

EESTI KUNSTIAKADEEMIA
Kunstikultuuri teaduskond
Muinsuskaitse ja konserveerimise osakond

Mihhail Staško

Conservation of painting „Saint John the Baptist“

Magistritöö

Juhendaja: Hillka Hiiop PhD
Merike Kallas MA

Tallinn 2017

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1. Introduction

The subject of the present thesis is related to the examination, conservation, and restoration of painting Saint John the Baptist. The idea of the master thesis degree work has been elaborated after the department of cultural heritage at Estonian Academy of Arts has received painting „Saint John the Baptist” for examination and recuperation. The painting has been retrieved from Estonian Art Museum depository where the painting has been stored since 1955.¹

By the time of first observation in Estonian Academy of Arts, it was evident that painting presents a number of practical and theoretical challenges. The work has been lined on a linoleum support, removed from taking edges, had a soiled thick and heavily decayed varnish, and most importantly exhibited a considerable loss and damage of pigmented layer, which visually distorted the paint surface to the ruin-like condition. Regarding aforementioned features, the question that arose was if the painting can still be recuperated or to which extent the „potential unity” of the painting can become visible and how promising will it be in terms of aesthetical representation? The further evaluation of painting’s condition through Cesare Brandi concept has indicated that the present painting is a ruin, where the historical aspect of value is brought forward while the aesthetical component of the artwork is reduced to the background.² However, the most important figurative elements of the painting still remain readable and thus allow to presume that the painting may be to certain limited extent recuperated. The main aspect of the present work consists in the practical intervention process that will consist of two main procedures, namely cleaning and retouching, as well as other procedures, however, less topical than the first two mentioned.

As an object of a “rich” material history, the painting presents interest as a witness to previous conservation interventions which led the painting to the present state of preservation. Thus one of the objectives of the work will be studying the previous conservation methods to determine the source of the damage effects visible on the surface of the painting as well as studying the lining method that is most rarely encountered on the wide scale practice.

In general, the theoretical part of the work will mostly consist of the methodological moment for finding the guidelines for practical restoration and conservation works. The art historical research will be mostly of secondary importance and have a superficial character. The damage

¹ Record of 19 march 1955, Document in the archives of the art Museum in Estonia

² C. Brandi , Theory of conservation I - Historical and Philosophical Issues in the conservation of Cultural Heritage , N. S Price , M. Kirby Talley Jr., A. M. Vaccaro , Getty Conservation Institute , Los Angeles , p 230-235

of the present painting is most likely the degree when the essential part of the painting is lost, making the stylistic analysis very difficult.

Thesis structural division and objectives

The work will start with the art-historical description that will include the overview of written documentation and description of several stylistic features of the painting that might provide a link to the painting's attribution. Considering the poor preservation state of the painting the stylistic analysis of the work is could be done only superficially.

The second section will describe the preservation state of the painting “Saint John the Baptist“ and will talk about the previous interventions in order to determine the possible source of the damage taken place on the painting during its material history.

The next section will return to the issue of paintings attribution and origin. Considering the stylistic analysis may not give a reliable link to the painting origin, a sufficient historical data is expected to be obtained through material-technical research which will include preparation layer cross-sections analysis, canvas fiber analysis and XRF analysis of pigmented layer in order to determine the structural composition of the painting materials.

The obtained data will be interpreted through the historical literature containing descriptions of painting materials employed in 17th and 18th centuries in different parts of Europe.

The possible treatments of structural and aesthetical damage of the painting will be described in the project design section that would allow to draw up some the ethical and practical guidelines for the treatment of painting “Saint John the Baptist”. The most important and extensive part of this section is cleaning. This part will make an overview of cleaning methods developments, starting from traditional solvent cleaning and moving to more recent aqueous cleaning formulations consisting of solvent gel formulations. The last section of the work will describe the intervention process including de-lining , cleaning, varnishing and retouching.

Literature and references

Technical research section

This research section will be composed of historical description of fabric supports, grounds, pigments and varnishes. The basic source for this section will be represented by the book "Conservation of Easel Paintings", the first comprehensive text on the history, philosophy, and methods of treatment of easel paintings that combines theory with practice. The additional sources are Y. Greenberg's book „Технология Станковой Масляной Живописи“, that contains overview of historical fabric supports, grounds, paints and varnishes, based on 17th-18th century treatises, Theodore De Mayerne „Pictoria, Sculptoria et quae subalternarum atrium” (1620), Francisco Pacheco „Arte de la Pintura“ and Paolo Palomino „El Museo pictórico y escala óptica” (1715).³ The technical extracts of original texts translated on Russian and can be found in Russian edition of Ernst Berger's book „Beiträge Zur Entwicklungsgeschichte der Maltechnik“.⁴ A comprehensive description of preparation systems development can be found in the texts of Prof. of University of Amsterdam Martje Stols-Witlox, describing recipes for canvas and wooden panel supports from 1500 and till 1900.⁵ History and technical data on pigments is available in books „Pigment Compendium”⁶, „Artists Pigments”⁷ and „Технология масляной живописи”⁸.

Previous interventions

The description of present lining method is considerably rare and is not encountered in the traditional literature or articles on the subject of lining. The only mentioning of linoleum lined painting was found in one of the abstracts of Rostov-on-Don Art Museum restorer V. V. Shulgin published in 1991⁹, describing the conservation of 17th century painting previously lined on a linoleum support. Materials used during the time period of 1600 -

³ Ю.И. Гренберг, Технология станковой живописи, Издательство изобразительное искусство, 1982

⁴ Э. Бергер, "История развития масляной живописи", Москва, Издательство Академии художеств СССР, 1961г.

⁵ M. Stols-Witlox, Historical recipes for preparatory layers for oil paintings in manuals manuscripts and handbooks in North West Europe, 1550-1900: analysis and reconstructions, Amsterdam School for Culture and History (ASCH), 2014

⁶ Pigment compendium: A Dictionary and Optical Microscopy of Historical Pigments, N. Eastaugh, V Walsh, Butterworth-Heinemann 2004

⁷ Artists' Pigments: A Handbook of Their History and Characteristics, Volume 3, E. West Fitzhough Washington: National Gallery of Art, 1986

⁸ А.В. Виннер, Материалы масляной живописи, под общей редакцией И.Э. Грабаря, Москва: Искусство, 1950

⁹ В. В. Шульгин, Особые случаи реставрации: Художественное Наследие. Хранение, Исследование, Реставрация. № 14. М.ГОСНИИР, 1991, p 42

1900.¹⁰ The other source will include book „Issues in the Conservation of Painting“ including a number of historical documentation describing the early methods employed in conservation.

