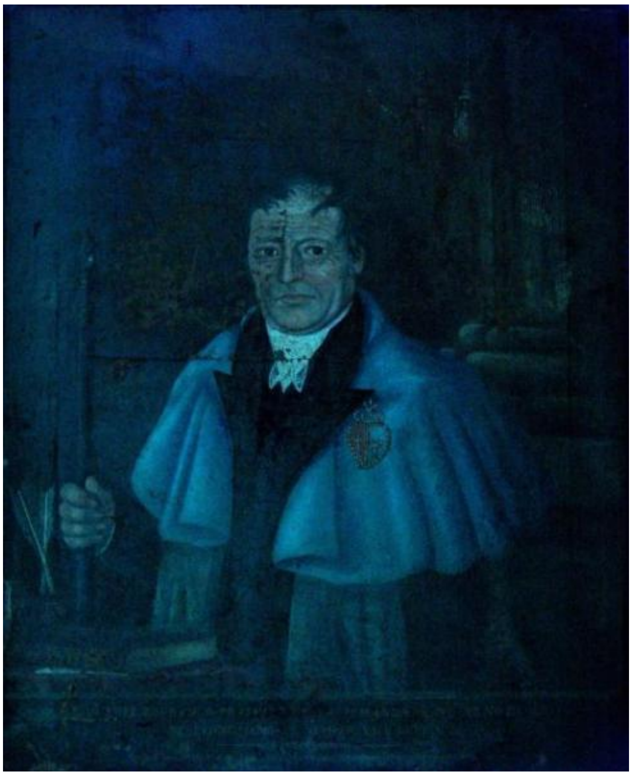
Before Treatment: Normal light back.



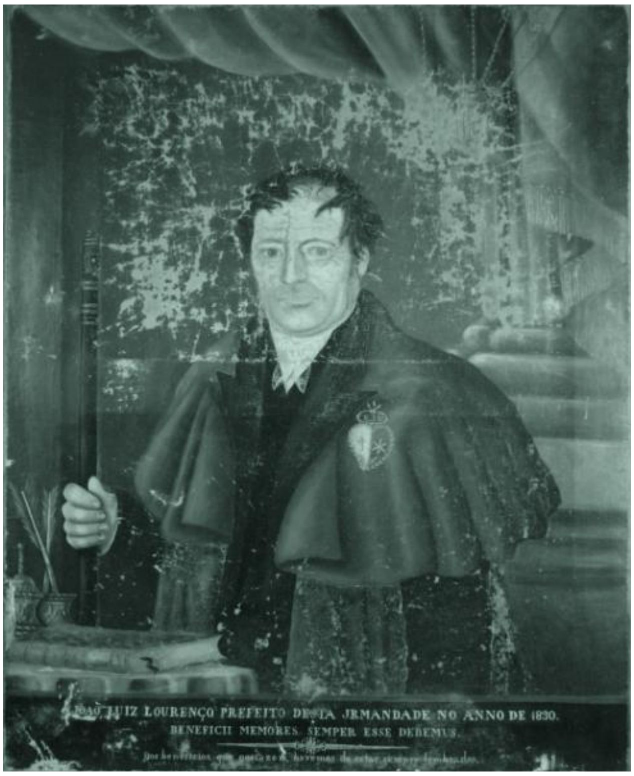
Before Treatment: Raking light photograph.



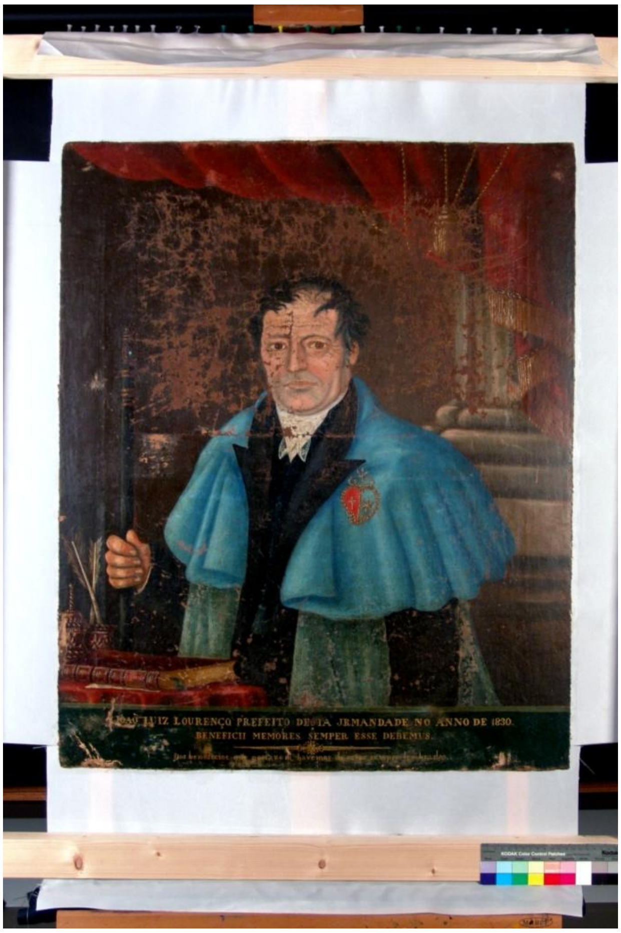
During Treatment: Raking light back, after the removal of the lining canvas, before flattening.



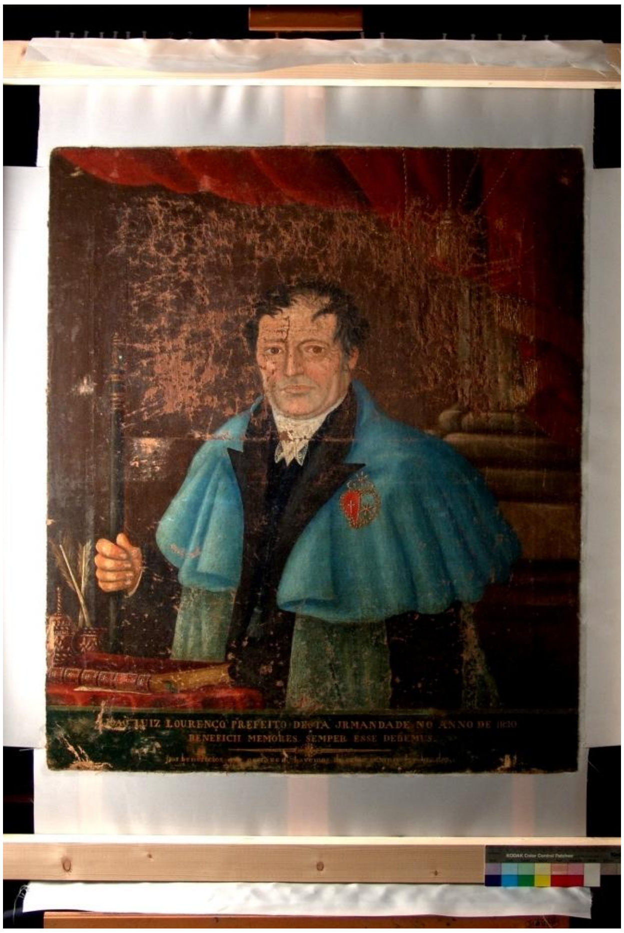
Before Treatment: Ultraviolet (UV) light


JOAO LUIZ LOURENÇO PREFEITO DESTA JRMANDADE NO ANNO DE 1830.
BENEFICII MEMORES SEMPER ESSE DEBEMUS.

Before Treatment: InfraRed (IR) light


JOAO LUIZ LOURENÇO PREFEITO DESTA JRMANDADE NO ANNO DE 1830.
BENEFICII MEMORES SEMPER ESSE DEBEMUS.

Normal light photograph of front of *João Luiz Lourenço.* During Treatment: after Flattening



Raking light photograph of front of *João Luiz Lourenço.* During Treatment: after Flattening.

Appendix II: *João Luiz Lourenço’* details photographs

II.1 Previous treatment

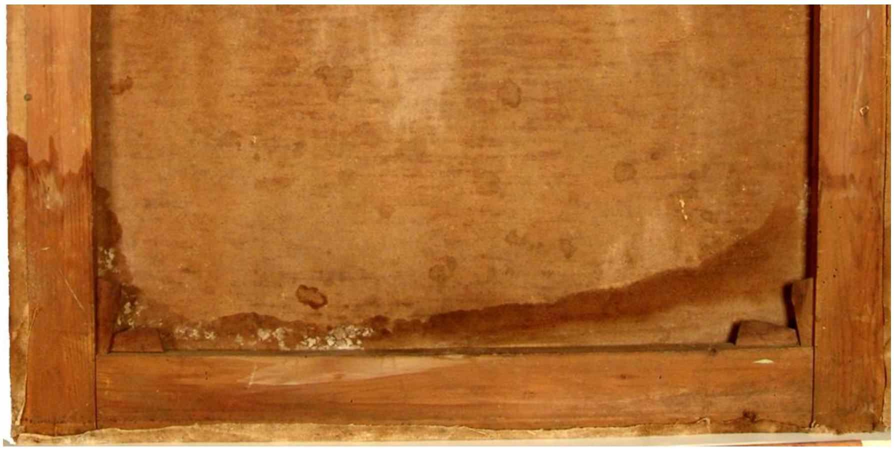


Figure 1: Signs that the painting had been in direct contact with water: dark tide line and significant spotting with dark and light areas likely due to the existence of fungi.

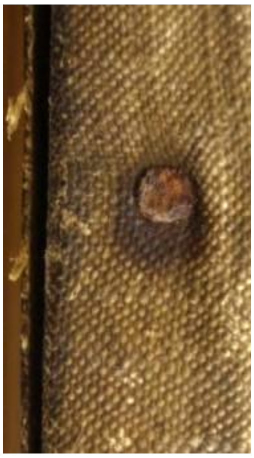


Figure 3: The tacks were in poor condition (rusted). The tacking margins of the lining fabric were deteriorated (brittle), extremely dirty, with poor attachment, in part due to the condition of the tacks.

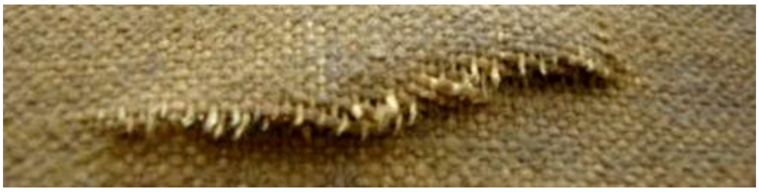


Figure 2: Small tear (4cm) through original and the lining canvas.

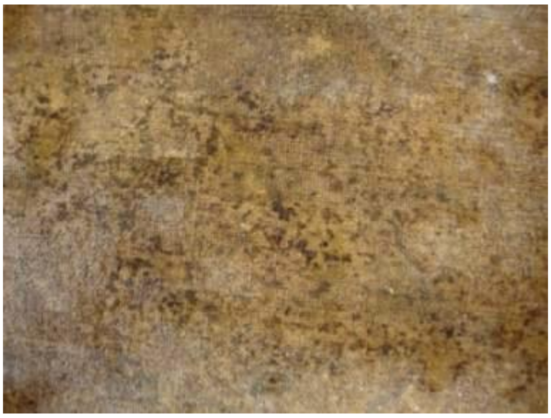


Figure 4: After removing the lining canvas, it was possible to see that the adhesive had been severely affected by microorganisms.

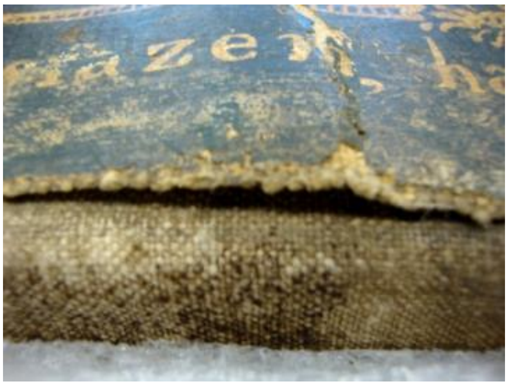


Figure 5: The adhesion between the lining and original canvas was very poor.

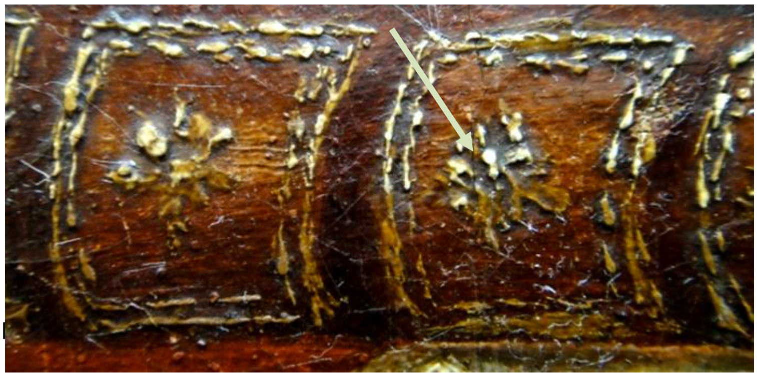
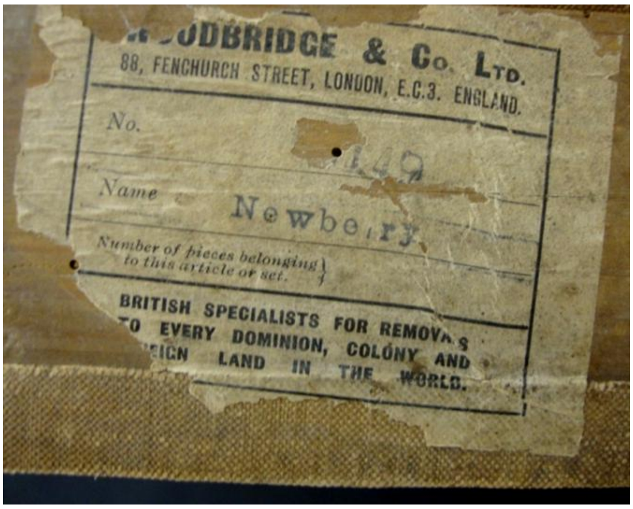


Figure 6: Flattening and loss of texture thought to be associated with the lining can be seen in the impasto.



ODBRIDGE & Co. LTD.
88, FENCHURCH STREET, LONDON, E.C.3. ENGLAND.
No. 49
Name Newberry
Number of pieces belonging to this article or set.
BRITISH SPECIALISTS FOR REMOVA S
TO EVERY DOMINION, COLONY AND
EIGN LAND IN THE WORLD.

Figure 7: Label of a British transport company, which includes the name of the family that donated the painting to Ecomuseu Municipal of Seixal. On the label can be read: "(...)ODBRIDGE & Co. LTD. 88, FENCHURCH STREETLONDON , E.C.3 ENGLAND. *No.* (...)49. Nam: Newberry. Number of pieces belonging to this article or set. }. British specialists for removals to every dominion, colony and (..) eign land in the world." .

II.3 Original support: fabric

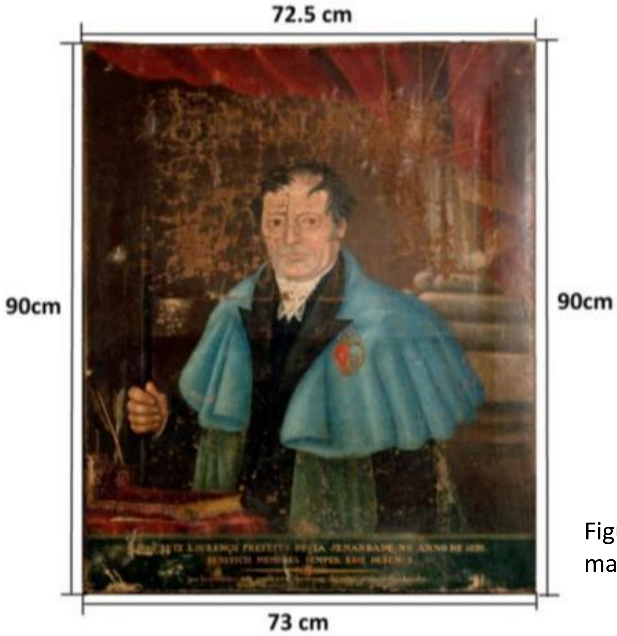
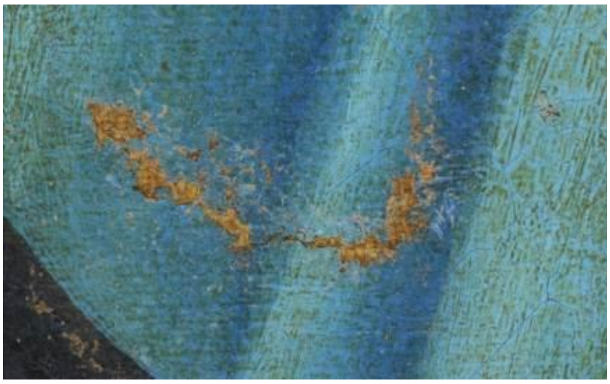


Figure 8: Measurements of the image area (tacking margins are missing).



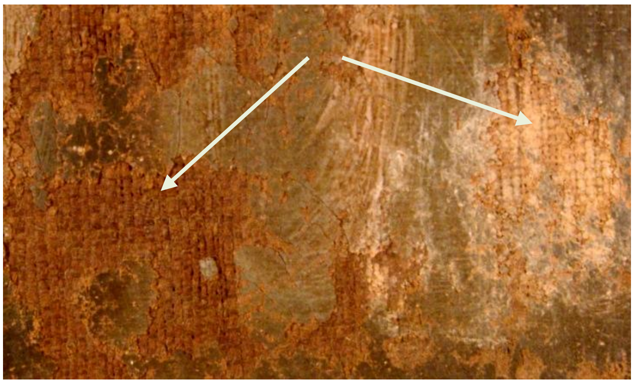


Figure 9: The tear (4cm) on the original support with loss of paint associated.

Figure 10: Difference in colour of the original canvas between old and more recent losses.

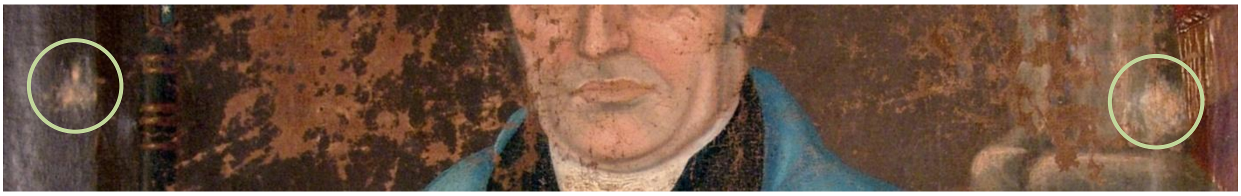


Figure 11: Damages (green circles) thought to be associated with projecting hanging hardware from another painting

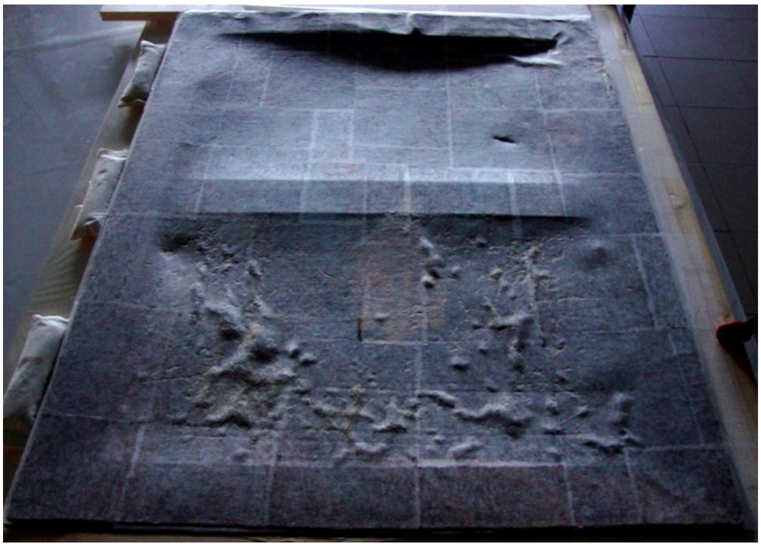


Figure 12: During treatment: After facing, raking light, demonstrating the severe distortions in the top half of the painting, and the major depression at the bottom edge (top of this image).