Project design

The project design section will provide guidelines for de-lining, cleaning, varnishing and retouching. The ethical guidelines for retouching and cleaning will be provided through the work of Cesare Brandi and his followers. Cesare Brandi was an art critic and historian, specialist in conservation-restoration theory. In 1939 he became the first director of the Istituto Centrale per il Restauro in Rome and in 1963 he published „Teoria del Restauro”¹¹, a landmark theoretical essay on restoration, where reflected a fundamental theoretical compromise between aesthetical and historical requirements of the artwork representations. The philosophical ideas of Brandi were further exploited by Laura and Paolo Mora and Paul Philippot, who elaborated an ethical and practical guidelines for paint loss reintegrative technique known as *tratteggio*.¹²

In terms of cleaning of easel paintings the conflict of aesthetical and historical representations of art object are reflected in the notion of patina. Basing on Brandi’s idea of patina Paul Phillipot in text “The Idea of patina and cleaning of paintings “¹³, has determined that extent of cleaning should be determined according to the normal state of art object which implies both aesthetical representation and the physical alteration of composite material that together establish the artistic reality of the art object.

The technical part of the project design will mostly consist of describing the cleaning methods. The texts of A. Phenix and Sutherland provide the detailed information on the traditional cleaning tools represented by organic solvents, describing properties and effects of solvents on oil paint films¹⁴.

The alternative cleaning methods are provided through the work of Professor of Delaware University Richard Wolbers describing the alternative cleaning methods that is known as aqueous cleaning.¹⁵ The main idea of this method is to either restrain or substitute the

¹⁰M. Stols-Witlox, Historical restoration recipes: the cleaning of paintings 1600-1900,

https://www.academia.edu/19949929/Historical_restoration_recipes_the_cleaning_of_oil_paintings_1600-1900

¹¹ C. Brandi , Theory of Restoration I: Historical and Philosophical Issues in the Conservation of Cultural Heritage, N.S. Price , N. Kirby Talley, Getty Conservation Institute 1996 p339-342

¹²•P Mora , L mora , P Philippot, Problems of Presentation , Historical and Philosophical issues in conservation of cultural heritage , The gettu conservation institute , Loss Angeles 1996., p 343-354

¹³ P. Philippot , The idea of Patina and the cleaning of Paintings: Historical and Philosophical Issues in the Conservation of Cultural Heritage, N.S. Price, N. Kirby Talley, Getty Conservation Institute 1996, p 372-376

¹⁴A. Phenix and K. Sutherland , The cleaning of paintings: effects of organic solvents on oil paint films, Reviews in Conservation, Volume 2,IIC, p.47-60

¹⁵ R. Wolbers , Cleaning Painted surfaces : Aqueous methods , Archetype Publications , 2000

organic solvent application as it usually leads to leaching and erosion of the paint film that is described by Alan Phenix and Ken Sutherland¹⁶. The recognition of uncontrolled diffusion issue of solvents had led R. Wolbers to developing a set of water based cleaning gels that improve the delivering system of traditional free solvent cleaning. The latter methods lead to highly controlled and selective cleaning process that allows to deal with the cleaning situations that can not be solved by traditional methods. The description of aqueous cleaning methods is available via video course with R.Wolbers, “New Methods in the Cleaning of Paintings” recorded in 1991¹⁷ and books „Cleaning Painted Surfaces: Aqueous Methods.”¹⁸

¹⁶ Alan Phenix , Ken Sutherland , Cleaning of paintings effects of organic solvents on oil paint films : Sutherland, K., 'The extraction of soluble components from an oil paint film by a varnish solution' Studies in Conservation 45, 2000, pp. 54-62. www.viks.sk/chk/revincon10.doc

¹⁷ New Methods in the Cleaning of Paintings , A video Course with Richard Wolbers, recorded in 1991, <https://udcapture.udel.edu/misc/cleaningpaintings/>

¹⁸ R. Wolbers . Cleaning Painted Surfaces: Aqueous Methods, Archetype publications , 2000

2. General description

The painting depicts a figurative composition comprised of five light-colored figures counterposed on a dark background. The figures include a man figure, lamb and three angels. In the center of the composition the painting depicts a young man, with long hair and beard. Man figure is, half naked and wearing a piece of clothing made of animal fur. The man's sight is directed upwards into the sky. The man's figure is turned three-quarter and drawn upon a light colored support, reminding of a rock, which accommodates a manuscript. The lamb figure is located in the lower right part of the painting surrounded by plants. The upper sky area accommodates three angle figures; each composed of a head and feathered wings. The background details are hard to observe due to the poor preservation state of the covering layer. The upper left and right sides of the painting exhibit green-blue color surface, which is most likely to be sky part of a background landscape.

The present painting represents a religious scene, considering figures of the painting certainly obtain a symbolist religious character. The animal fur clothing and lamb figure on the right are attributes referred to Saint John the Baptist.

3. Historical background

The painting „St. John the Baptist” arrived to Estonian Art Museum in 1955. The painting has been stored in the building of former Estonian embassy in Moscow until in 1954 it was decided to move the painting along with the other 27 painting, 4 sculptures and a number of furniture objects to Estonian Art Museum in Tallinn. One of the objects transferred along with the painting “Saint John the Baptist” was the known painting „Samson and Delilah” . The arrival of the painting was recorded in the reception report where the present painting was mentioning under inventory number 342 and under the title “Mythological theme“. Both author and owner of the painting are not mentioned.¹⁹

Considering the poor preservation state of painting it is difficult to proceed with stylistic analysis because of greater part of the visual properties of the painting is lost. The observation of the remaining part of the painting allows to make a general presumption for the painting style and make a few parallels regarding the composition and some typical stylistic elements evident through the comparison with the other artworks .

¹⁹Record of 19 march 1955, Document in the archives of the art Museum in Estonia

The present painting is most likely refers to the beginning of the 18th century. The later can be red by the sense of grandeur and overt emotional content that is reflected by the lightning effect (on best preserved parts) and face expressions of Saint John and angels.

The similar pose and some of the composition elements can be found in one of Charles le Brun`s paintings „The Repentant Magdalena” dated to 1655.²⁰



Figure 1 . „The Repentant Magdalena”,
by Charles le Brun



Figure 2 . „Saint John the Baptist” unknown author

The angel figures located in the upper part of the present painting can be correlated with the panting „Baptism of Christ“by Francesco Trevisani (1656–1746).²¹

²⁰ C. Le Brun , „The Repentant Magdalena”, http://www.wga.hu/html_m/l/le_brun/magdalen.html
²¹ One of the paintings by Francesco Trevisani is preserved in Estonian Art Museum ,



Figures 3 - 6 . Left: fragments of painting “Baptism of Christ” by Francesco Trevisani (1656 – 1746) ; Right: fragments of painting “Saint John the Baptist “ by the unknown author.

Iconographical overview

John the Baptist is one of the most worshiped Saints in Christian tradition.

During his early life he began living in the desert an ascetic life, later began preaching and used baptism as a central symbol of sacrament. One of the most famous quotes of St. John is referred to prediction of Christ`s outcome:

“Look, the Lamb of God, who takes away the sin of the world. “²²

This verse is important both because it sees Jesus as the antitype of the Passover lamb whose blood protected the Israelites in Egypt.²³

In Western European painting tradition St. John is usually depicted in two appearances. The earliest tradition of Saint John`s portraiture depicts him as a middle aged man with long hair and wearing a beard. Later in 15th through the 16th century`s Renaissance artists started to depict John the Baptist as a beautiful youth or a handsome and well-muscled

²²John 1:29-27

²³R. Stracke, St. John the Baptist: The Iconography, Prepared in 2014, June 24 , august 29 , <http://www.christianiconography.info/johnBaptist.html>

young man. The hair, which is often an unruly mop in earlier images, is in later images a luxuriant mass of curls.²⁴

The important attributes that distinguishes St John are camel skin clothes, book, rarely a manuscript, leather belt, lamb and a cross. In Orthodox tradition St John can be also recognized by angel wings.²⁵

The given painting depicts John's life scene in the wilderness. The clothing symbolizes the ascetic life. The manuscript, similarly to the book denounces the start of preaching. Lamb is a symbol of Jesus Christ outcome.²⁶

²⁴R. Stracke, St. John the Baptist: The Iconography, Prepared in 2014, June 24 , august 29 , <http://www.christianiconography.info/johnBaptist.html>

²⁵ Е. Савкина , Иконография Иоанна Предтечи : "МИР ПРАВОСЛАВИЯ"№ 07 (136) июль 2009, <http://www.baltwillinfo.com/mp07-09/mp-10.htm>

²⁶Same

4. Present preservation state description



Figure 7. Front side



Figure 8. Back side

4.1 Support

The painting has a complex multilayered support structure consisting of a wooden wedge stretcher, linoleum lining, coarse canvas and original canvas. The last three layers of support were secured on the stretcher with metal nails applied from the front side of the painting.



Figure 9. Support structure

Stretcher

Wedge stretcher exhibits a satisfactorily preservation state. After the separation of the lined canvas from the stretching frame it has been revealed the present stretcher is smaller than the original canvas and thus can not be referred to the original part of the painting.

Lining

The initial observation of edges revealed that the lining consist of three layers:

1. Black linoleum
2. Coarse loosely woven cloth
3. Reddish brown adhesive

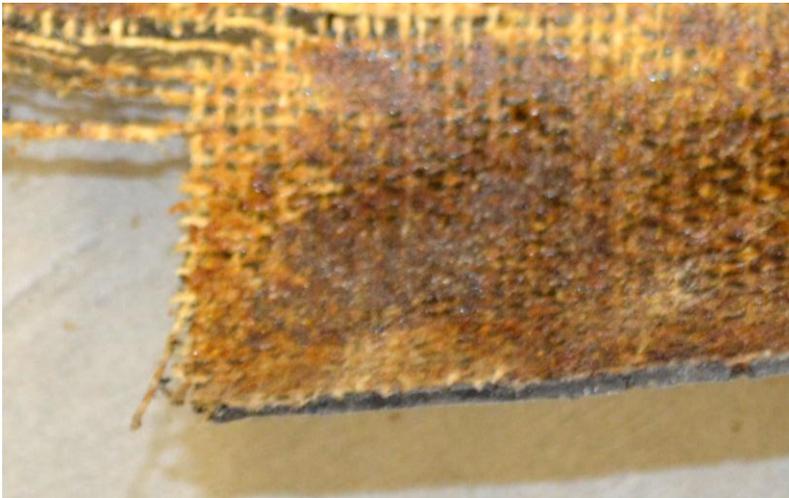


Figure 10. The fragment of lining support after the varnish removal

The linoleum and the coarse canvas support can be considered a single layer as the fabric was originally employed to serve as a support for linoleum film. For present lining structure it possibly functioned as a buffering layer that was used to reduce structural difference between original canvas and linoleum. The examination of the adhesive glue sample with ATR-FT-IR has indicated the presence of natural resin and no wax or oil additions consisting in the adhesive. The evidence of ironing has not been found neither on front nor on the backside of the painting. A presumption can be made that the lining was done using cold method.