II.4 Sizing and Preparation Layers:

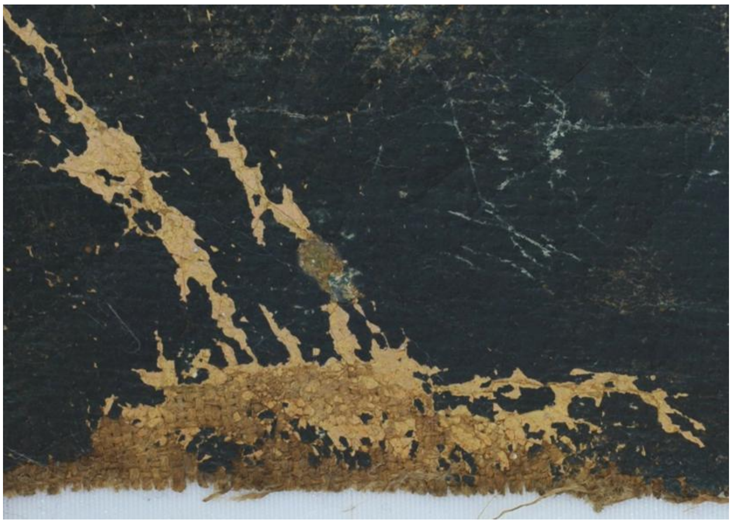


Figure 13: Loss of the paint layer on the bottom of the painting where it is possible to observe the ground layer.

II.5 Paint layering

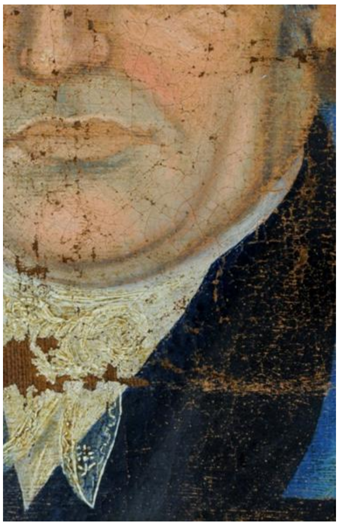


Figure 14: Abrasions on the paint surface due to mechanical damages and probably also due to over-cleaning.

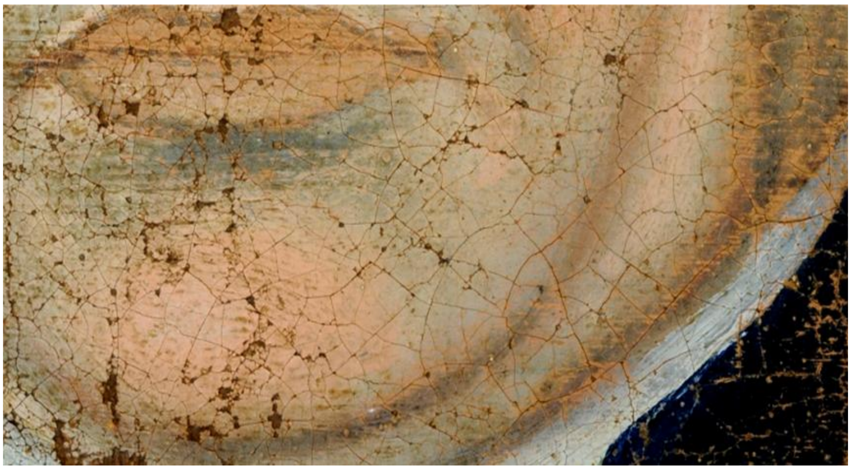
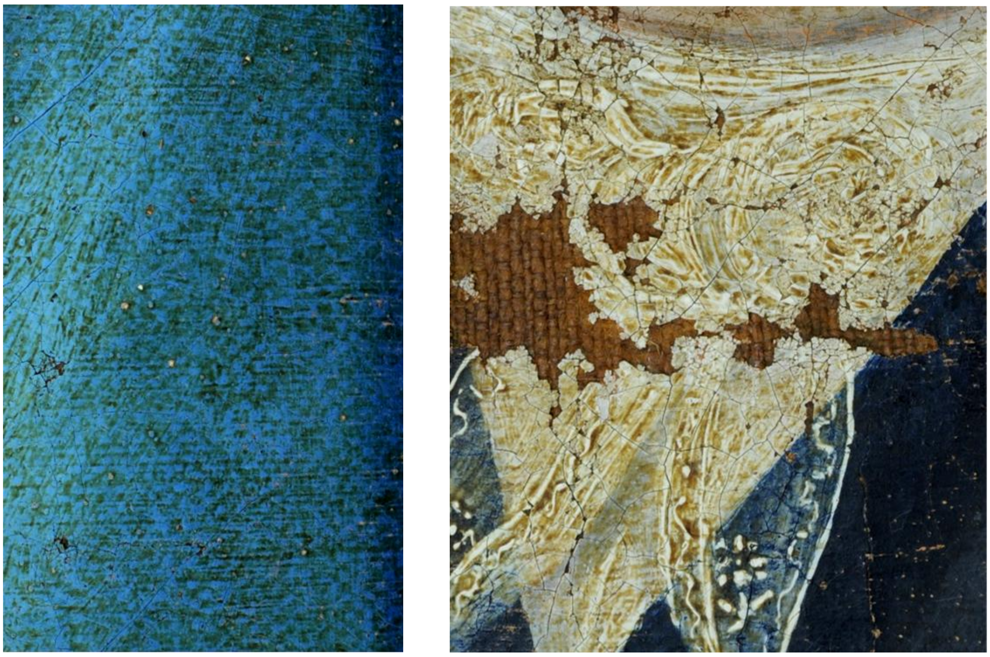


Figure 15: Mechanical cracking in the paint.

II.6 Coatings: varnish



Figures 16 and 17: Areas where it is possible to see varnish residues, significantly yellowed and degraded.

Appendix III –Description of the support and condition

III. 1 Auxiliary support: stretcher

The auxiliary support is a stretcher, measuring 74cm x 91cm (two vertical bars: 94x7x1.8 cm; two horizontal bars: 74x7x1.8 cm and a cross bar: 59.5x7x1.2 cm). Nine out of ten keys are present and they are all sound: two at each corner and one at each side of the cross bar - one upward and one downward. The missing key is in the bottom right corner. On left side, the key in the cross bar is inclined downwards in the direction of the canvas which may have caused some damage in the paint layer. The corner is a simple mortise & tenon construction with square corners. There are two nails at the top and one on the sidebar of the stretcher that are protruding and have damaged the lining canvas's tacking margins (Fig.19).

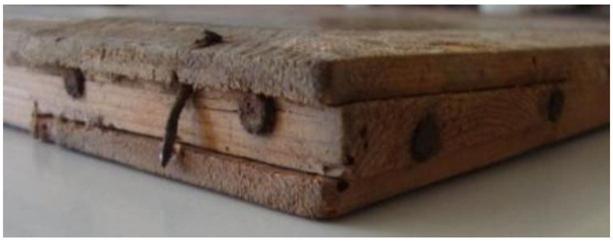


Figure 19: Corner detail: simple mortise & tenon with square corners. Protruding nail is evident.

The stretcher is in good condition overall, the wood is sound and the corners are well secured (although part of the bar is slightly protruding at each corner, a fault of this type of corner design). On the back of the stretcher, there are several small circular holes (1 mm) distributed randomly that indicate the presence of an insect infestation (no longer active), (Fig. 20). On the front, there is evidence of previous mould growth and insect infestation (carcasses from insects are present) (Fig. 21).

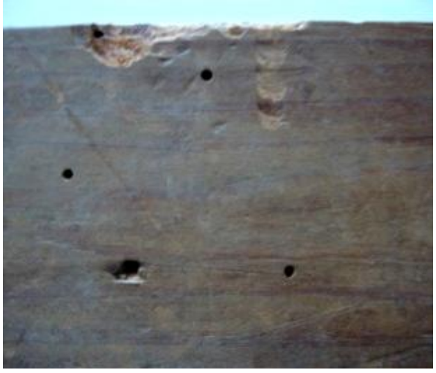


Figure 20: Exit holes from wood boring insects: small circular holes distributed randomly.

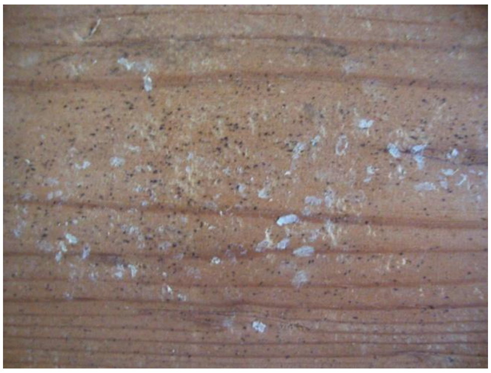


Figure 21: Signs of fungi and insect debris (carasses) on the surface of the stretcher.

As in the case of the lining canvas, the stretcher has a tide line, visible signs that this was in direct contact with water (Fig.22).

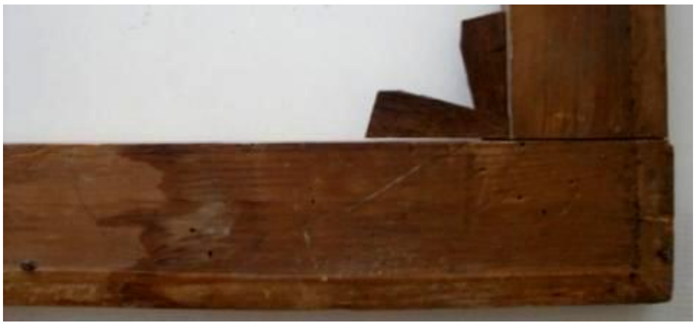
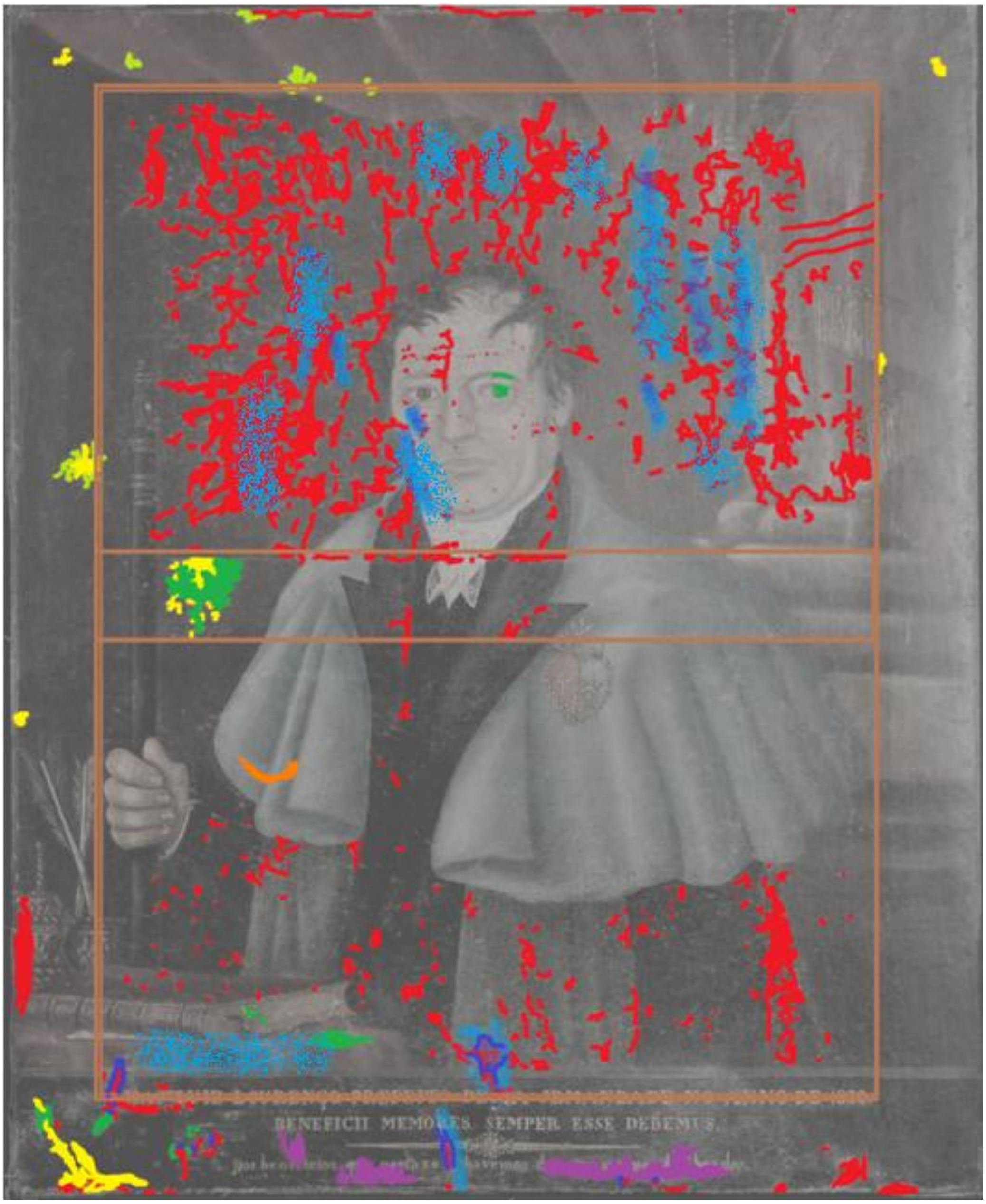


Figure 22: Tide line on the stretcher

III.2 Original support: fabric

The original fabric appeared to be in good condition, but was badly distorted. There are several different types of deformations: undulations, sharp depressions, stretcher-bar creases, and bulges (see appendix I, Before Treatment: Raking light photograph). The areas protected by the stretcher bars are significantly less damaged, probably due to the buffering effect of the wood moderating fluctuations in relative humidity and because the fabric was supported beneath by the stretcher bars (the extreme distortions in the canvas related to stretcher bar creases suggest that the painting was left in a horizontal position while in a plastic state induced by water and moisture- e.g. it was laid flat after having stood in water).

Appendix IV –Map of damages


BENEFICII MEMORES SEMPER ESSE DEBEMUS

Paint composite loss canvas exposed	🟥	**Stretcher mark**	🟫
Loss of the upper layer ground exposed	🟨	**Main deformation of fabric**	🟦
Flaking	🟩	**Tear**	🟧
Abrasion	🟦	**Blanching**	🟪

Appendix V– Fibre identification: lining and original support

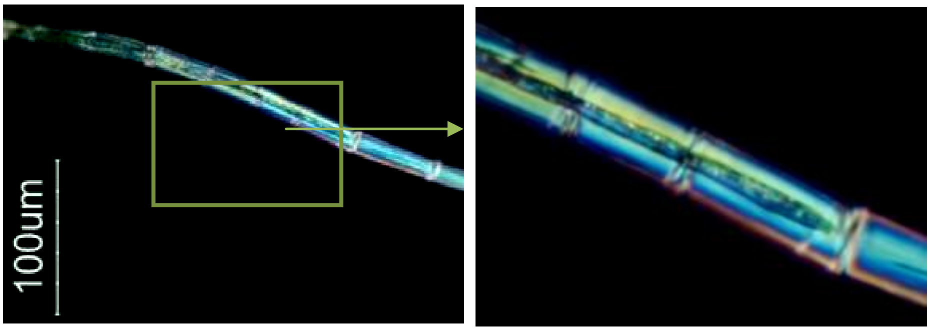


Figure 23: Longitudinal view of a fibre from the lining canvas under OM: dark field, total magnification 200x. On the left is a detail where it is possible to see the dislocations on the cell wall of the fibre.

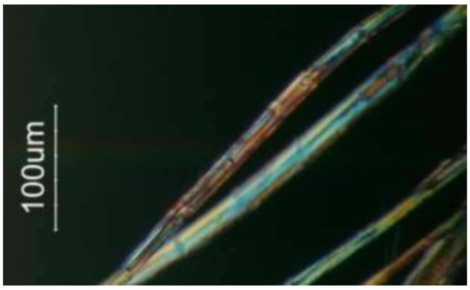


Figure 24: Longitudinal view of a fibre from the original canvas under OM: dark field, total magnification 200x.

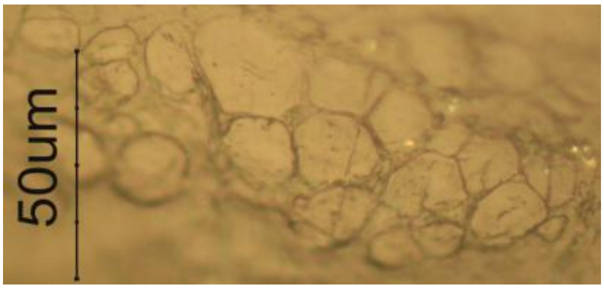


Figure 25: Transverse view of a fibre from the original canvas under OM: bright field, total magnification 500x.

Appendix VI: Lining adhesive: **Iodine test and observation of a sample with and with Polarized Light Microscopy**

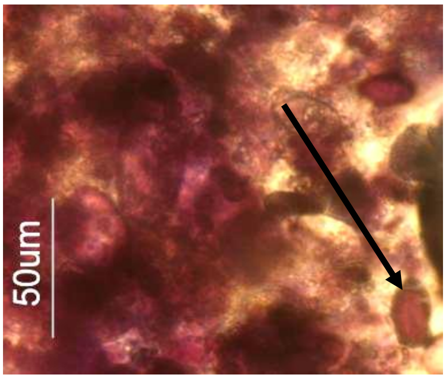


Figure 26: OM image of the lining adhesive stained with iodine solution. The purple colour indicates the presence of starch [11]. This image shows the particular shape of the starch [12] - total magnification 500x, plane polarized light

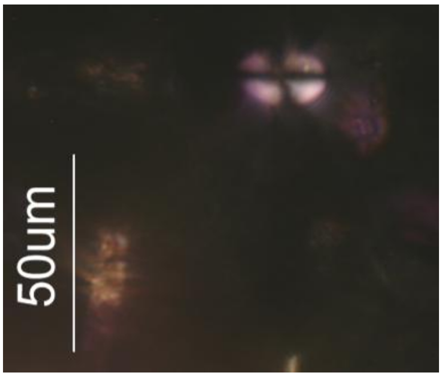


Figure 27: OM image from another area of the sample showing a centred extinction cross characteristic of starch under crossed polarized light [12] - total magnification 500x.