In oil painting conservation the use of linoleum for lining support for canvas painting can be considered exceptional. Historically the lining methods employed in canvas painting conservation can be distinguished by the types of lining adhesives which generally include:

wax-resin lining, developed in Northern Europe (Holland , Flanders) , animal –chalk lining known as *pasta coletta* , developed in Italy, and sturgeon glue method developed in Russia.²⁷ The backing for all three lining adhesives generally consisted of canvas. The only evidence of linoleum lining method similar with the one used for the given painting has been found in the abstract of Rostov-on-Don State Art Museum restorer V. V. Shulgin describing conservation of painting «Cleopatra» by a Dutch painter Yan de Ban (17th century). The painting has been lined on linoleum which was fixed on a wooden frame with screws from the front side of the painting. The chemical analysis of the glue has indicated wax-resin paste which is different from the adhesive used for „Saint John the Baptist“. The resin component of the adhesive contained synthetic resin prepared on the basis of terpenes and colophony resin acids. Considering the surface observation Shulgin mentions the paint underneath the thick varnish layer has several burns resulted in the course of ironing of the painting from the front side to increase the adhesive bond between the original canvas and the lining support.²⁸ The latter procedure is less likely to have been applied to the present painting as it does not exhibit any signs on ironing and could have possibly employed cold lining method. In result of the ageing process linoleum has lost elasticity and became brittle and physically unstable. However the stable mounting on the stretching frame prevented it from deforming or forming cracks. The single hole can be observed from both back and front sides of the painting. This defect has possibly emerged in result of mechanical impact occurred on the front side of the painting.

Original support

The original fabric support represents a pieced canvas. The connection seam locates on the left side, which is visible on the front side by the fissure running down the surface of the paint.

The canvas is heavily impregnated with the lining adhesive (resin). None the less it seems that original canvas has preserved elasticity and fiber strength. The left part of the canvas exhibits a single hole near the head of St John and a 16 cm tear running down the lower left section of the canvas. The tear contains structural loss and during the previous treatment has been filled with a white water soluble putty.²⁹ The back side of the canvas additionally exhibits a scratch

²⁷M. Kallas , Conservation of Canvas paintings , lecture, Estonian Academy of Arts october 2014

²⁸ В. В. Шульгин , Особые случаи реставрации :Художественное Наследие. Хранение, Исследование , Реставрация. № 14. М.ГОСНИИР, 1991, р 42

²⁹ Possibly of animal glue origin

and a small area of weakened canvas where fissure in the picture layer has produced an additional weakening of the original canvas support.



Figure 11. A hole and a crack of visible from the front side of the canvas



Figure 12. A tear in the same section of the painting, and paint the structural paint losses

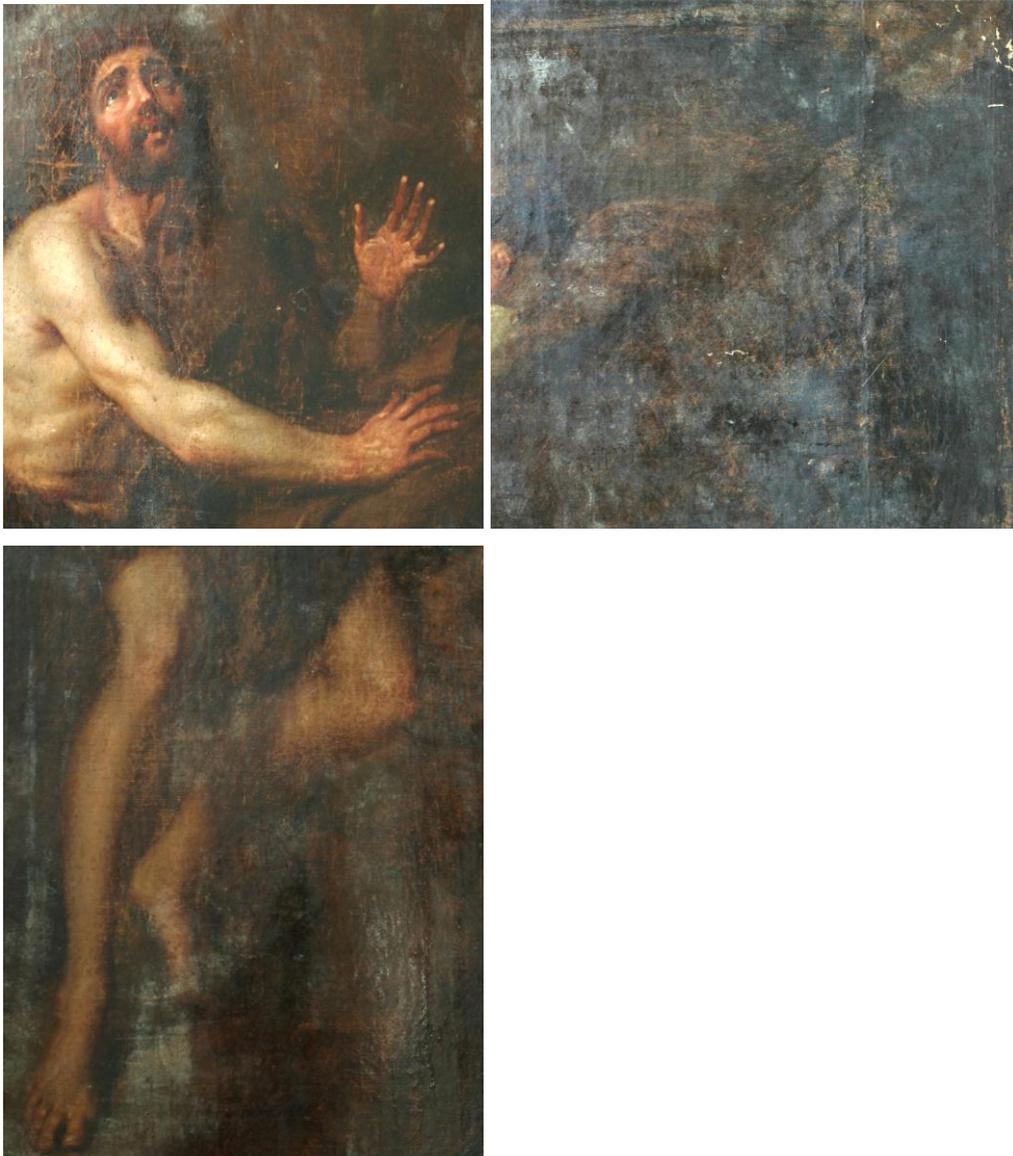


Figure 13. Lifted part of the original canvas

4.2 Paint layer and preparation layer

The paint layer of painting St John the Baptist represents an oil paint, which is evident by the saturation of color, impasto brushstrokes laid in the incarnate areas and a typical ageing cracklier. The paint layer exhibited a considerably poor preservation state and a number of structural damage types that were most possibly produced in the course of inappropriate cleaning and handling. The lower part of the painting is obscured by a heavy crazing or destructuring of varnish and can not be properly observed. The visible parts of the paint exhibit a total overcleaning damage with the image partially or entirely disfigured by the

damage. The larger part of the overcleaning damage is concentrated in the dark passages of the paint, both in and outside the incarnate area. The highlights of figures on the other hand remain considerably less damaged as they contain a strong lead white pigment.



Picture 14-16. Pictures illustrating effects of overcleaning on the painting „Saint John the Baptist“

Considering the scale of visible damage, it can be presumed that the glazing and scumbling that were commonly used by 18th century painters are likely to be lost together with the opaque layers of paint.³⁰ Regarding the scale and character of paint losses it can be presumed that the previous cleaning procedure had been performed using a very alkaline solution or an ethanol containing solvent. Another reason for the presence of paint damage consists in the lack of critical attitude.

³⁰ V. Elliott, *Traditional Oil Painting. Advanced Techniques and Concepts from the Renaissance to the Present*. New York: Watson-Guption Publications, 2007, p. 77

The left section of the paint exhibits a pronounced fissure about 2 cm in length running through the paint.

A part from overcleaning the painting surface exhibits structural losses especially prominent next to the tear area and in the lower section of the painting. The lower right corner of the painting exhibits small areas of lifted paint.

Both paint and preparation layer are partially missing on the edges of the painting and exhibit numerous fissures, paint and preparation layer losses, part of which were produced after nailing the canvas to the stretcher.

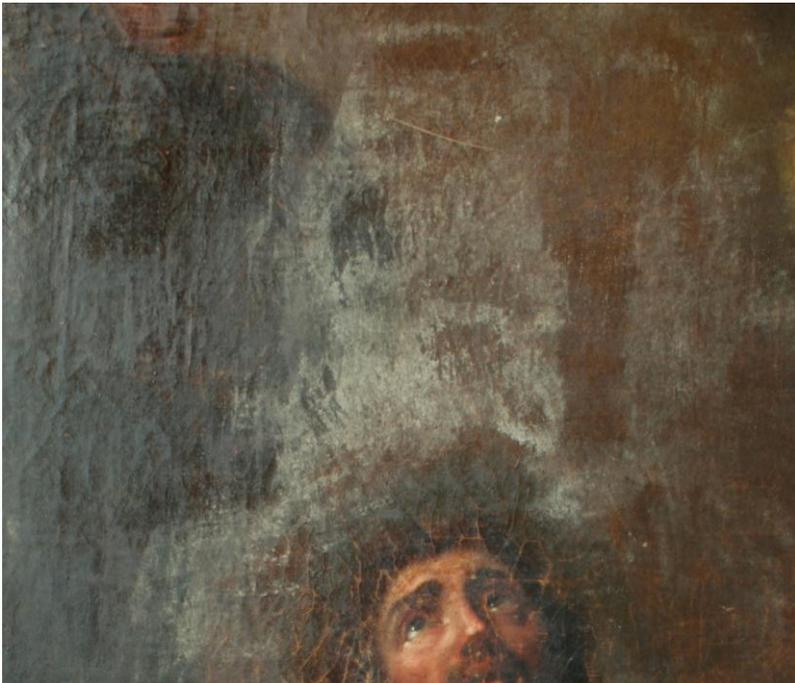
4.3 Varnish

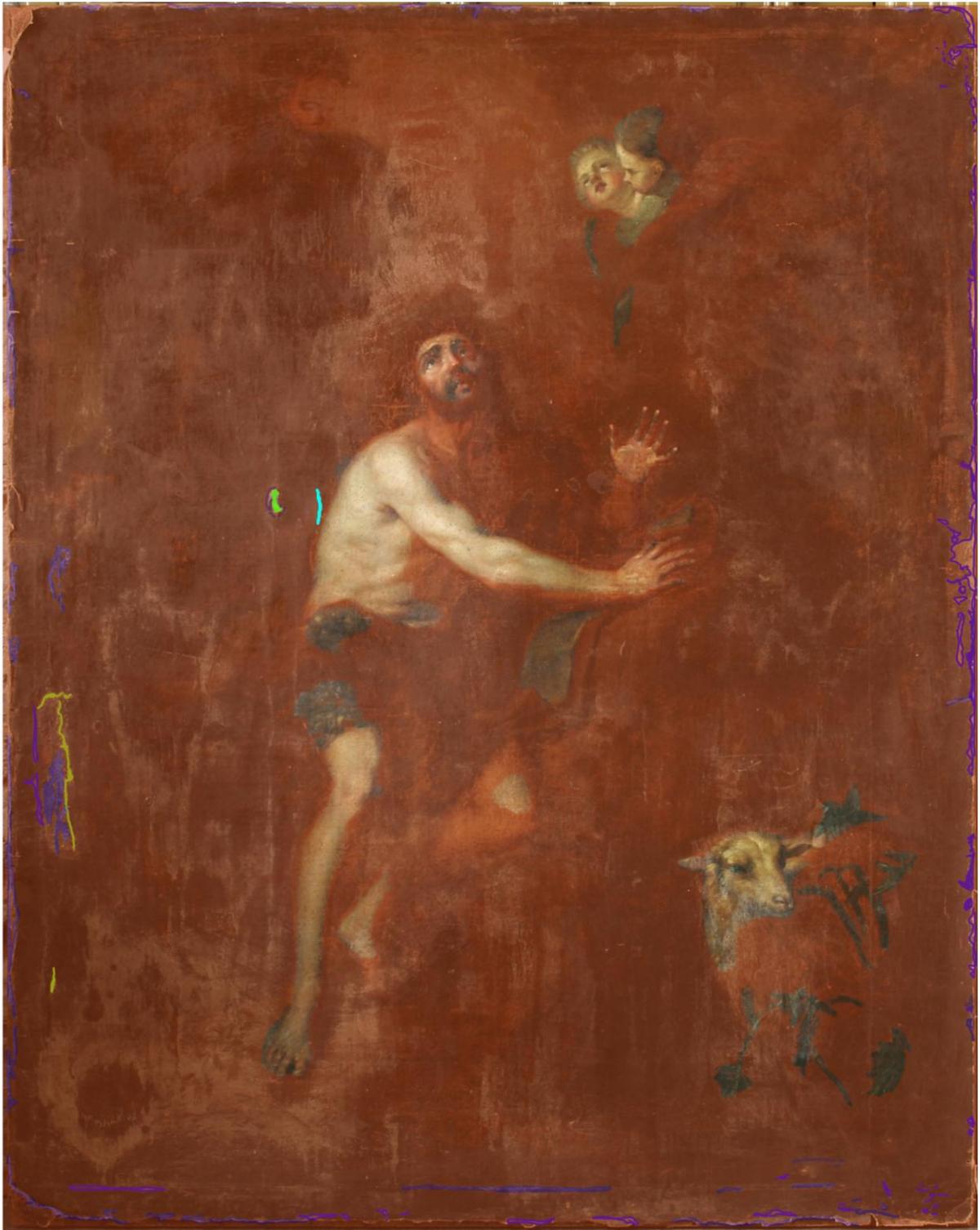
The gross observation of varnish has indicated numerous deterioration signs visible across the entire surface of the painting. The surface of varnish exhibit extensive blached areas which entirely obscured the paint. Light-colored areas of St John`s incarnate , angel heads and a small round piece on the lower left side remain relatively unbleached however the rest of the surface is either intermediately or entirely obscured by the light scattering surface of the varnish. The slightest mechanical stress produced by hand rubbing leads to powdering, which indicates destructuring of varnish known as crazing. Crazing represents formation of a large number of micro fissures leading to the ultimate loss of cohesion in the varnish layer. This defect is determined by the number of factors including low mechanical durability of triterpenoid resin varnishes and natural aging effect. The areas of varnish layer that have to certain degree preserved transparency exhibit a prominent aging and yellowing effects produced by the oxidation process.³¹