Appendix VII: Characterisation and documentation of Lead soap aggregates

VII.1: Introduction: Lead soap aggregates in oil paintings

Drying oils are natural vegetable oils consisting of triglycerides that chemical dry by a number of different mechanisms that occurring simultaneously to form a hard film [14,15,22,58]. As the oil ages, degradation reactions of the oil network occurs leading to the formation of low molecular weight breakdown products, for example, among others, free fatty acids [14,15,58]. This process results in a polyanionic network [14]. It was expected that this would lead to a complete failure of the paint, but, as Boon explains, this does not happen because paintings have a *self-repair mechanism* in which these fatty acid groups are stabilised by metals ions (such as lead, originating from the pigment or a drier) [15,23,27,32]. Free fatty acids migrate to the lead pigment surface to react and the formation of lead soaps occurs [31]. The metallic ions and the fatty acids form metal carboxylates - metal soaps. Conversion of the fatty acids into the lead carboxylate anion is thermodynamically favoured [30]. Lead soap formation is vital for the stability of oil paintings and is assumed to happen in all the paintings that contain lead and oil [23]. The formation of metal soaps is not dependent on the pigment alone, but is determined by the availability of free monocarboxylic acids from the binder [23]. When more free fatty acids are available more metal soaps are formed and an area around the metal-containing pigment develops [23]. The release of fatty acids can occur during hydrolysis of oil paint or also later on because of environmental exposure and acidification [32]. Hydrolysis is a normal process in an aged oil paint, but its degree is not the same for every painting, or even in all layers [23]. The availability and release of these fatty acids depends on the original paint composition, the build-up of the layers, and the conservation history and history of environmental exposure of the painting [23].

Frequently, but not always, metal carboxylates aggregate and change volume, sometimes to the point of protruding through the surface. K. Keune states that local high concentrations of lead soaps in the paint film may act as a nucleation point and lead to aggregation [15, 27]. The critical concentration of lead soaps in a matrix to form aggregates is still unknown. As noted by Boon, Hoogland and Keune lead soaps are dispersed as separate entities in the paint system and they are organise like liquid crystals [27,32]. At higher temperatures these chains are disorganised, becoming more flexible [27,32]. This flexibility of metal soaps allows a potential movement in and between paint layers [27]. Therefore, these usually do not remain in place: they migrate or diffuse within the paint system, which is semi-permeable [31]. This ability to move may be the reason why metal soaps tend to form aggregates in paintings that appear to grow as time progress [32]. It is also proposed that lead soaps aggregate/migrate when there is no further interaction with the mineral matter [15]. As a drying oil paint film ages the degree of cross-linking increases, and as oxygen becomes incorporated into the film and degradation reactions occur, the polarity increases [30]. Thus, the aggregates formation might be linked to the increasing incompatibility between the oil matrix and more mobile components such as free fatty acids and lead carboxylates causing a phase separation [27, 30].

Often, a heterogeneous structure with lamellar bands (enriched in lead) is seen in the centre of aggregates [23,31]. The striations are interpreted as precipitation bands of a new lead compound - lead carbonate [31]. It is assumed that the lead soaps formed react with atmospheric carbon dioxide (CO_2), the carbonate source [15,28]. It seems likely that the lead carbonate associated with the inclusions forms via the lead soaps, because of the lamellar structure seen in some of the larger inclusions, which suggests that it is 'precipitating' from the lead carboxylate [U].Mineralization processes might be beneficial because it can stabilize the system [15,23,32,27]. However, these fatty acid-rich hydrophobic regions are a potential sink for more free fatty acids that separate out of the less hydrophobic anionic oil network [15].

There is some speculation about why some paintings have metal soap aggregates and others not. One hypothesis, suggested by some researchers, is that aggregates can form due to exposure of the painting to high temperatures and/or humidity [27]. Moisture and high temperature are two factors, which promote the hydrolysis of the oil, therefore releasing fatty acids that can react with the lead based pigment and originate soaps [15]. However, this is not the only factor since the role of the metal is probably also important [15]. It is know that pigments like lead oxide and lead white encourage the de-esterification of the paint, which can explain why metal soap inclusions are seen in layers that contain these pigments [15,25].

Specific characteristics of metal soap aggregates dependent on the paint composition, so this implies that many aspects determine or influence their formation [15].

As yet, the mechanism of metal carboxylate's formation into aggregates is not understood, and basic questions remain such as the time in the life of the painting when they form, and their rate of formation. A scheme has been suggested by J. Boon[1] which describes the development of lead soap aggregates in lead white-containing paint[32]. See the illustrations from Boon in Fig. 28. 1., the lead white particles react with free fatty acids and the resulting lead soaps are dispersed in the paint layer; 2.-4., as the lead soaps aggregate and grow in volume, they can break up the overlying paint layer and protrude through the surface of the painting; 4., during and after aggregation, remineralisation is thought to take place inside the aggregate [14].

Lead soap aggregates have been found in many oil paintings without any geographic or temporal relationship and they are now understood to be a widespread phenomenon in paintings [15,23].

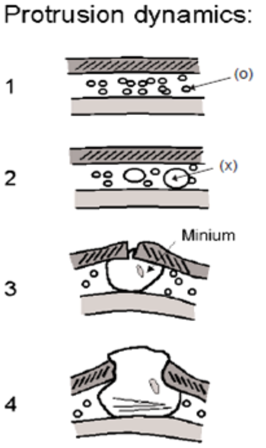


Figure 28: Diagram from Boon[1]: schematic diagram of protrusion formation in ground/intermediate paint layers.

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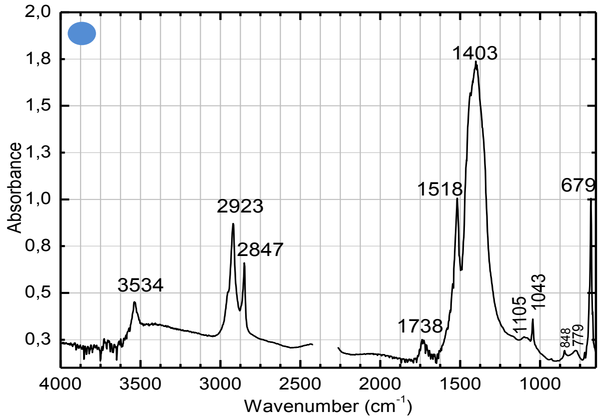
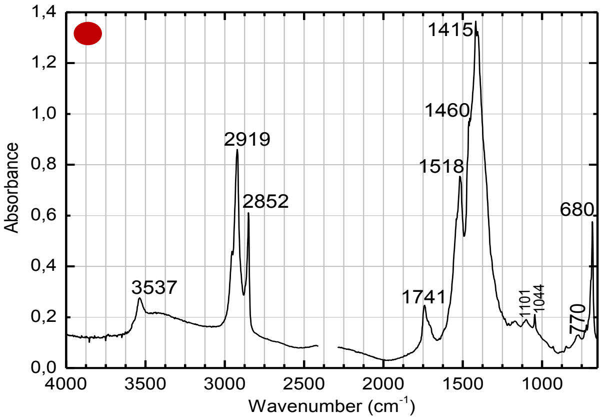
[32] Boon, J. J., van der Weerd, J., Keune, K., Noble, P., Wadum, J., 2002, Mechanical and chemical changes in old master paintings: dissolution, metal soap formation and remineralization processes in lead pigmented ground/intermediate paint layers of 17th century paintings'. In *ICOM Committee for Conservation, 13th Triennial Meeting, Rio de Janeiro, Preprints,* ed. R. Vontobel, James and James: 401- 406.

VII.2: Lead soap aggregates in *João Luiz Lourenço*: analyses

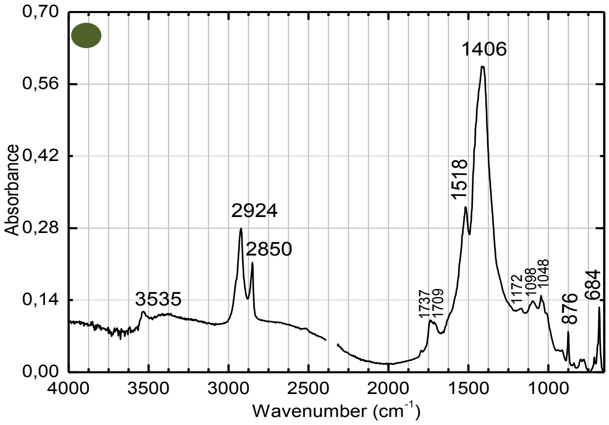
µ-FTIR spectra



IR Spectrum of a lead soap aggregate on a blue area (sample F1).



IR Spectrum of a lead soap aggregate on a red area (sample F2).



IR Spectrum of a lead soap aggregate on a green area (sample F3).

Wavenumber (cm^{-1}) **Average**	Vibration associated
3534-3537	ν O-H
1738-1741	ν(C-O)
1518	**ν_{as} (COO$^-$)**
1403-1415	**ν_s (COO$^-$) and ν_{as} (CO_3^{2-})**
1043-1048	ν (CO_3^{2-})
848-876	δ_{as}(CO_3^{2-})
679-684	δ_{as}(CO_3^{2-})

IR absorption peaks for Lead soap aggregates

SEM-EDX Mapping

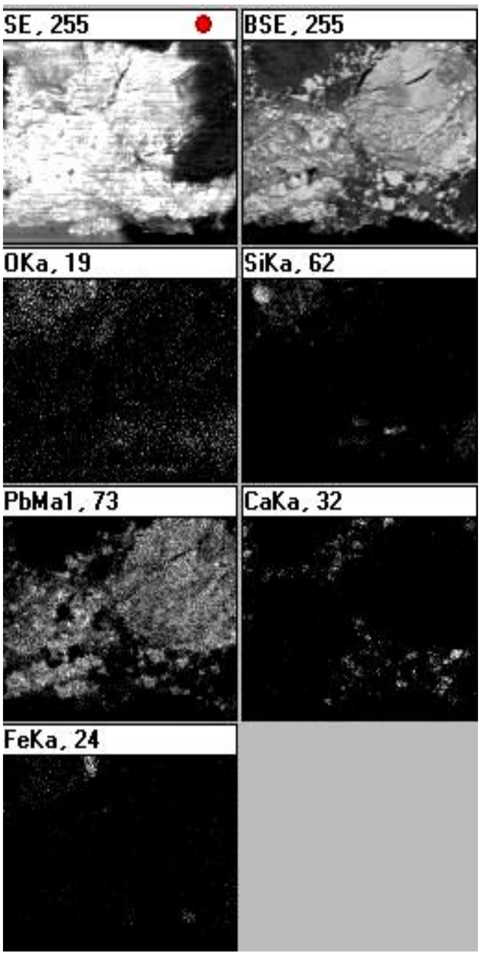

SE, 255
BSE, 255
OKa, 19
SiKa, 62
PbMa1, 73
CaKa, 32
FeKa, 24

Figure 29: SEM-EDX mapping of the sample

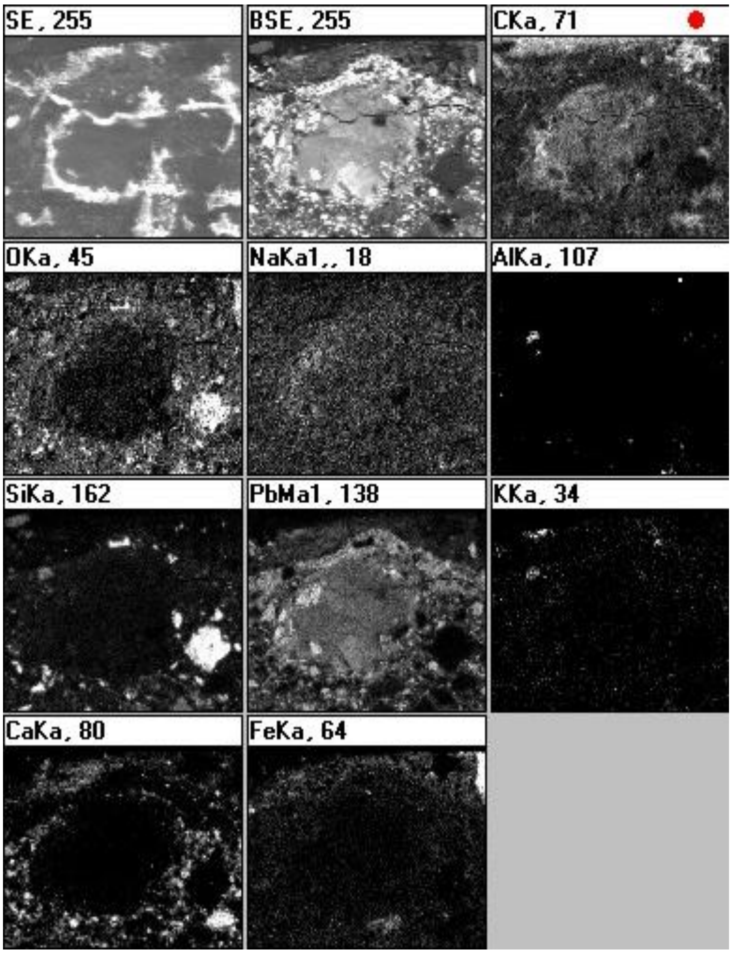

SE, 255
BSE, 255
CKa, 71
OKa, 45
NaKa1,, 18
AlKa, 107
SiKa, 162
PbMa1, 138
KKa, 34
CaKa, 80
FeKa, 64

Figure 30: SEM-EDX mapping of the sample X15

The SEM-EDX mapping show that lead is the only metal inside the aggregates, and that its amount is higher than in the surrounding area. The amount of carbon is also higher inside the lead carboxylate aggregate. The mapping also demonstrates the distribution of elements such as oxygen, silica, calcium, carbon, sodium, aluminium, potassium and iron present around lead soap aggregates.

VII.3: Lead soap aggregates documentation

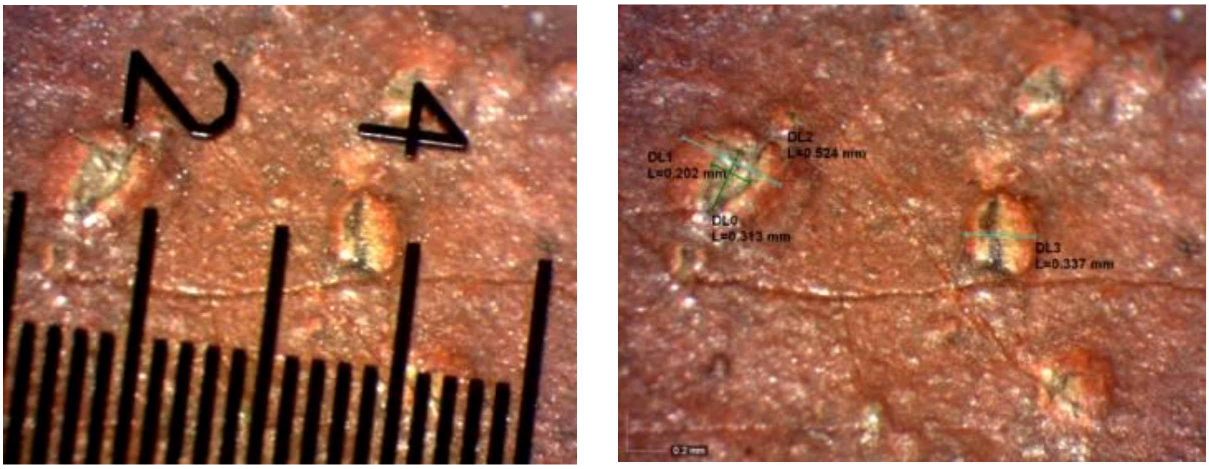

2
4
DL1
L=0.202 mm
DL2
L=0.524 mm
DL0
L=0.313 mm
DL3
L=0.337 mm
0.2 mm

Figure 31a: Paint surface imaged with a Dino-eye Microscope Eye-Piece Camera with a micro-scale, Figure 31b: Protrusion dimensions illustrated using the Dino-eye software.

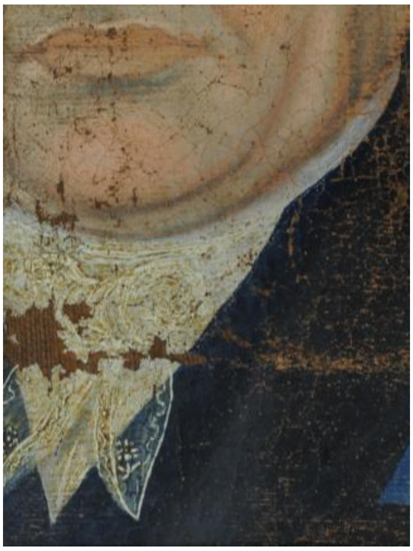


Figure 32: Initial efforts to document the distribution of the protrusions at the surface of the painting. Problems with discriminating lead soap protrusions from other surface defects was encountered, so that imaging did not provide exclusive evidence of lead soaps for the mapping desired.