³¹ IAP: Science Refresher , Surface Cleaning Science for Painting ConservatorsBronwyn Ormsby, 8.5.14, Estonian Academy of Arts: Merike Kallas



Pictures 17-18. Close up photos illustrating varnish crazing process on the painting „ Saint John the Baptist“





- Filling/Putty
- Structural loss
- Hole
- Fissure
- Overcleaning, degraded varnish

Figure 19. Damage area mapping

5. Technical research

5.1 Support

Both of parts of the canvas have plain wave, intermediately coarse and exhibit thread count of 16 weft to 13,5 wrap fibers per one square centimeter . The original color of the canvas can not be visible due to the large amount of resin covering the canvas from the backside; however the samples taken from both pieces were cleaned with ethanol and exhibited a warm light color. The similar appearance of fibers taken from both canvas pieces allow to presume that the present canvas is most likely made from a single material.

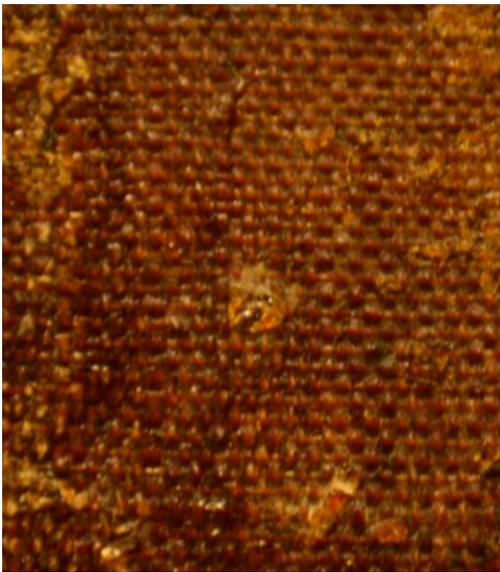


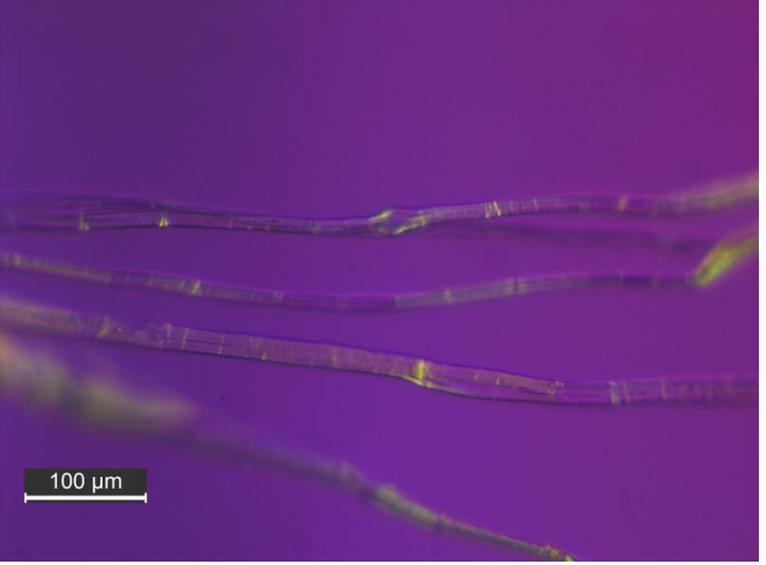
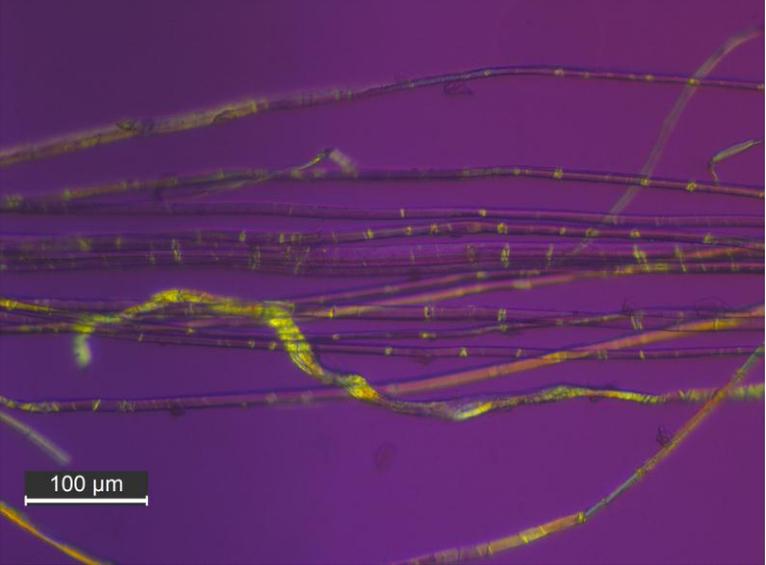
Figure 20. Plain wave canvas