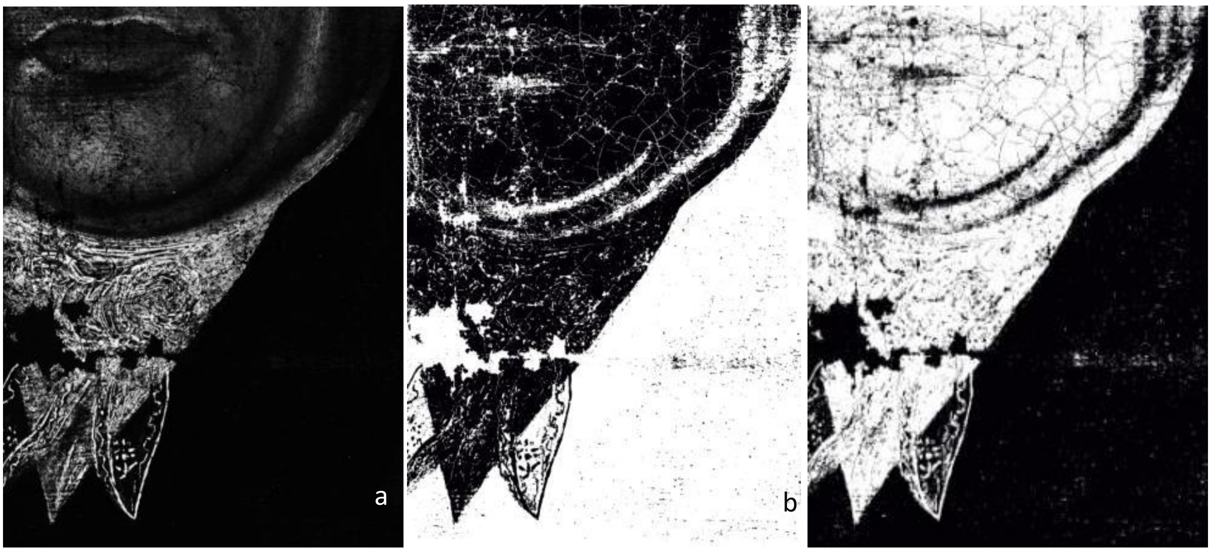


Figure 33: Application of a series of Photoshop filters, in an attempt to highlight the protrusions.
a) Black&white image with increased contrast. b) Filter “Torn&Edges” c) Filter “Torn&Edges” (inverted)

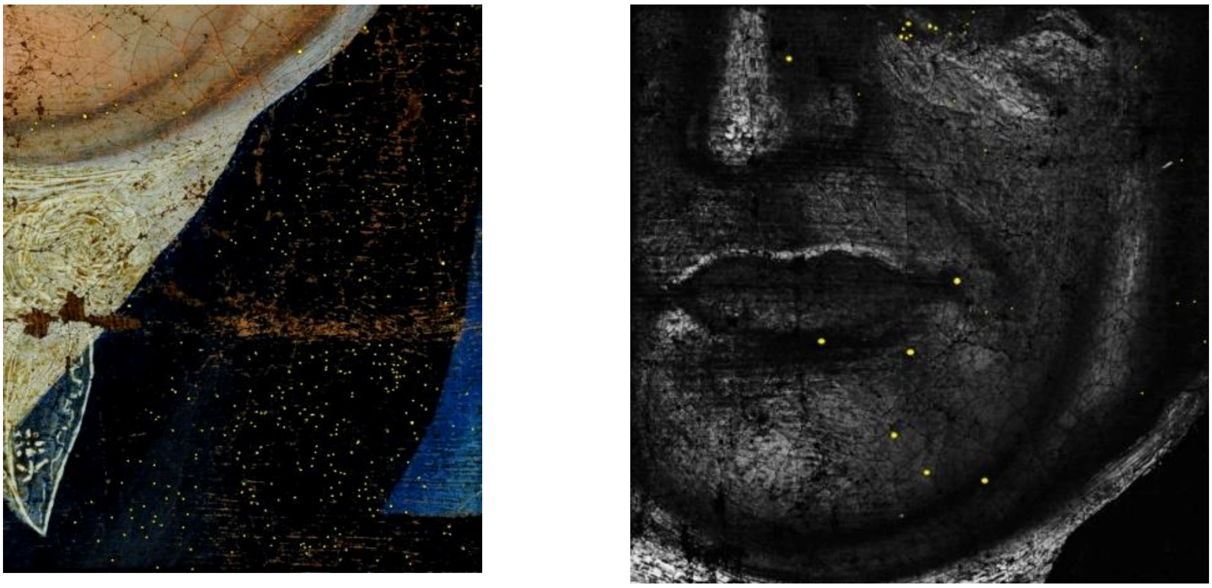


Figure 34a: Highlighted protrusions with yellow dots on the surface without a filter (left image) and Figure 34b: black&white image with increased contrast image (right)

Appendix VIII- Analytical section

VIII.1 Description of the instruments used

- **Photographic documentation**

The photographic documentation was performed with a Sony digital camera (DSC-F828, Cyber-shot, Zeiss, Super HAD CCD, 4 color. 7x optical zoom. 8.0 Mega-pixels). For photographs with Ultraviolet (UV) light, the machine was equipped with a UV filter (Hoya Pro1Digital Filter: Tokina Co., Ltd. DCM, 58) and for photographs with Infrared (IR) light with an IV filter (Hoya, 58mm Infrared R72). The photographs for document the distribution of the protrusions were acquired with a Nikon D700 camera (AF-S Micro Nikkon1:2.8 GED).

- **Optical Microscopy (OM)**

The optical microscope is an Axioplan 2ie Zeiss microscope equipped with a 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 can be analysed with 10x ocular lenses and 5x/10x/20x/50x objective Epiplan lenses (giving total optical magnification of 50x, 100x, 200x, and 500x).

For the incident and transmitted light 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], set 9 [BP 450-490, FT 510, LP 515] and set 2 [BP300-400, 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-rayfluorescence 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 primaryradiation (Ø ~70 μm) at the sample. Elemental compositions were obtained from the average of three independent spots, analysed with a tube voltage of 40KV, a current intensity of 300μA and live time of 200s.

- **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 a 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). The spectra are shown as acquired, without corrections or any further manipulations.

- **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, in 50-100 mm areas, resolution setting 4 cm-1 and 128 or 256scans, using a Thermo diamond anvil compression cell. When necessary, the system was purged with nitrogen prior to the data acquisition. The spectra are shown here as acquired, without corrections or any further manipulations, except for the occasional removal of the CO_2 absorption at ca. 2300-2400 cm^{-1}.

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

A Zeiss DSM 962 scanning electron microscope of CENIMAT/I3N in FCT/UNL was used with SE (secondary electron) and BSE (back scattered electron) detectors coupled with an INCAx-sight X-ray-EDS (energy dispersive spectrometer) from Oxford Instruments. Samples were covered with a layer of carbon (a three-second pulse/ one nanometer of thickness). The spectra were acquired with voltage of 20 kV (high voltage), 25mm of working distance and present real time of 30 s.

VIII.2.EDXRF points

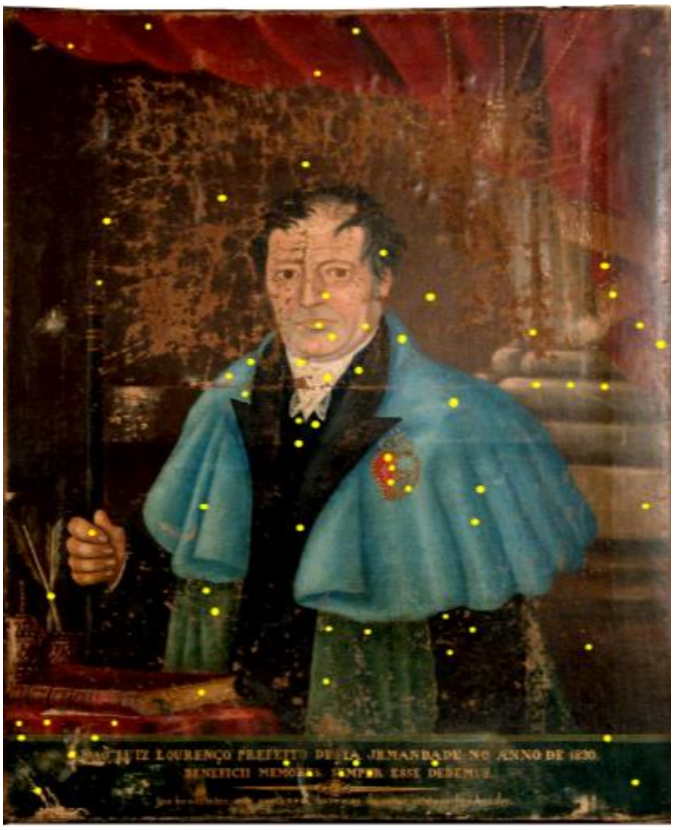

LUIZ LOURENÇO PREFEITO DESTA IRMANDADE NO ANNO DE 1830
BENEFICII MEMORES SEMPER ESSE DEBEMUS

Figure 35: EDXRF points marked with yellow dots.

VIII.3. Areas sampled for mounting into cross-sections (X) and for µ-FTIR (F)

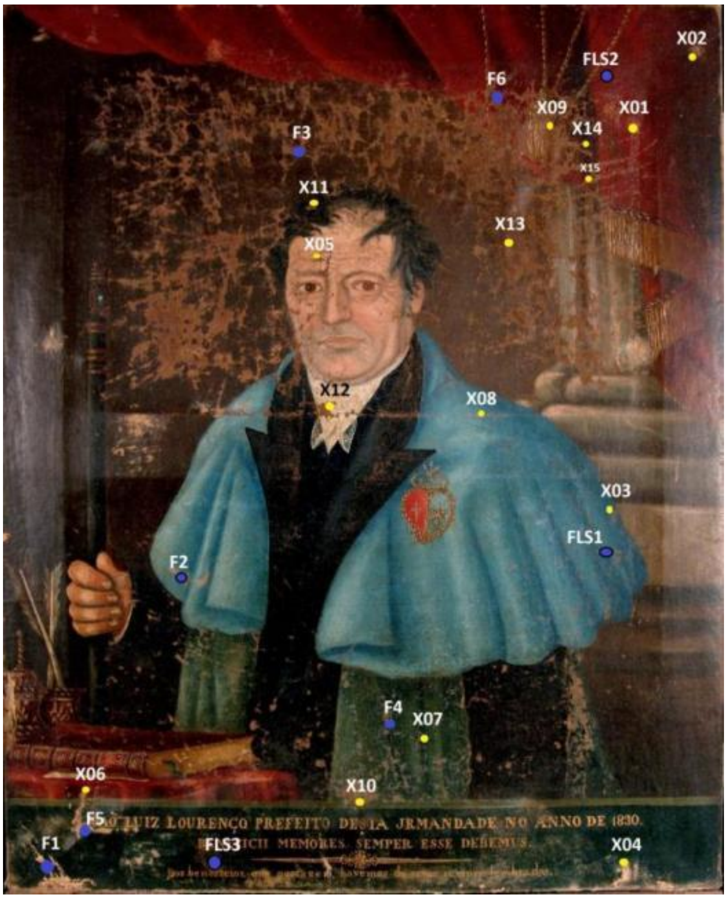

X02
FLS2
F6
X09
X01
X14
F3
X15
X11
X13
X05
X12
X08
X03
FLS1
F2
F4
X07
X06
X10
F5
LUIZ LOURENÇO PREFEITO DESTA IRMANDADE NO ANNO DE 1830.
F1
FLS3
ICII MEMORES SEMPER ESSE DEBEMUS.
X04

Figure 36: Areas sampled for mounting into cross-sections (X, signed with yellow dots) and for µ-FTIR (F, marked with blue dots)

Codes for samples' identification

Cross section identification: **FCTPNT.26 EMS158**	**Colour**	**Area**
X01	Red	Red curtains
X02	Dark red	
X03	Dark Blue	Blue coat
X04	Dark Green	Bar letters
X05	Flesh Tones	Face
X06	Red	Table
X07	Green	Jacket
X08	Lead soap in a Blue area	Jacket
X09	Lead soap in a Red zone	Curtains
X10	Light green	Bar letters
X11	Black	Hair
X12	White	Scarf
X13	Brown	Background
X14	Lead Soap	Curtains
X15	Red	Curtains

µ-FTIR Sample identification	**Area/Colour**
F1	Ground
F2	Blue
F3	Brown
F4	Green
F5	Dark green
F6	Red
Lead soaps	
FL1	Blue
FL2	Red
FL3	Green

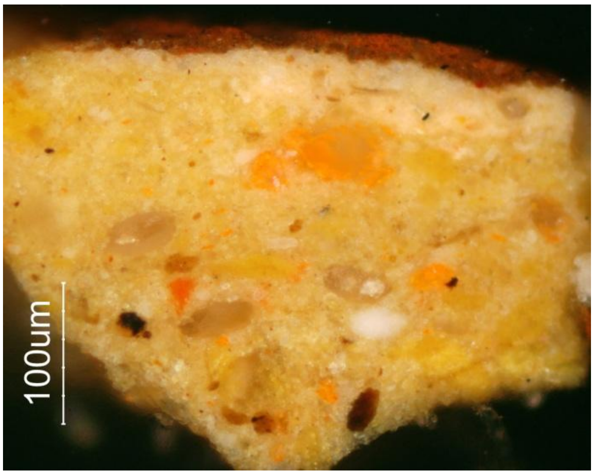
VIII.4. Pigment analyses results

Sample		Pigments identified	EDXRF	µ-FTIR		µ-Raman	
				wavenumber (cm^{-1})	assignment	wavenumber (cm^{-1})	assignment
⬛	X 11	**carbon based pigment**	Pb, Fe, Ca, Mn, K	n.a.		1324	sp$_3$ (C-C)
						1600	sp$_2$ (C-C)
🟦	X 3	**Prussian Blue** ($Fe_4[Fe(CN)_6]_3$)	Pb, Fe, Ca, Mn	2090	v $[Fe(C=N)_6]^{3-}$	275	δ (C-Fe-C)
						536	δ (Fe-C≡N)
						950	
						2090	ν (C≡N)
						2150	ν (C≡N)
		lead white ($2PbCO_3.Pb(OH)_2$)		3530	v OH	1048	ν_s CO_3^{2-}
				1734	v C-O		
				1398	v_{as} CO_3^{2-}		
				1046	v CO_3^{2-}		
				839	$\delta_{as}CO_3^{2-}$		
				679	$\delta_{as}CO_3^{2-}$		
🟫	X13	**carbon based pigment**	Pb, Fe, Ca, Mn	-	-	1335	sp$_3$ (C-C)
						1563	sp$_2$ (C-C)
		calcium carbonate $CaCO_3$		-	-	1086	ν_s CO_3^{2-}
		lead white ($2PbCO_3.Pb(OH)_2$)		3530	v OH	1047	ν_s CO_3^{2-}
				1732	v C-O		
				1407	v_{as} CO_3^{2-}		
				1037	v CO_3^{2-}		
				873	$\delta_{as}CO_3^{2-}$		
				678	$\delta_{as}CO_3^{2-}$		
		iron oxide (haematite) α-Fe_2O_3		-	-	227	
						289	δ_s (Fe-O)
						409	δ_s (Fe-O)
						609	ν_s (Fe-O)
						1311	
		quartz SiO_2		1090	v SiO_3^{2-}	462	
		alumino-silicate Al_2O_3. $2SiO_2$.$2H_2O$		3624	hydroxyl ion bands	655	Al-O-Si
				1037	Si–O–Si		
				911	Al–O–H		
🟧	X5	**lead white**	Pb, Ca, Fe	n.a.		1047	vs CO_3^{2-}
		iron oxide?				-	-
🟩	X7	**Prussian blue** ($Fe_4[Fe(CN)_6]_3$)	Pb, Fe, Ca, Ba	2096	v $[Fe(C=N)_6]^{3-}$	2158	ν (C≡N)
		barium sulphate $BaSO_4$		1117		-	-
				1121	v_{as} SO_4^{2-}		
				1071			
		lead white ($2PbCO_3.Pb(OH)_2$)		1419	v_{as} (CO_3^{2-})	1048 1053	ν_s CO_3^{2-}
				1071	v (CO_3^{2-})		
				671	$\delta_{as}CO_3^{2-}$		
🟩	X4	**Prussian blue**	Pb, Ba, Fe, Ca, Cr	2090	v $[Fe(C=N)_6]^{3-}$	2150	ν (C≡N)
		chrome yellow $PbCrO_4$		-	-	358 838	δ CrO_4^{2-} ν_s CrO_4^{2-}
		barium sulphate $BaSO_4$		1181	v_{as} SO_4^{2-}	987	ν_s SO_4^{2-}
				1122	v_{as} SO_4^{2-}		
				1079	v_{as} SO_4^{2-}		
				981	vs SO_4^{2-}		
⬜	X12	**lead white** ($2PbCO_3.Pb(OH)_2$)	Pb, Ca, (Fe)	n.a.		1053	vs CO_3^{2-}
🟥	X6	**red lead** Pb_3O_4	Pb, Fe, Ca, Mn	-	-	121	ν (Pb-O)
						152	PbO_2
						220	δ(PbO_2)
						310	
						391	PbO_2
						480	
						548	ν (Pb-O)
		iron oxide (haematite) α-Fe_2O_3		-	-	226	
						245	
						334	δ s (Fe-O)

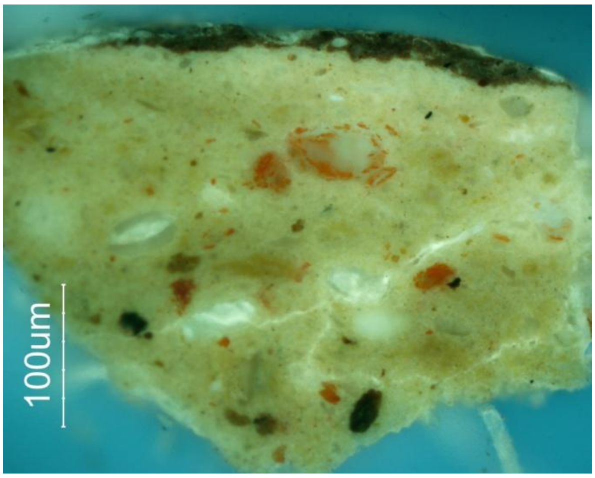
🟥						410	δ s (Fe-O)
						652	vs (Fe-O)
						1316	
		gypsum $CaSO_4.2H_2O$		-	-	1005	v SiO_3^{2-}
		lead white **($2PbCO_3.Pb(OH)_2$)**		1405 680	v_{as} (CO_3^{2-}) $\delta_{as}CO_3^{2-}$	-	-
		quartz SiO_2		1140	v Si-O-Si	-	-

n.a.=not analysed

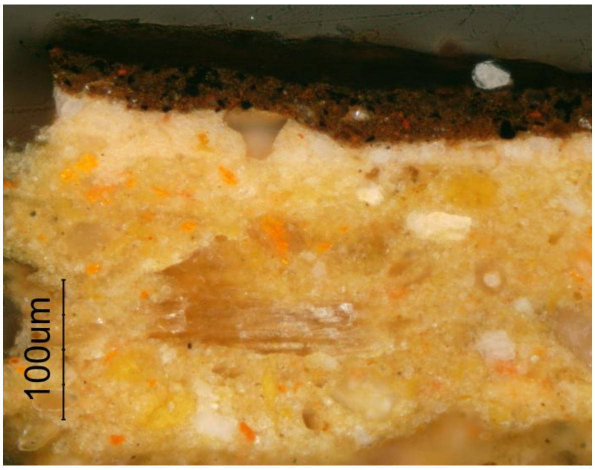
VIII.5. Cross- sections X1-X15 – Normal light and Ultraviolet light



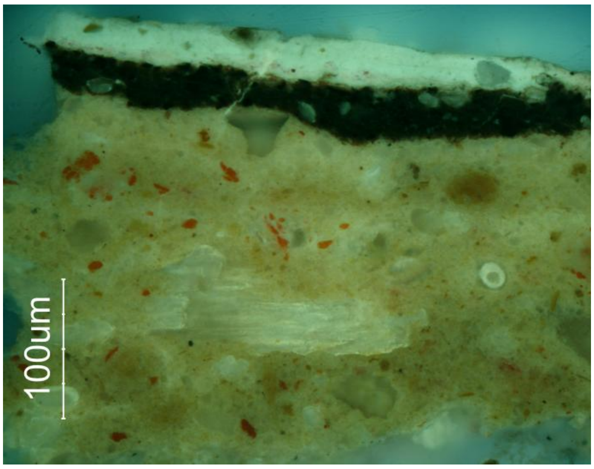
X1: OM Vis-Light - Polarized Light: total magnification200x



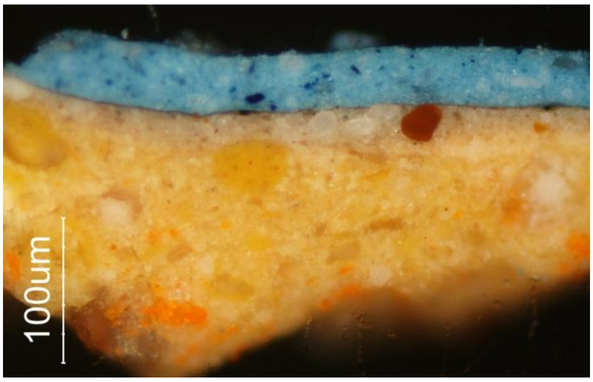
X1: OM UV Filter set 5: total magnification200x



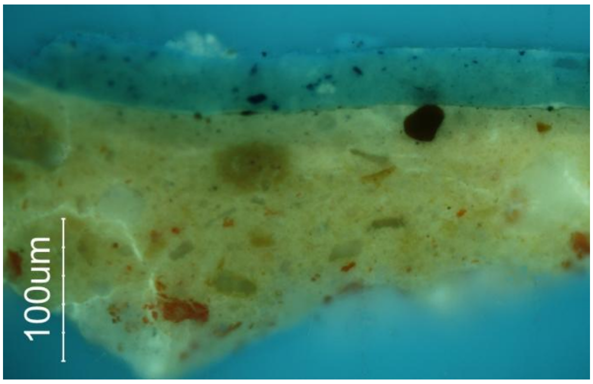
X2: OM Vis-Light - Polarized Light: total magnification200x



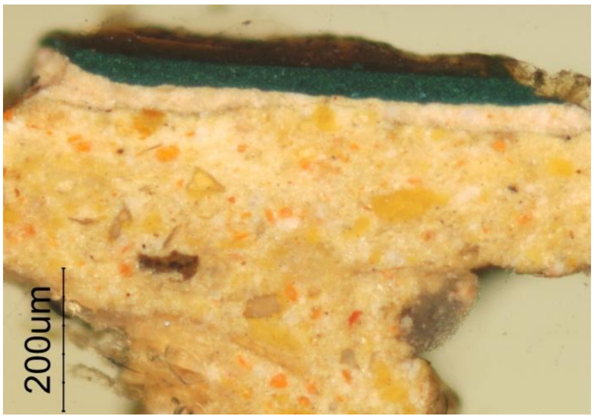
X2: OM UV Filter set 5: total magnification200x



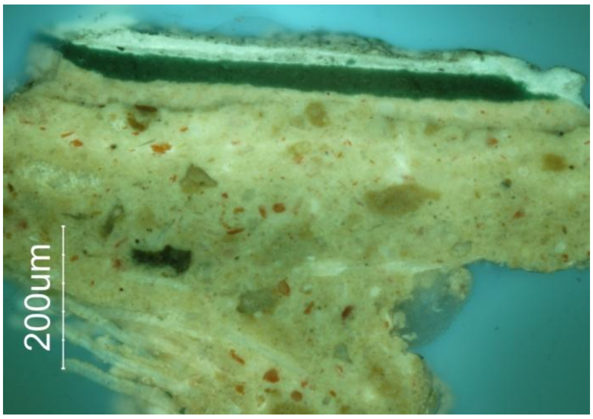
X3: OM Vis-Light - Polarized Light: total magnification200x



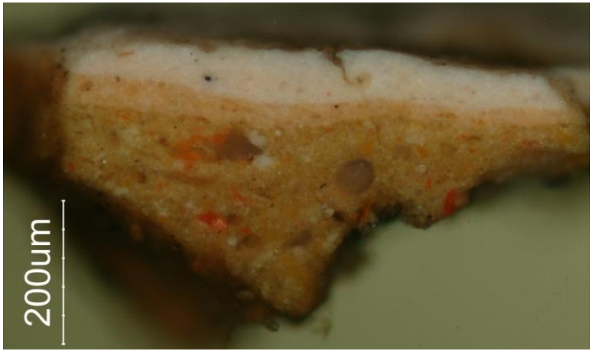
X3: OM UV Filter set 5: total magnification200x



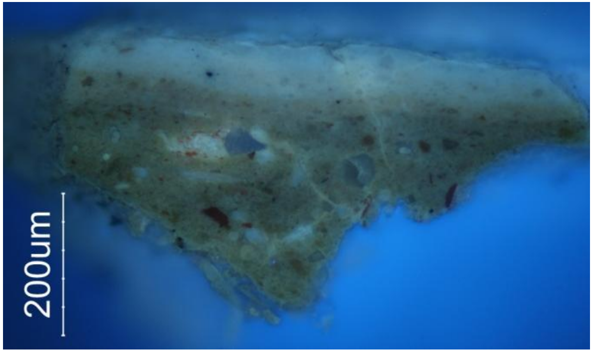
X4: OM Vis-Light - Polarized Light: total magnification100x



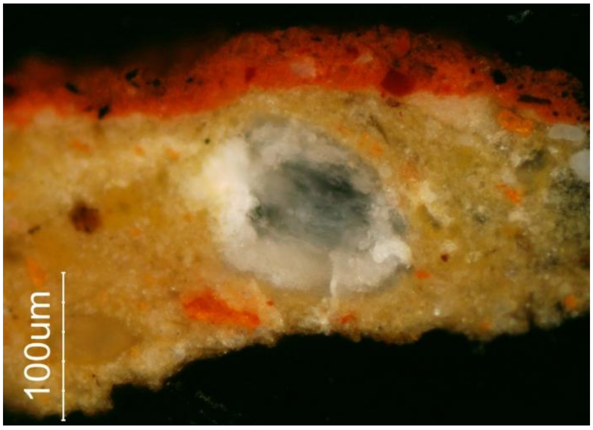
X4: OM UV Filter set 5: total magnification100x



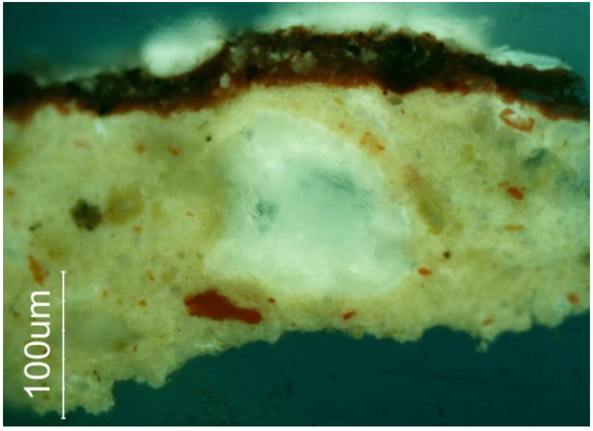
X5: OM Vis-Light - Polarized Light: total magnification100x



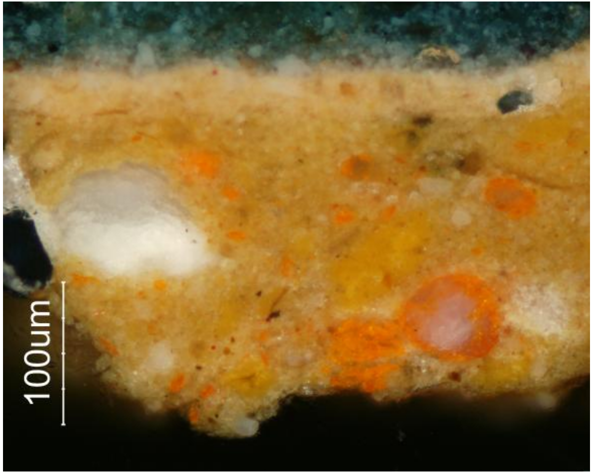
X5: OM UV Filter set 2: total magnification100x



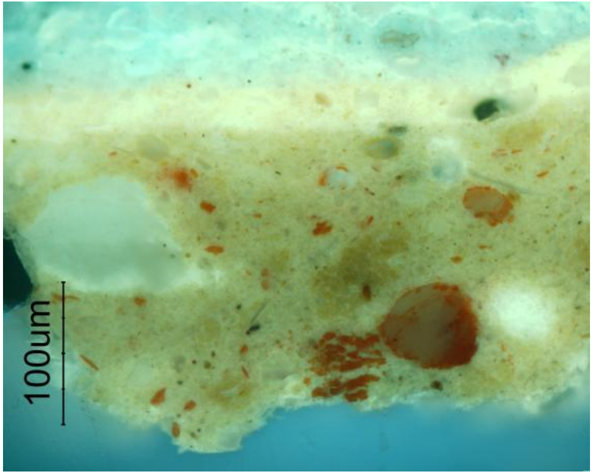
X6: OM Vis-Light - Polarized Light: total magnification200x



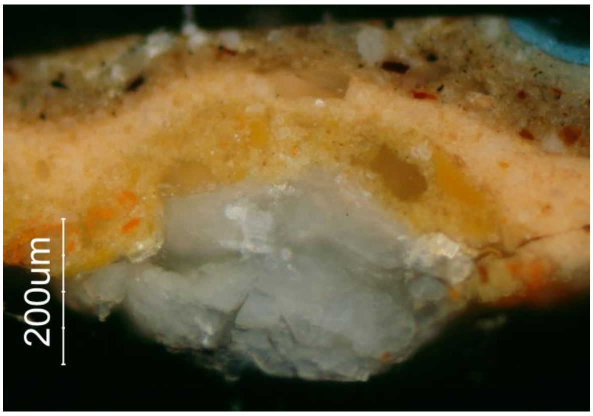
X6: OM UV Filter set 5: total magnification200x



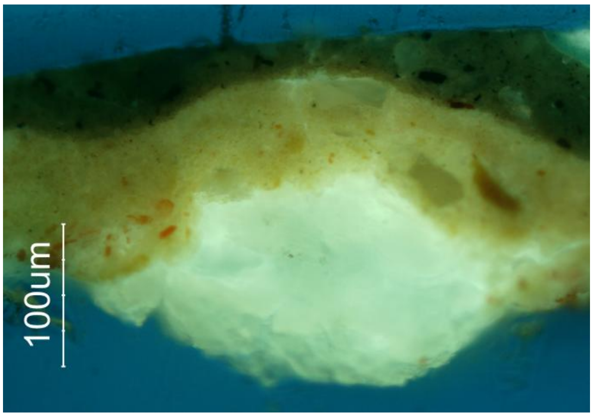
X7: OM Vis-Light - Polarized Light: total magnification200x



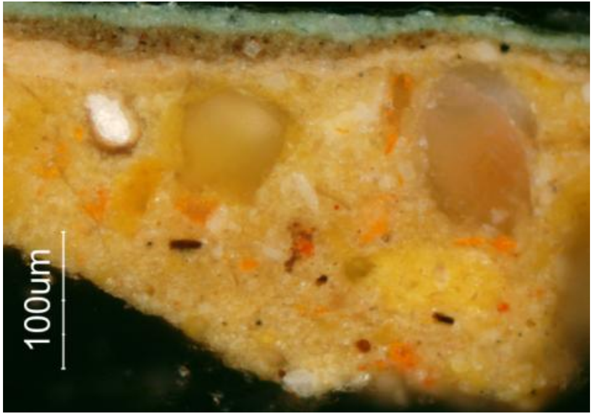
X7: OM UV Filter set 5: total magnification200x



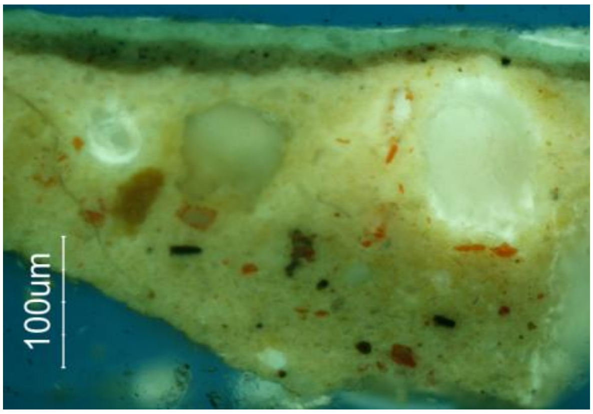
X8: OM Vis-Light - Polarized Light: total magnification200x



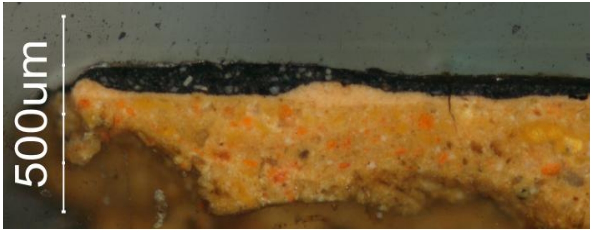
X8: OM UV Filter set 5: total magnification200x



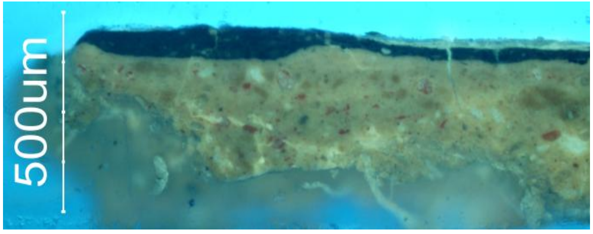
X10: OM Vis-Light–Polarized Light: total magnification200x



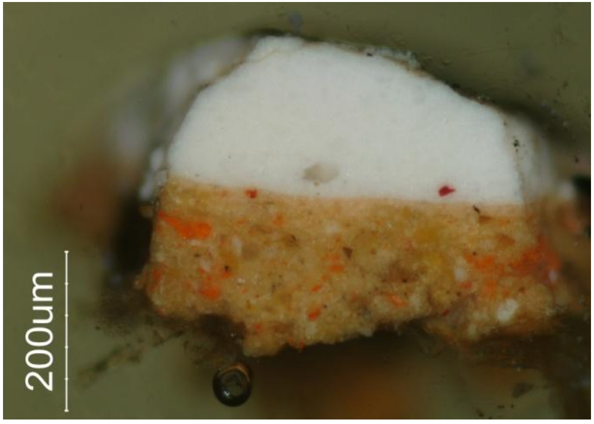
X8: OM UV Filter set 5: total magnification200x



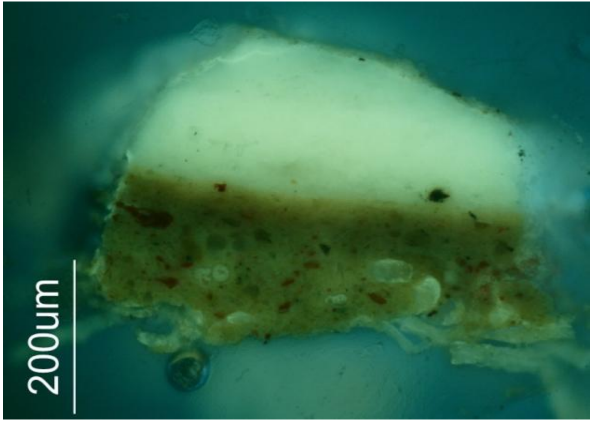
X11: OM Vis-Light - Polarized Light: total magnification50x



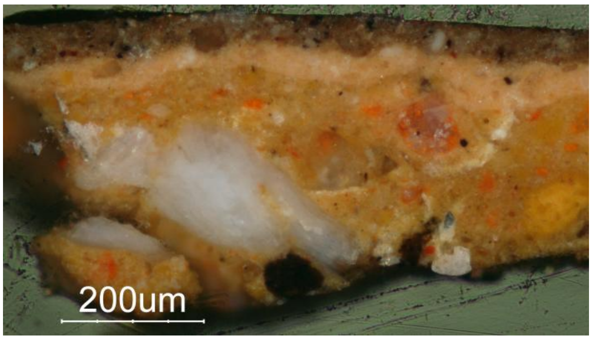
X11: OM UV Filter set 5: total magnification50x



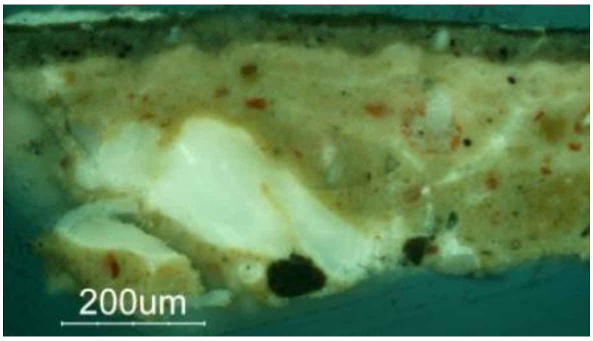
X12: OM Vis-Light - Polarized Light: total magnification100x



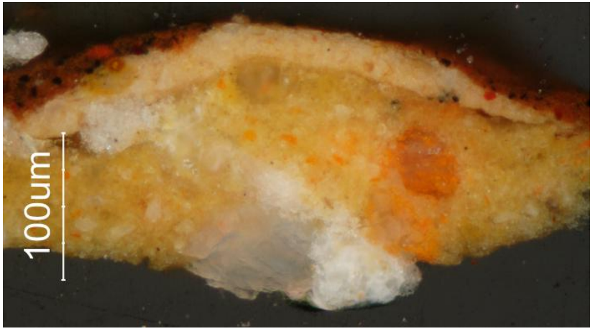
X11: OM UV Filter set 5: total magnification50x



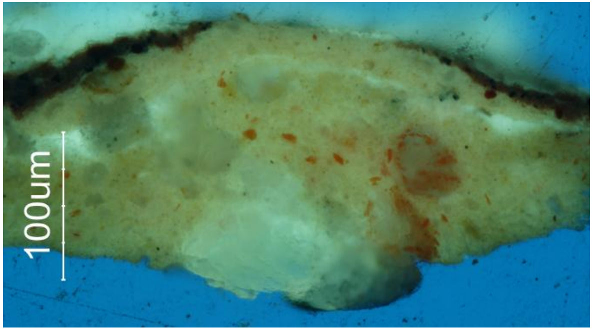
X13: OM Vis-Light - Polarized Light: total magnification100x



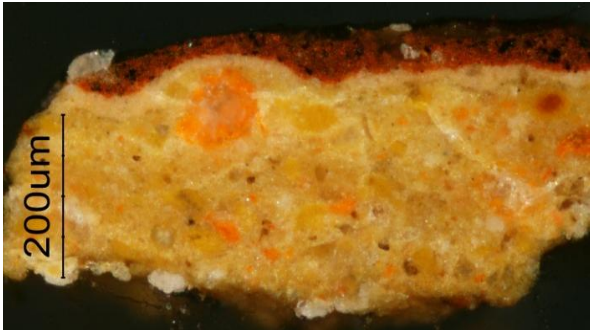
X13: OM UV Filter set 5: total magnification100x



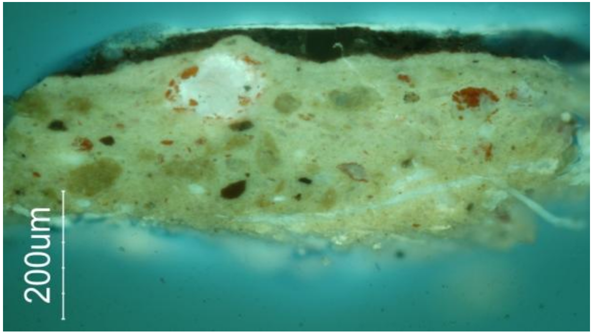
X14: OM Vis-Light - Polarized Light: total magnification200x



X14: OM UV Filter set 5: total magnification200x 5



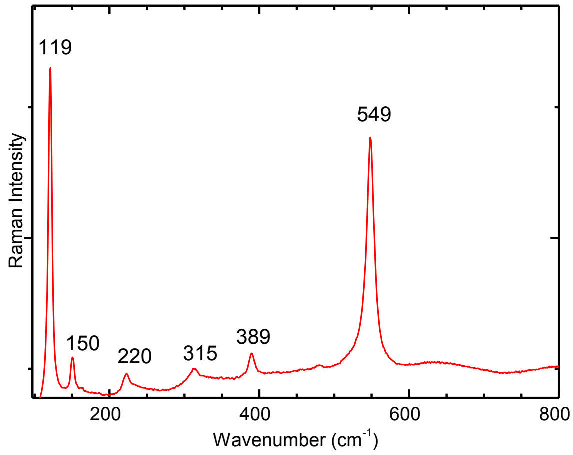
OM image of the sample X15: total magnification100x; Vis-Light Polarized Light