Figure 21.. Canvas thread colour

Fiber identification

Fiber sampling	
Sampling methodology (steps)	<ol style="list-style-type: none">1. The fibers were separated from the surface with scalpel2. The fiber has been embedded into aqueous surrounding on a glass slide3. The yarn is separated onto a few single fibrils and covered with second glass slide.4. The sample is pictured under 200 X magnification using a polar filter

Sampling area and fiber type	Photo	Interpretation
Weft , upper right edge of the canvas		<p>The pictures indicate the presence of either flax or hemp. The ultimate fibers of hemp are similar to flax with subtle differences that are not always distinguishable microscopically on a small sample. The present sample exhibits two fibril alignments characteristic both for hemp and linen. Linen fibril alignment is visible in form of vertical lines running across the stem of the fiber. The fibril alignment of hemp can be recognized by cross or X fibril alignment visible inside the fiber.</p>
Wrap , upper right edge of the canvas		<p>The pictures indicate the presence of either flax or hemp. The ultimate fibers of hemp are similar to flax with subtle differences that are not always distinguishable microscopically on a small sample. The present sample exhibits two fibril alignments characteristic both for hemp and linen. Linen fibril alignment is visible in form of vertical lines running across the stem of the fiber. The fibril alignment of hemp can be recognized by cross or X fibril alignment visible inside the fiber.</p>

Drying twist method

Method description:

The general mean of distinguishing hemp from flax fiber is that the micro fibril spiral around the fibre axis in opposite directions. Relying to this feature fiber identification method has been developed. The drying twist test method is used to identify the predominant direction the micro fibrils wrap around a fibre, which for flax and hemp are in opposite direction. The spiral direction of the microfibril is species dependent and is described as a 'Z-type' or an 'S-type' twist. The test is preformed on single fiber or a fiber bundle of about 2 cm long. ³³

³²D. D. Mayer , Identification of textile fibers found in common painting supports, Conservation of Easel Paintings, Joice Hill Stoner, Rebecca Rushfield , Routledge, 2012 , p 322-323

³³D. D. Mayer , Identification of textile fibers found in common painting supports,..., p 325

Testing methodology :

1. A single or a number of fibrils are separated from the yarn in the water using needle.
2. As the sample fibril is sufficiently moistened in water it is dried with a drier or by holding it with the distant end of the fibril pointed down.

This method may not always work and may require several attempts to achieve a satisfactory result. ³⁴

Testing results:

During the several attempts with 4 fibers examined, only one fiber produced a counter clock-wise twist (s-type twist) indicating the fibers to be made of hemp, while other fibers have twisted in different directions simultaneously. Hence no confirmation of the obtained result has been obtained. To obtain a more certain result an additional examination is required using a more complex SEM observation.

Historical context

The two main types of fabric support used from the 15th to 18th century were mostly represented by either linen or hemp canvases. ³⁵

During the middle ages the fabric supports were known to be used for painting both in Southern and Northern European countries. In general fabric support were employed for portrait paintings, wings for wooden altarpieces, organ shutters, tapestries, banners and temporary street decorations. The Florentine Cennino Cennini (around 1400) in his tractate *Il Libro de Arte* described the preparation of unspecified canvas and taut stretched on the wooden frame which was used for painting, although the exact purpose and type of painting not specified. ³⁶

The relatively recent research of historical resources from 14th and 15th century has indicated that the use of textile support stems from the Northern European painting tradition. The 15th and 16th century Italian resources show that distemper paintings were imported from Flanders and were considered as a speciality of these area. „*Tüchlein*“ is the common term for early glue distemper paintings prepared on canvas support. This type of painting usually employed a fine plain weave linen and occasionally silk. Before painting the canvas was lightly sized with glue or gum and occasionally covered by a pigmented wash. In Brugge, the centre of canvas painting during the renaissance period, the painters were generally divided on two groups: the ones specialized in panel paintings and the others specifically employed with glue painting on canvas. Despite this professional

³⁴D. D. Mayer, Identification of textile fibers found in common painting supports,..., p 325

³⁵Ю.И. Гренберг, Технология станковой живописи, Издательство изобразительное искусство, 1982, p 70

³⁶C. Cennini, *Il Libro dell' Arte*, around 1400 - Translated by Daniel V. Thompson, Jr. New York: Dover Publications, Inc. 1933, <http://www.noteaccess.com/Texts/Cennini/10M.htm>

deviation some of the panel painting masters like Dirk Bouts and Dürer in Germany took advantage of this technique on par with panel painting. One of the most remarkable examples of *Tüchlinen painted by Dieric Bouts (1415 – 1475)* is represented by the painting „The Entombment” (1440-1455).³⁷

In Italy the painting on fabric support was known as „*German method*“ and was used mostly with a gesso ground for both glue distemper and egg tempera painting. The use of canvas has been seen in the works of Paduan artist Andrea Mantegna by (1431-1506). Forty one glue distemper paintings assigned to this artist were executed on fine linen support. Among the total number of canvases six exhibit twill wave while rest have plain wave.³⁸ The 15th and 16th century Venetian artists used coarse, usually twill or plain wave hemp canvases.³⁹ In the beginning of the 16th century the plain wave canvases were used by Venetian artists including Bellini (1430-1516), Titian (1485-1576) and Catena(1480-1531). Titian late works mostly include plain wave canvases of fine and coarse waves. Twill wave can be also seen in Titian work „*Ecce Homo*“. A herringbone twill has been found in Titian's work “*Vendramin Family*”. Twill wave canvas can be seen in the works of identified Bellini, Antonio da Venri, Girolamo dai Libri, Moretto, Moroni, and Veronese.⁴⁰

During the end of 16th and beginning of 17th century a trend towards coarser plain wave, sailcloth-like, canvases has been established.⁴¹ Although both hemp and linen could have been originally used both in Northern and in Southern Europe, some local trends still existed in 17th century. For instance in Holland artists preferred a tightly woven plain-weave linen canvases.⁴² By the 1680s, typical thread counts are down to 10 threads/cm to 16 threads/cm. Among the wave types plain and twill waves were the most common. A more complex damask twill wave canvases were mostly used for the ceremonial objects such as banners, or paintings of particular religious significance.⁴³

A detailed information on French artists fabric support is given by Katarina Vanderlip Carbonnel through study of 116 French artists canvases from the period of 1600-1700.