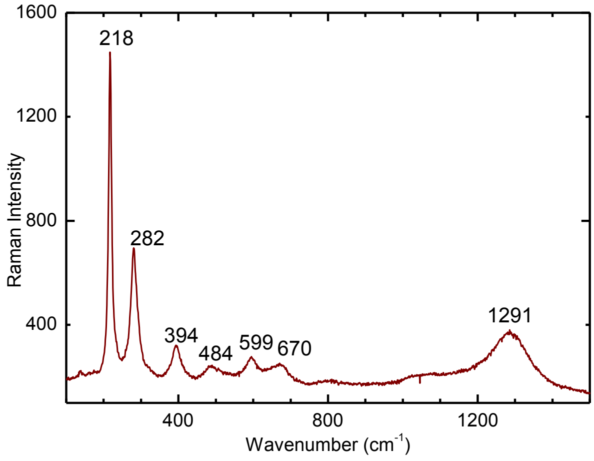
OM image of the sample X15: total magnification100x; **UV-Light** Filter set 5

VIII.6. µ-Raman spectra

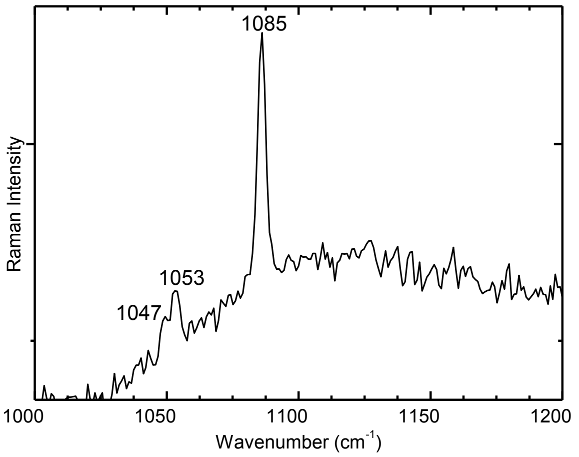
XI.6.1 Ground Layer samples X07, X05, X03



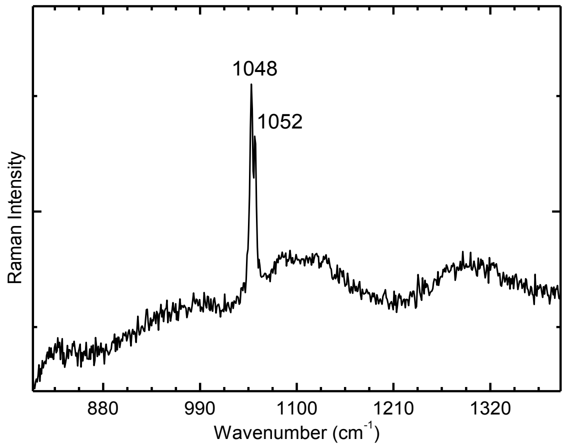
X07: the first ground layer showing the main peaks of red lead (minium): 119, 150, 220, 315, 389 and 549 cm^{-1} [33, 60].



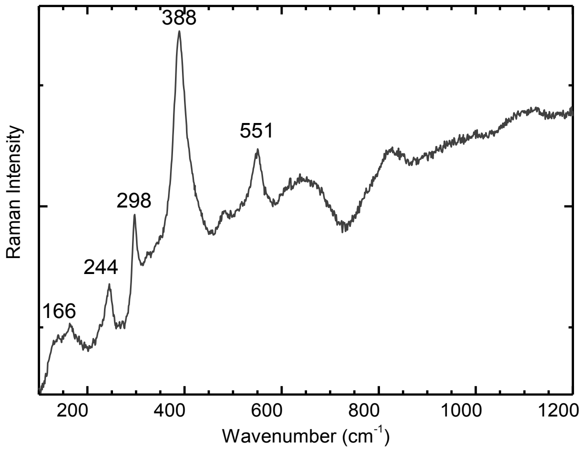
X05: the first ground layer showing the main peaks of an iron oxide: 218, 282, 395, 484, 599, 670 and 1291 cm^{-1}) [20, 33,61].



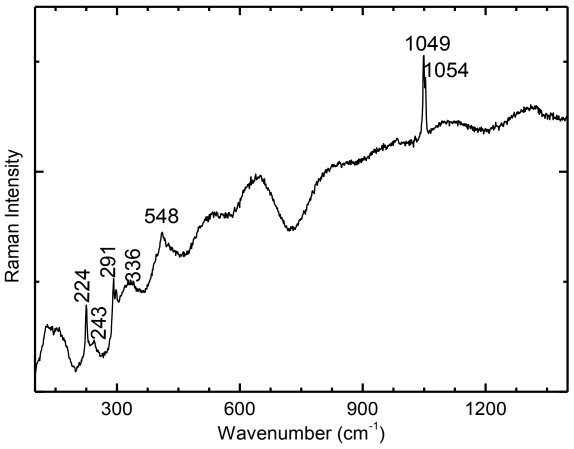
X07: the first ground layer showing the main peaks of lead carbonate (1047 and 1053 cm^{-1}) and calcium carbonate (1085cm^{-1}) [33,34].



X05: the first ground layer showing the main peaks of lead carbonate (1048 and 1052 cm^{-1}) [33,34].

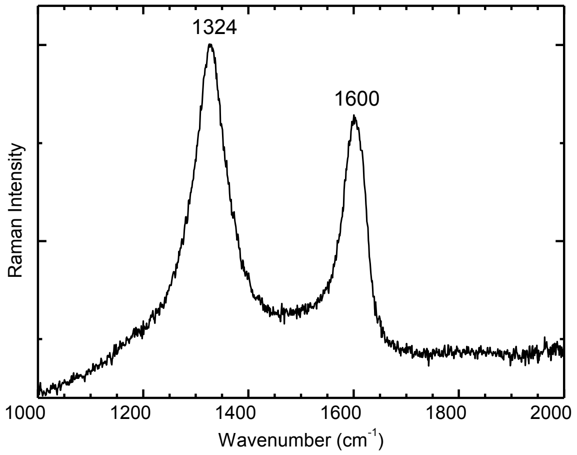


X03: the second ground layer showing iron oxide (goethite): 166, 244, 298, 388 and 551cm^{-1} [61].

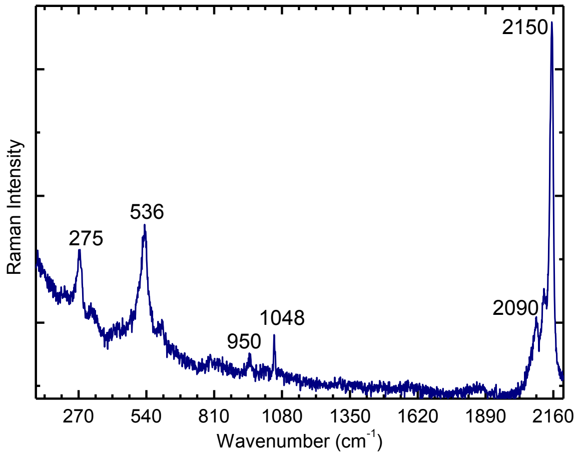


X05: the second ground layer showing the main peaks of an iron oxide (haematite): 224, 243, 291, 336 and 548 cm^{-1} [E1,E4] and lead carbonate (1049, 1054 cm^{-1}) [20].

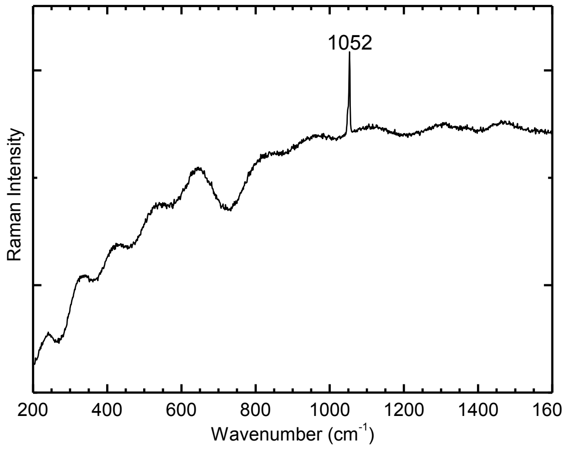
VIII.6.2 Paint Layer samples X3, X4, X6, X12, X11, X13:



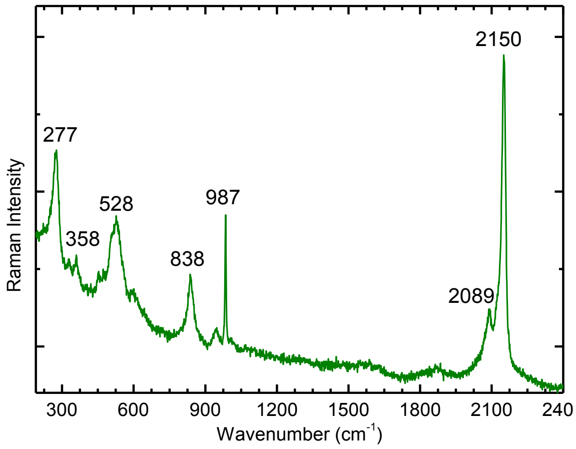
X11: Black pigment. Showing characteristic peaks of a carbon-based pigment: 1324 and 1600 cm^{-1} [33,34]



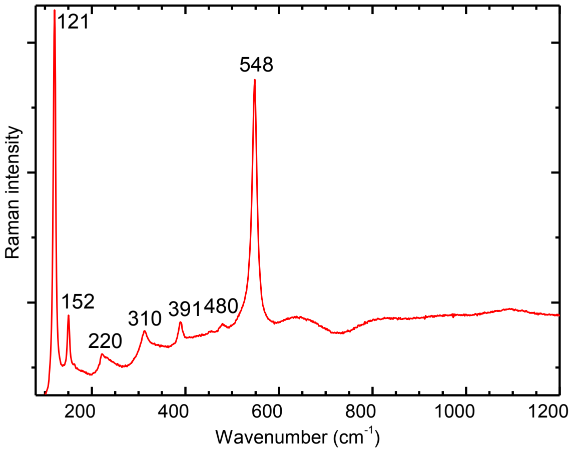
X3: Blue pigment. Showing peaks associated to Prussian blue (275, 536, 950, 2090 and 2150 cm^{-1}) and lead white (1048 cm^{-1}) [33,34]



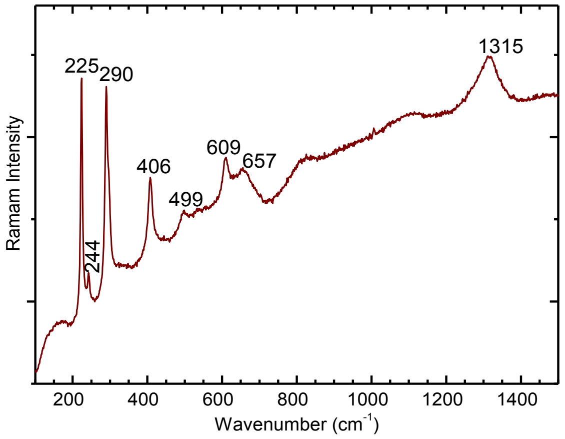
X12: White pigment. Showing the main peak associated to the presence of lead white pigment at 1053cm^{-1} [33,34].



X4: Dark green pigment. Showing characteristic absorbance for chrome yellow (lead chromate) at 358 and 838 cm^{-1}. The strongest band is at 838cm^{-1} is associated to vibration of CrO_4^{2-} (symmetric stretching) [59] and to Prussian Blue (277, 528, 987, 2089 and 2150 cm^{-1}) [33,34].



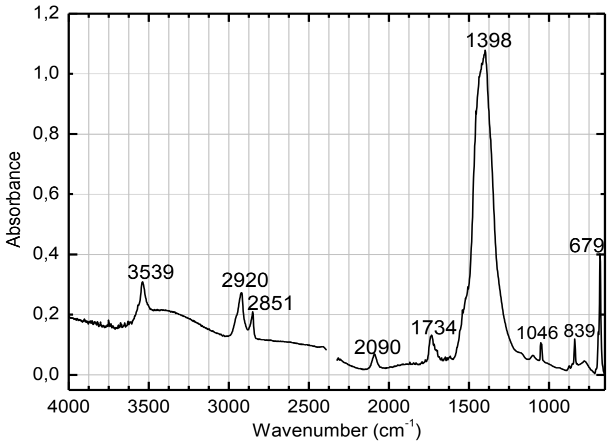
X6: Red pigment. Showing the presence of minium: 121, 152, 220, 310, 391, 480 and 548 cm^{-1} [33, 60]



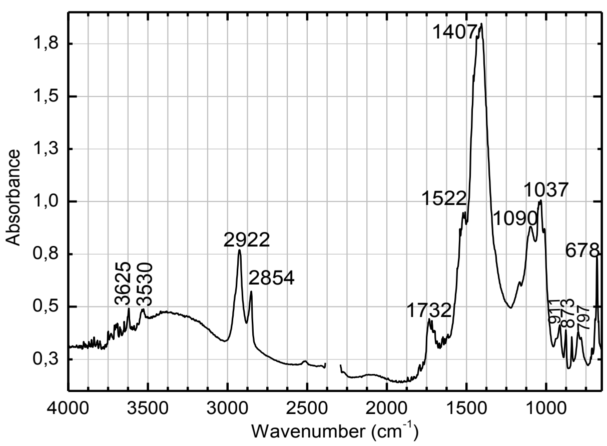
X13: Brown pigment. Showing the presence of an iron oxide (haematite): 225, 244, 290, 406, 499, 609, 657 and 1311 cm^{-1} [61].

VIII.7. µ-FTIR spectra

Paint Layer: samples F2,F3, F5

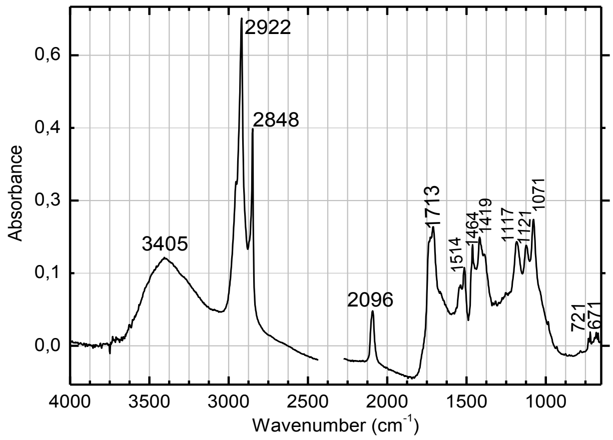


F2: Blue pigment. A mixture of Prussian blue and lead white. The µ-FTIR indicates the presence of the ion $[Fe(C{=}N)_6]^{3-}$ (Prussian blue) stretching band at 2090cm^{-1} [5] and the main peaks of lead white at 3530 cm^{-1} (OH stretch), 1734 cm^{-1}



F3: Brown pigment. A mixture of lead white (3530, 1732, 1407, 1037, 873 and 678 cm^{-1} [22]), aluminosilicate kaolinite (3624 cm^{-1} (hydroxyl ion bands), 1037 cm^{-1} (Si–O–Si) and 911 (Al–O–H) [21]). Normally, low amounts of quartz are found

(C=O stretch), 1398 cm^{-1} (C-O stretch), 1046 cm^{-1} (CO_3 symmetric stretch), 839 cm^{-1} (CO_3 out of plane rocking) and 679 cm^{-1} (CO_3 in plane rocking)[22].



with kaolinite, which is identified by the bands at 1090 and 797 cm^{-1}[21]. It was not possible verify the presence of an iron oxide. In this spectrum the metal carboxylates' peaks at 1407 and 1522 cm^{-1} (COO^- symmetric and asymmetric stretch, respectively) [14-16,23] are detected.

F4: Green pigment. Confirmed the presence of Prussian blue through the band at 2096cm^{-1} and barium sulphate ($BaSO_4$) by the IR bands at 1117, 1121 and 1071 cm^{-1} [E2].

It is possible to observe a peak at 1713 cm^{-1}, associated with the presence of carboxylic acids [A], and peaks related with metal carboxylates at 1464 and 1514 cm^{-1} (COO^- symmetric and asymmetric stretch, respectively) [14-16,23].

Appendix IX- João Luiz Lourenço' future environment[33]

For the most appropriate decision-making at the level of treatment of the painting *João Luiz Lourenço*, it was necessary to know the future environment in which the painting will be exposed, in particular to determine parameters like temperature and relative humidity (RH). In this context, information was requested and data was provided by Ana Duarte, a staff member of the division of Historical Heritage and Museums/ Ecomuseu Municipal - Conservation Service and General Inventory of the Center Quinta da Trindade. Through this, it was possible to establish that: Ecomuseu Municipal do Seixal is a decentralized organization with multiple locations, only some of which have a museological function. In the case of *João Luiz Lourenço* its location is *Quinta da Trindade* in the *storage of the Core of Quinta da Trindade of Ecomuseu Municipal do Seixal of the Division of History Heritage and Museums of the Municipality of Seixal*. This storage does not have any environmental control systems. According to Ana Duarte, the monitoring of this storage indicates a cold, moist but very stable environment for the daily cycles with gradual seasonal changes. This is related to the location of the storage (ground floor, with an exterior wall) and also with the characteristics of the building (old with very thick walls - approx 80cm). The RH in the storage is always above 60% and most of the year is between 65% and the 70%, but only very exceptionally reaches 80%. The temperature fluctuates annually between 10/12ºC and 18/20ºC, and for the majority of the time it is around 15ºC. For the most sensitive objects those responsible try to create a more favourable microclimate through packaging systems and materials, including the use of a desiccant (silica gel).

For temporary exhibitions, similar problems arise as the exhibition spaces are also not environmentally controlled. These are often located in industrial buildings with original architecture, where environmental control with reference values of conservation of collections would be unsustainable and in some cases incompatible with the preservation of the buildings themselves.

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[33] Duarte, A. 2012.24 July. [personal communication]

Appendix X: Evaluating Treatment Options

X.1 Facing adhesives

X.1.1 Cyclododecane (CDD)

A comparison of melted and sprayed CDD on glass slides: after 60 days the glass plates with melted CDD continued to show a white residue, whereas the CDD spray sublimed more quickly (around 4 days) and no residue was left on the slides after 9 days. According to Rowe, S. & Rozeik, C. (2009), the sprayed film sublimes at least 10 times faster than a film with the same thickness applied as a melt. It proved extremely difficult to achieve an even film when the CDD was applied in a molten state. In view of these initial results, the evaluation concentrated on the spray application. CDD Spray was applied at a distance of 15cm from the surface to form a uniform film. Since CDD itself does not have adhesive properties, facing tissue was then placed over the sprayed film and fixed in place using two different methods: a hot spatula and a hot air gun. The use of the hot air gun was rejected since it took too long to achieve the CDD melting point. Therefore, the hot spatula (around 60 °C) resulted in a more useful fixing method. After sublimation, no residue of CDD nor changes to the surfaces tested was evident. The evaporation time for the sprayed CDD proved to be quite short (less than one month for complete sublimation but the film was becoming thinner quickly). The main disadvantage however, was that the film formed was very brittle, and would easily crack under the mild pressure needed for mechanical removal of the lining adhesive (scraping). Also of concern was a mention in the literature that CDD may act as a solvent for certain substrates, including oil films and varnish [39]. There is also a lack of literature, scientific studies and tests related to CDD toxicity. Further research is needed to establish whether CDD can interact with materials in aged oil paintings and to understand its possible toxicity.

X.1.2 Sodium carboxymethyl cellulose (CMC): *Tissue Comparison*

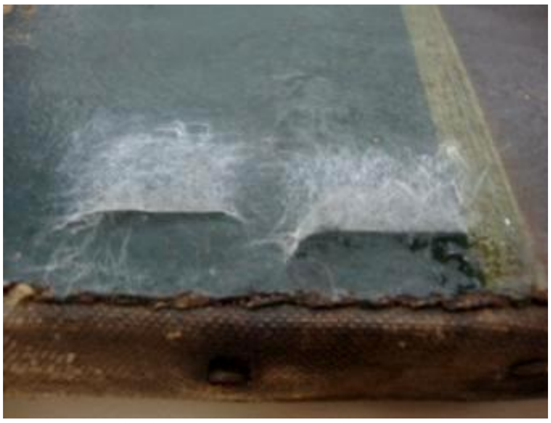

Figure 37: Two facing papers were considered, one thin[34] (left) and one thicker[35] (right). Rectangles (3cm x 4cm) of each tissue were applied with the 3% CMC solution.

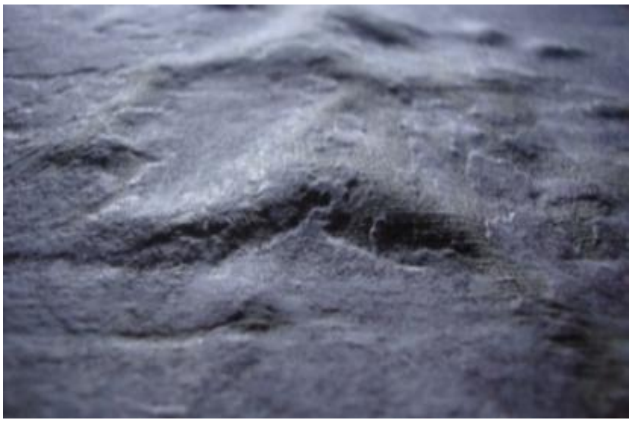

Figure 38: Painting after facing. The thick tissue still provided good conformation to all deformations.

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[34] Tengucho 20m, MMNR-01; Neschen Portugal. S.A. FAO: Maureen Weinstein . Pel Tissue paper 5gsm 965mmx20M

[35] FilmoplastT J 50 M X 31 CM K 50; NESCHEN Documents; No. 13906027498; 50,000 M x 0,310 M; Neschen AG.

X.2 Exploration of moisture delivery methods for lining adhesive removal

To control moisture delivery and avoid excess water during lining adhesive removal, two agents used to form a gel in water were tested: CMC (carboxymethyl cellulose) and Agar (a high molecular weight polymer extracted from the Gelidium and Gracilaria seaweeds [B3]). Finally, the use of moisture introduced into blotting paper was tested.

CMC: a gel of CMC (3% solution) and water was painted onto the lining adhesive using a brush, then left to swell the glue. This method was difficult to control and the glue/canvas appeared to become quickly saturated with water.

AGAR: Agar and water were mixed then cast into a thick film which set to form a moist gel that could be cut to size. A small (1x 2 cm) piece was applied to the glue/canvas. While it was effective in restricting the area receiving moisture, it was evident that the glue/canvas became wet very quickly.

Moistened blotting paper: This method avoided damaging the canvas fibres and allowed good control of the level of moisture introduced to the back of the painting. A square of slightly moist blotting paper was placed on top of the glue and covered by a piece of polyester film (Melinex) to slow moisture loss. A light weight was placed over the Melinex (Fig. 39) to obtain better contact between the glue and the blotting paper and left for ten minutes. After this time, the glue appeared dark and was soft, but the canvas did not appear to be significantly wet. The blotting paper was then removed and a dental instrument followed by a scalpel blade were used to gently scrape the adhesive. The process was repeated two to three times, removing two to three layers of adhesive (Fig. 40).

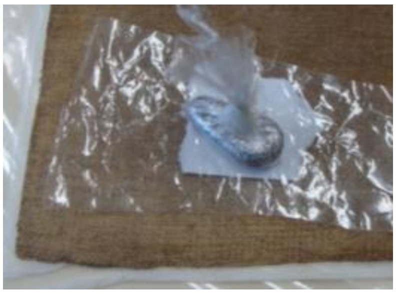

Figure 39: A light weight was placed over the Melinex to obtain better contact between the glue and the blotting paper.

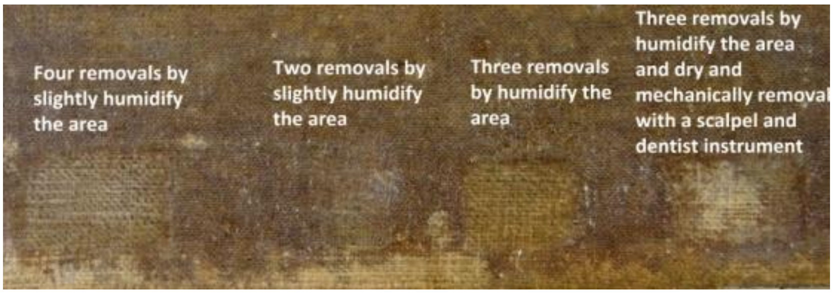
Four removals by slightly humidify the area
Two removals by slightly humidify the area
Three removals by humidify the area
Three removals by humidify the area and dry and mechanically removal with a scalpel and dentist instrument

Figure 40: Aspect of the canvas after the removal (with moisture) of the lining adhesive.

X.3 Choosing an appropriate infill material

As summarised in the literature [7,42] infill materials for paintings should be:

- dimensionally stable to humidity and temperature change, in terms of stiffness, strength, and resistance to fracture
- reversible
- physically and chemically stable in both the short and long term
- resistant to fungal and bacterial attack
- non-toxic
- flexible
- strong

- compatible and mechanically similar to the painting. Both fillers and paint should be able to support similar environmental oscillations and behave in a similar way
- easy to remove
-

Table 1: Infill Recipes Explored

Binder		
Animal based	**Gelatine + PVA**	9% gelatine in water+ PVA
	Rabbit skin glue	5% RSG in water
		7% RSG in water
	Isinglass	4% Isinglass in water
		10% Isinglass in water
Synthetic	**Mowiol Resin (PVAL)**	20% Mowiol in water

Table 2: Observations of the behaviour of the fillers during and after application[36]

Group	**Recipe**	**Observation**	**General results - summary**
Glue Fillers	**1** **Gelatin: 2gr** **Chalk: 8gr** **PVA: 2 gr**	The filler nº1 was easy to manipulate but it was also very sticky (because of the amount of PVA). When it dried, this filler contracted more than the other two gelatine formulations. However, after drying this fill was also the most flexible.	↑ good to work with ↑ easy to apply and control ↓ short working time. It was necessary to keep the gelatin mixtures warm and add water during the experiment. ↓ After drying the gelatine fillers change colour slightly and suffered some deformation.
	2 **Gelatin: 2gr** **Chalk: 6gr** **PVA: 1 gr**	Filler nº2 was good to work with and it was less sticky than Filler nº 1. After drying this filler also contracted. In the thinner parts, the film was flexible. In thicker parts, it was brittle, but it stands some pressure before breaking.	
	3 **Gelatin: 2gr** **Chalk: 5gr** **PVA: 0.5 gr**	Filler nº3 was quite difficult to spread out but it was also good to work with. This filler contracted less than the others did. It was very brittle in both thicker and thinner areas.	
	5% RSG (in water)	After drying, this filler with chalk nº2 on Melinex had several cracks. On canvas the fillers with both chalks presented drying cracks. This filler was also extremely brittle (more than the 7%RSG filler).	↑ easy to apply and control ↑ good to work, but less than gelatin fillers. ↓very sticky ↓When a new portion of RSG fillers were applied on top of a layer that was already dried some cracks were created.
	7% RSG (in water)	After drying this filler was brittle, but in the thinner areas it was fairly flexible. When 7% RSG filler was applied on the fabric, some cracks appeared after drying. When it was applied on Melinex only, chalk nº2 had drying cracks. On canvas both chalks had cracks. There was also a large deformation of the fabric.	
	4% Isinglass (in water)	It was good to work with. The film formed by this filler was very brittle after drying (with both chalks and supports). Chalk nº1 did not contract after drying but chalk nº2 contracted when applied on fabric. Both chalks had drying cracks.	↑ very easy to apply, work and control. ↑reasonable working time

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[36] It should be noted, that the tests performed on pieces of fabric were not very realistic, because the fabric was not under tension (not stretched, as painting would be). Thus, when the fillers started to dry, deformation presumably due to the contraction of the fill materials was observed, however when the same fillers were also applied to the model painting none of them exhibited visible deformations or drying cracks.

	10% Isinglass (in water)	This isinglass (10%) filler was very good to work with and easy to manipulate (slightly better than the 4%filler). The working time was also reasonable (higher than fillers with gelatine and RSG). However, it was not as good as Mowiol. After drying this filler did not crack or shrink.	
Mowiol Fillers	**20% Mowiol** (in water)	Mowiol filler was very easy to handle. This filler was brittle after it dried, but appeared to be less brittle than the isinglass filler. It did not exhibit drying cracks.	↑easy to control. ↑ good working time

X.4 Investigating and choosing the re-lining technique:

Mist lining method was identified as the best choice for relining *João Luiz Lourenço*. Therefore, this process was tested with variations using an untreated lined canvas with similar characteristics to the original. In two of the three lining trials the adhesives were applied using different ratios of the two acrylic dispersions (tests nº1 and 2. see: adhesive application). In the third case, the glue on half of the canvas was sprayed to form a thin and even layer while on the other half the glue was not applied evenly (test nº3).

The variables tested are presented in Figures 41 and 41 and were the same for the tests nº1 and 2.

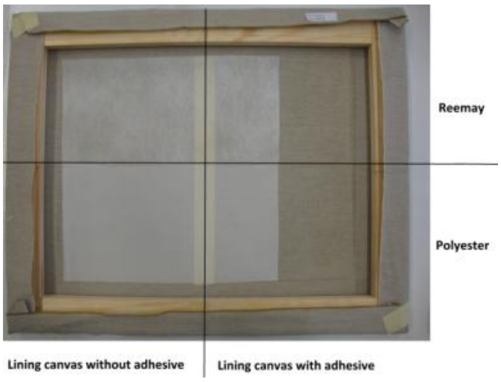
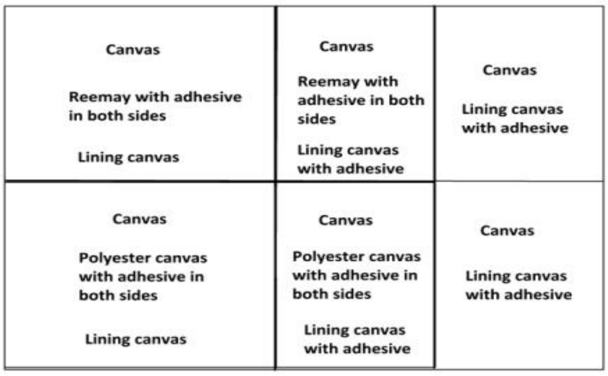


Figure 41: Lining canvas with adhesive (on one-half) and with the two interleafs. Interleafs had adhesive on both sides. On top of this, a piece of fabric was placed to simulate the "painting" to be lined.



Canvas Reemay with adhesive in both sides Lining canvas	Canvas Reemay with adhesive in both sides Lining canvas with adhesive	Canvas Lining canvas with adhesive
Canvas Polyester canvas with adhesive in both sides Lining canvas	Canvas Polyester canvas with adhesive in both sides Lining canvas with adhesive	Canvas Lining canvas with adhesive

Figure 42: Diagram representing the different 'layers' on each lining trial.

The tests performed were based on two articles by Och [43,44], a DVD about Lining[37] and on notes taken by Dr. Leslie Carlyle, Sara Babo and Diana Conde during a *Mist Lining* workshop in S.R.A.L. Maastricht, Netherlands (2011).

1) **Preparation of the Lining Canvas and Interleafs:**

Natural or synthetic lining fabric can be utilised [43], the selection depends on the requirements of the painting and on the environmental conditions expected for the painting after the treatment [43]. If a painting will be subject to relatively extreme climate conditions, then an inert lining canvas can be the best option [43]. Polyester fabric satisfies many criteria: high uniaxial tensile stiffness, good isotropic behaviour, resistance to degradation, stress relaxation and relative humidity [48]. Natural linen is reactive to RH (relative humidity) fluctuations, thus, the characteristics mentioned above of the polyester canvas are advantages over linen [48].

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[37] ICOM- CC Paintings group workshop current practice and developments in the structural conservation of paintings on canvas supports [DVD]. Helsinki Metropolia University of Applied Sciences. Degree Programme in conservation. Vantaa, Finland 16-18 September 2010

Considering that the painting will be stored in an uncontrolled environment with relatively moist conditions in winter (appendix IX), the most suitable choice for *João Luiz Lourenço* was determined to be a coloured polyester fabric (see suppliers, appendix XII). It has a similar appearance to linen but with more advantages than the natural fabric.

The lining fabric has to be slightly bigger than the painting to be lined – so three pieces of polyester fabric were cut larger than the fabric that was simulating the "painting". Each lining canvas was stretched onto a loom and using sandpaper it was roughened in both horizontal and vertical directions to increase and raise the nap of the fabric before the application of the glue (Fig. 43). A vacuum cleaner was used to remove any loose fibres, sand, and to further raise the fibres [43]. This operation promotes an open adhesive network, because the fibres "hold" the adhesive at the surface. The three looms were covered with plastic and sealed with masking-tape. The tape was used also to cover the tacking margins' areas before the application of the glue (Fig. 44). The area that is going to be sprayed must have the same footprint as the painting.

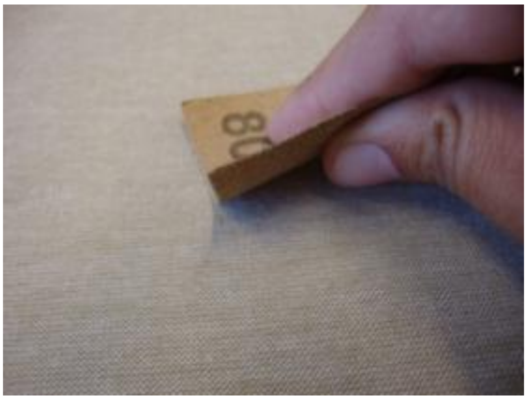

Figure 43: Each lining canvas was stretched onto a loom and using sandpaper it was roughened.

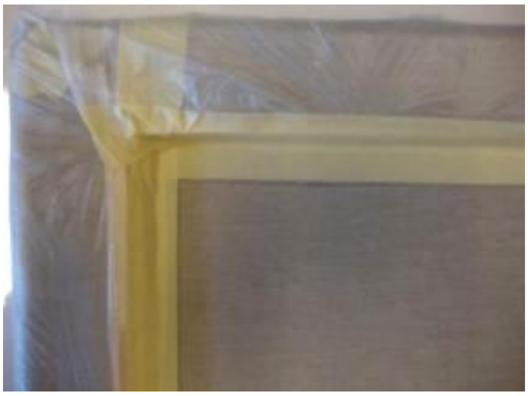

Figure 44: The three looms were covered with plastic and sealed with masking-tape. The tape was used also to cover the tacking margins' areas before the application of the glue

The two interleafs were also sanded in both sides. However, fibres could not be raised properly on the polyester fabric.

2) **Adhesive application:** Two formulations were tested.

- 70% Plextol K360, 30% Plextol D540. This formulation is the one generally proposed by Jos van Och[38]
- 60% Plextol K360, 40% Plextol D540: it was decided, at the suggestion of Jos van Och[39], to increase the amount of Plextol D540 (the harder material) to achieve a stiffer less flexible adhesive specifically for *João Luiz Lourenço* in an effort to reduce the painting's tendency to deform in response to humidity changes.

The amount of the glue mixtures was calculated according to the recommendation in the literature: 200ml/m^2.[7] The use of a thickener inhibits penetration of the adhesive into the fabric's fibres [43]. To both formulations the thickener Acrylic Rohagit SD was added. Because the thickener requires a neutral pH, and Plextol K360 is extremely acid (pH ~3), the pH of the K360 was increased with ammonia to a neutral pH 7.[6] To ensure that the glue layer forms an open web at the surface of the lining fabric (to enhance regeneration with solvent vapours

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[38] Och, J. March, 2011. [personal communication]. S.R.A.L. Studios for Paintings Conservation, Maastricht, Netherlands

[39] Carlyle personal communication, S.R.A.L. Maastricht, Netherlands, June 2012

[43]), a very thin layer was applied with vertical strokes at an angle around 45^0 using a spray gun held 10cm from the canvas surface (Fig. 45)[40]. The glue was sprayed in both sides of the interleaves, and on just one side of the lining canvas. The back of the painting is never sprayed; this facilitates removal of the lining in the future. In the case of Reemay and the lining fabric an open glue network was easily created (Figs. 46 and 47). In the case of polyester canvas this did not happened, because the polyester's fibres could not be roughened and raised properly. The adhesive was left to dry for 24 hours to allow the moisture and the solvent content to evaporate.

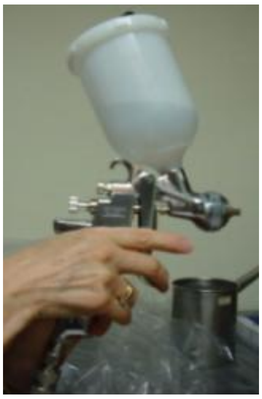

Figure 45: The spray gun used during the lining trial.

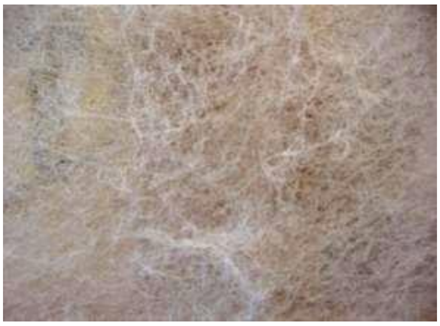

Figure 46: Reemay interleaf after the glue application.

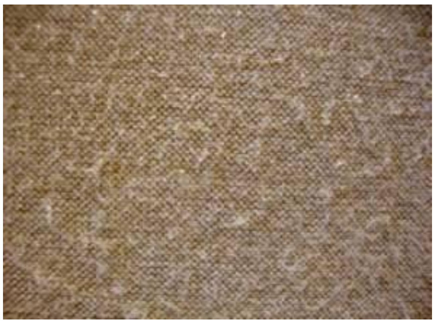

Figure 47: Lining canvas with glue dispersion.

3) Vacuum system

During the lining, a uniform and mild pressure is achieved on a vacuum table optimize the adhesion between the two canvases [43]. The sequence of the materials used in the vacuum table during the lining tests is represented in the following diagram (Fig.48).

1. The thicker *cheesecloth,* a cotton fabric with a close weave, was placed over the table surface; it allows better air circulation into the system.
2. A thin sheet of foam (0.3cm thick) provides a cushion to encourage any remaining deformations from plane to be forced into the back of the painting instead of the front during lining.
3. A very thin (approx. 10μ) Melinex sheet on top of the foam sheet allows the foam sheet to deform easily but isolates it from the lining fabric which will contain solvent that could attack the foam sheet (not available for testing, but included here as it will be used for the final lining)[41].

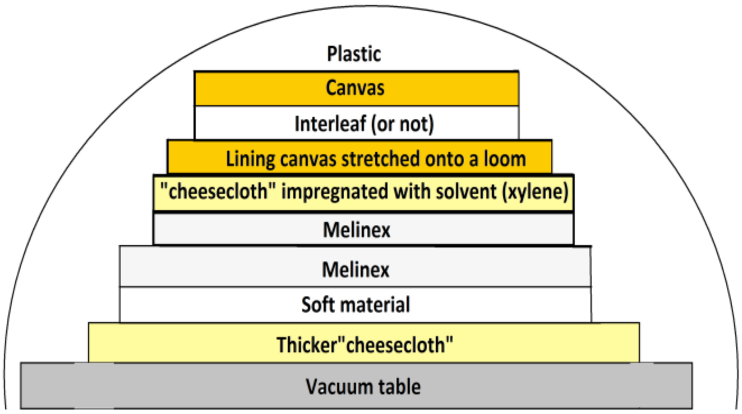

Figure 48: Diagram illustrating the various layers of materials used in the table top of vacuum during the lining

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[40] The 1.3 nozzle was used on the spray gun. This was oriented in the horizontal position and it was used at a pressure of 3bar. The glue was filtered before being placed in the spray gun.

[41] A sample of the extra-thin Melinex was kindly supplied by the Canadian Conservation Institute, with thanks to James Bourdeau, Nancy Binne and Jane Down.

4. A second sheet of Melinex is in place only while the *cheesecloth* with solvent is on the vacuum table, to facilitate removal of the cheesecloth when the adhesive is activated.
5. C*heesecloth,* an open weave cotton fabric, is used to deliver the solvent' vapours quickly and evenly through the reverse of the lining canvas.
6. The lining fabric with sprayed adhesive stretched over a loom
7. The painting registered exactly over the area coated with adhesive
8. A thin flexible plastic sheet is placed over the painting to create the top layer of the vacuum system. This sheet has two functions: to prevent the evaporation of the solvent and to allow a vacuum to be created in the lining system.

4) Reactivation of the adhesive layer

The dried lining adhesive is reactivated using solvents [44]. The choice of solvent and its quantity depends on the ratio of the two dispersions used in the mixture, but also it depends on the desired bond strength[7].
Solvents which may be used are[7]: Xylene; Xylene and Isopropanol; Ethanol; and a mixture of Shelsoll A and Isopropanol (8:2). Xylene was chosen as it provides the strongest bond. Solvent tests on *João Luiz Lourenço* determined that while xylene has a minor affect on the varnish layer, it does not damage the paint layer. During the Mist-Lining process, the reactivation of the adhesive is made by solvent vapours alone; the probability that the xylene vapours will affect the varnish layer is considered minimal, furthermore the varnish will be removed after the lining.
The reactivation of the adhesive took place as follows: the fabric that was simulating the painting was measured to determine the size of *cheesecloth* - it should be 10% bigger than the painting, because impregnation with the solvent can cause shrinkage of the tissue. Osh recommends the use of 30 - 60ml per square metre of xylene to evenly moisten the *cheesecloth* [44]. In tests nº1 & 2, 60ml of xylene was used, whereas in test nº3 30 mls were used. The goal was to explore how the quantity of solvent influences the adhesive bond.
Prior to the lining tests, the *cheesecloth* was folded and sealed with cling film and xylene was injected into the package with a syringe (Fig. 49)[42]. A second layer of cling film was then placed around the cheesecloth to cover the needle holes and the package was put under pressure to enhance even distribution of the solvent (it was placed between wooden boards and pressure was applied with two clamps) (Fig. 50). The solvent was left to diffuse for 2 hours.

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[42] The resistance of the cling film had been tested previously and in immersion in the solvent did not appear to suffer any changes.

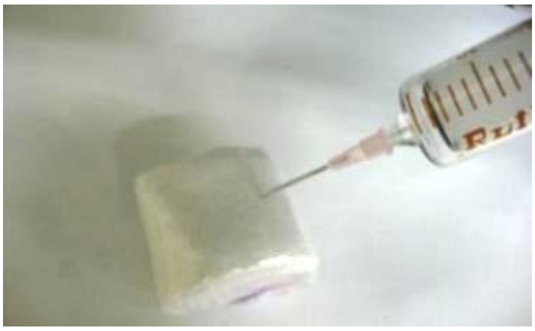


Figure 49: Xylene being injected into the '*cheesecloth*' package with a syringe.

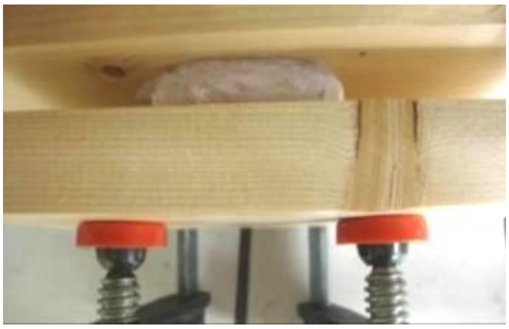


Figure 50: '*Cheesecloth*' package under pressure between wooden boards with two clamps.

After two hours the *cheesecloth* was unwrapped (Fig.51) and rolled out in on top of Melinex in the vacuum system (forming layer 5 see diagram above). The vacuum was turned on for 20 minutes while the adhesive was reactivated (Fig.52).

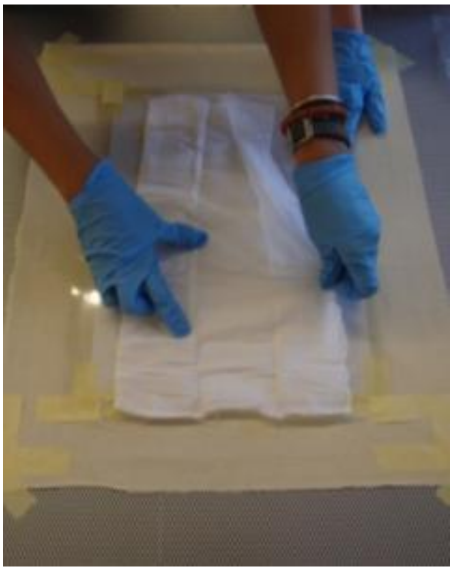


Figure 51: *Cheesecloth* being unwrapped.

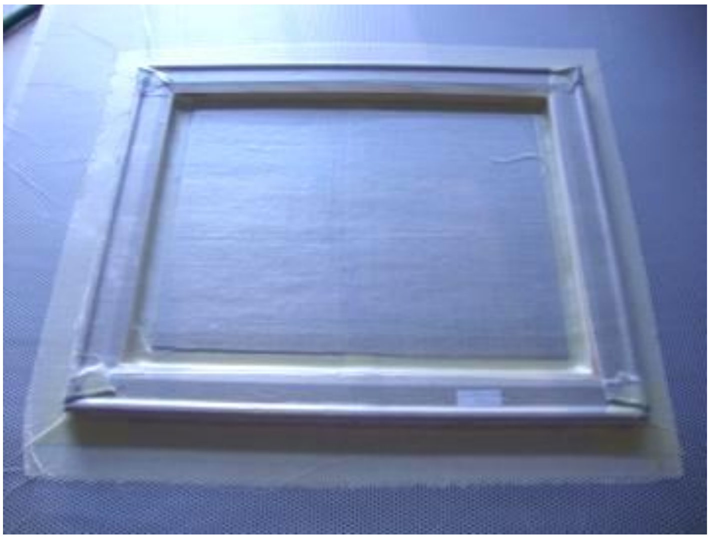


Figure 52: Adhesive being reactivated. The trial canvas under vacuum.

The lining process

After reactivation, the adhesive became tacky- at this point, the vacuum was stopped, the top covering of plastic was opened and the *cheesecloth* was removed. The system was covered again with the plastic and the vacuum was again turned on, leaving the system under pressure for about 2 hours. The amount of time and pressure determine the strength of the adhesive bond [43].

Appendix XI – Treatment Details

XI.1 Removal of stretcher and lining canvas

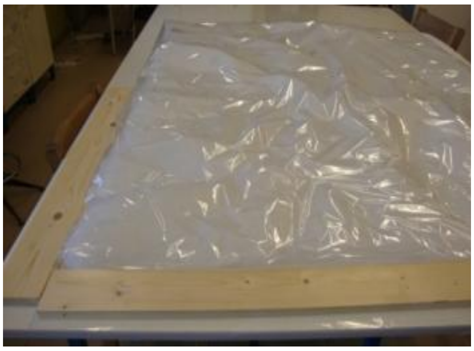


Figure 53: Cushioning material to accommodate and provide some support to the badly distorted painting while face down.

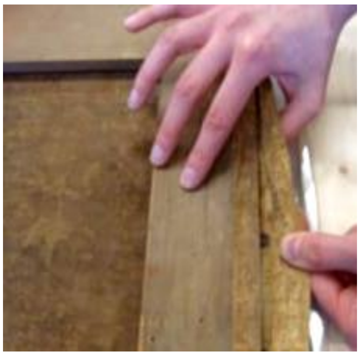


Figure54: Lining canvas being pulled away from the stretcher along the tacking margins.

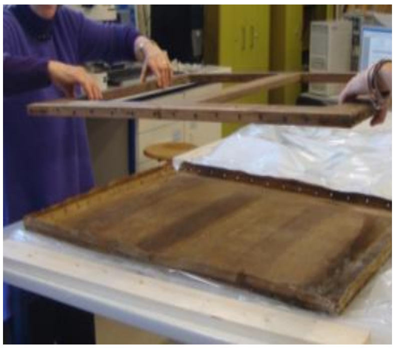
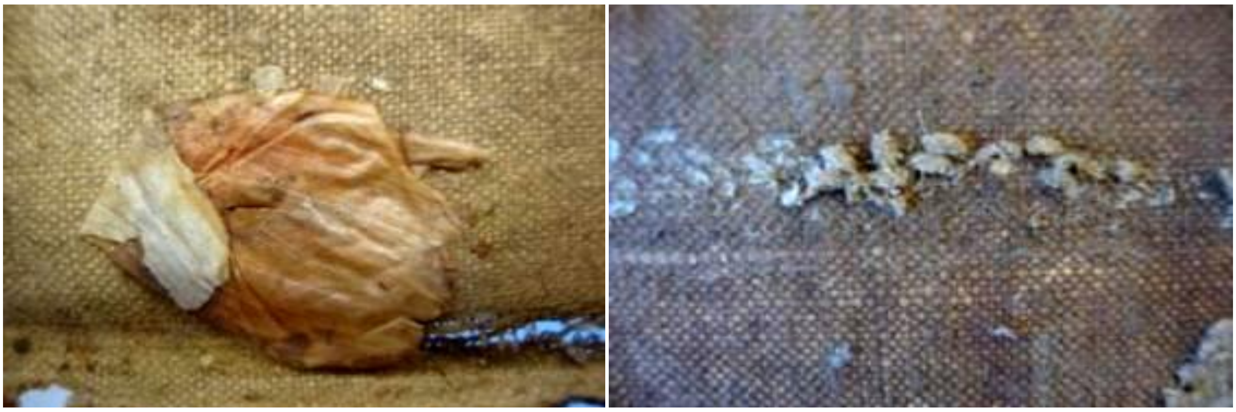


Figure 55: The stretcher being lifted off the back of the lined painting.



Figures 56a & 57: Lining canvas debris- a: a piece of old onion skin, and b. insect casings

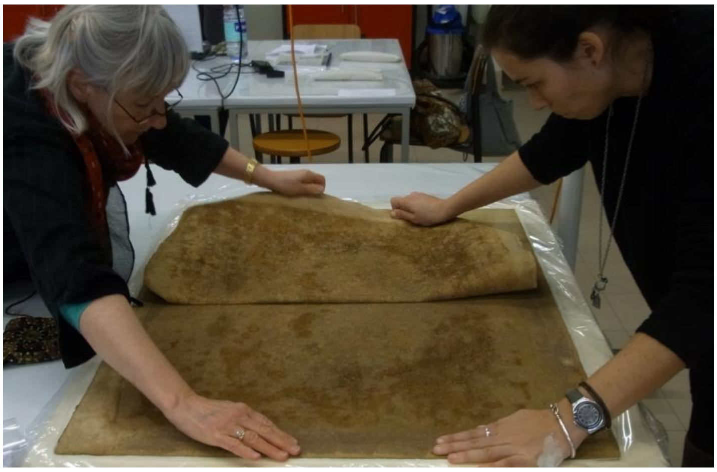


Figure 58: The lining canvas being

XI.2 Strip-lining and looming

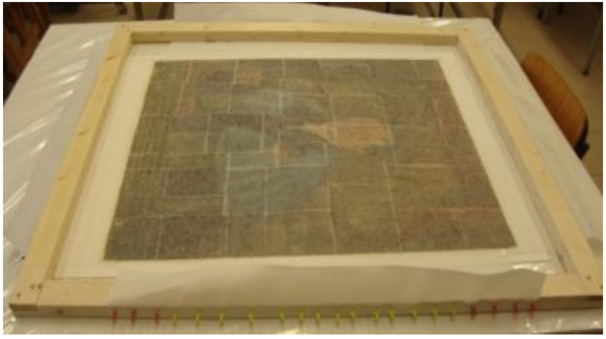


Figure 59: The painting is attached to the loom such that it is face up with the canvas back flat on the table.

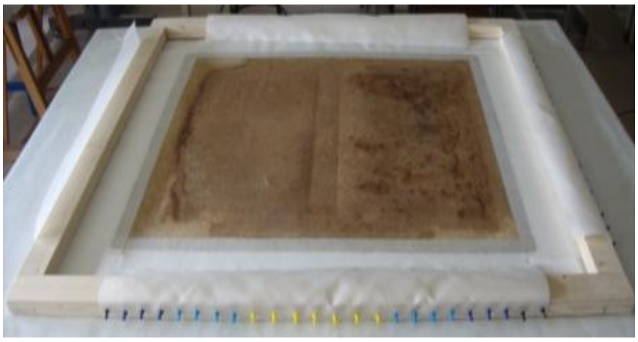


Figure 60: The painting is attached to the loom such that the canvas is face up with the paint surface flat on the table.

XIII.3 Treatment of deformations (flattening)

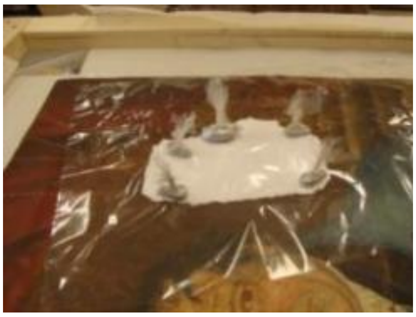
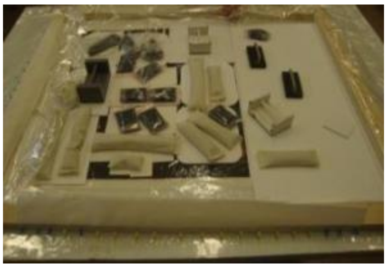
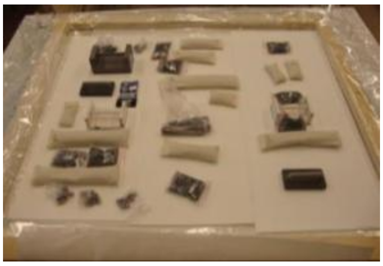


Figure 61: A slightly moist blotter on the surface of the painting to plasticise the paint/ground composite. Blotting paper had been moistened with water spray and left to equilibrate 3 to 24 hours before use to ensure uniform moisture delivery.





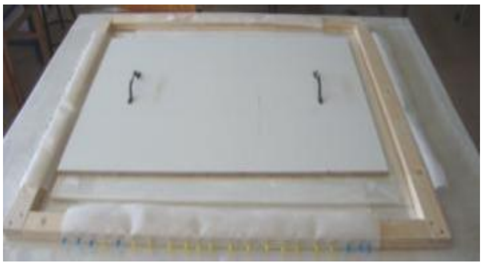


Figure 62: The painting protected with a Melinex sheet and with a series of small flat light-weight boards placed on top covered with weights

Figure 63: Three light-weight flat boards covering the entire painting with weights on top.

Figure 64: In the last phase of the flattening a card-board (heavier than those used before) was placed on top of the painting. Above this, a very flat and heavy particle board was used.

After the overall moisture treatment a sequence of weights were applied on top of the painting.

Appendix XII. Suppliers

Material	Suppliers
Gelatine	Super Cook. Select fine leaf gelatine platinum grade. 100% Pork- SUPERCOOK, Sherburn-in-Elmet Leeds, LS25 6JA, England. www.supercook.co.uk FCT Paintings Laboratory Stock[1] (purchased 2010, Dr Carlyle)
PVA	Neutral pH Adhesive. Archival Quality. INC. Lineco. FCT Paintings Laboratory Stock[1]
Rabbit Skin Glue	Kremer Pigmente GmbH & Co KG[2]. Hasengraupen aus Kaninchenfellen. Nº 63028. 1kg
Isinglass	L.CORNELISSEN & SON, isinglass 50gr. 22. Great queen street, Convent Garden, WC2B (purchased early 1999, Dr Carlyle)
Mowiol Resin	Kremer Pigmente GmbH & Co KG.Mowiol 4-88. Nº 67760. FCT Paintings Laboratory Stock[1].
Thin flexible sheet of plastic	Adeo Services: Rue Chanzy – Lezennes – 59712 Lille Cedex 9 – France. Leroy Merlin BricolalaJ SRL 0.007 mm; 2mx50m
Polyester fabric	Polyester Restoration Fabric – Russel & Chapple (purchased 2012, Dr Carlyle).
Coloured polyester fabric	Deffner & Johann: Polyestergewebe P110 ecru 215gr/m2 Breite 314 cm Nr. 2742320 http://www.deffner-johann.de/
BEVA371	Gustav Berguer's Original Formula 371 40% solution CTS s.a.s. FCT Paintings Laboratory Stock[1]
Plextol K360	Kremer Pigmente[2]: 76101. FCT Paintings Laboratory stock (purchased February 2012)
Plextol D540	Kremer Pigmente[2]: 76202. FCT Paintings Laboratory stock (purchased February 2012)
Acrylic Rohagit SD 15	Kremer Pigmente[2]: 76910. FCT Paintings Laboratory stock (purchased February 2012)
Akawipe Powder white	Kremer Pigmente[2]: 780638.12500.900. FCT Paintings Laboratory stock[1]
Chalk 1	Kremer Pigmente[2]: Champagner Kreide PW 18, naturliches Calciumcarbonat, nº 58000. FCT Paintings Laboratory stock[1]
Chalk2	Kremer Pigmente[2]: Leicht naturlich, nº 58490. FCT Paintings Laboratory stock[1]

[1] acquisition date not recorded

[2] http://kremerpigments.com/