³⁷ H. Dubois, H. Khanjian, M Schilling, A late 15th century Italian Tüchlein, ZKK, 19.11.1997, Eesti Kunsti Akadeemia: Hilka Hiio

³⁸ C. Young, History of fabric supports, Conservation of Easel Paintings: Joice Hill Stoner, Rebecca Rushfield, Routledge, 2012, p 126

³⁹ The hemp manufacturing was flourishing in Italy until 1500, extract from Ю.И. Гренберг, Технология станковой живописи, Издательство изобразительное искусство, 1982, p 71

⁴⁰ C. Young, History of fabric supports: Conservation of Easel Paintings, Joice Hill Stoner, Rebecca Rushfield, Routledge, 2012, p 128

⁴¹ C. Young, History of fabric supports: Conservation of Easel Paintings, Joice Hill Stoner, Rebecca Rushfield, Routledge, 2012, p 128

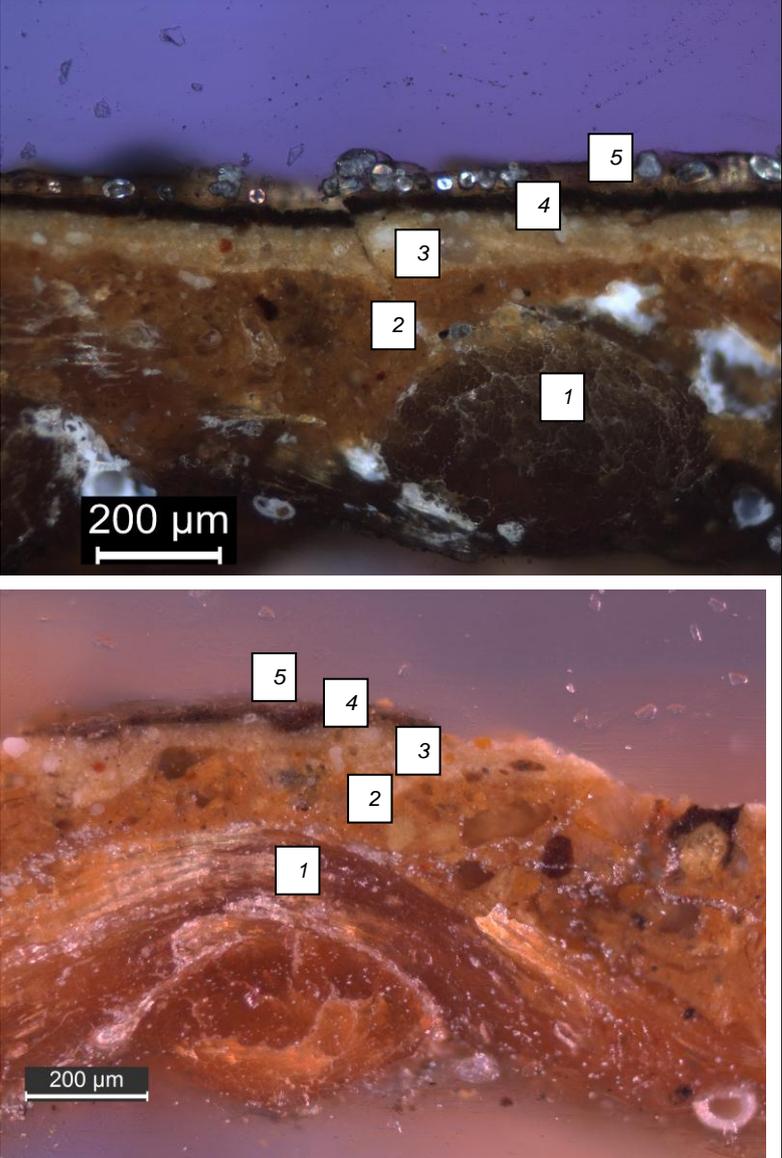
⁴² Ю.И. Гренберг, Технология станковой живописи, Издательство изобразительное искусство, 1982, p 70-73

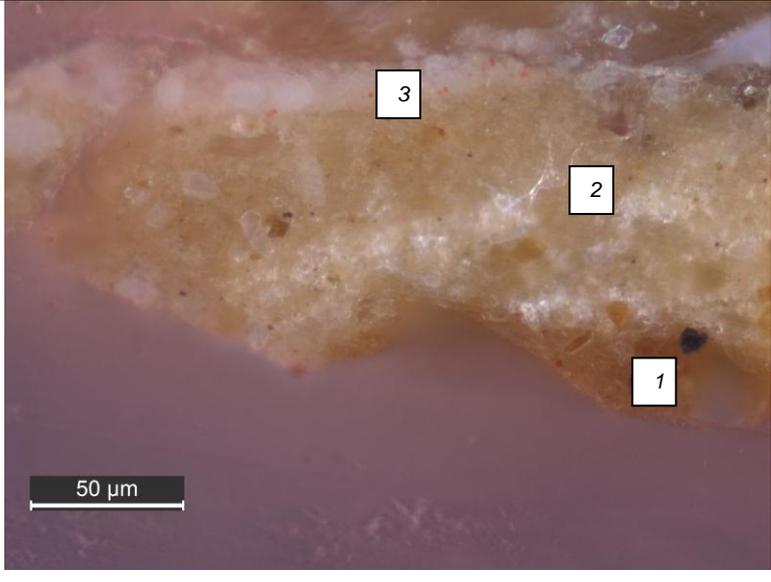
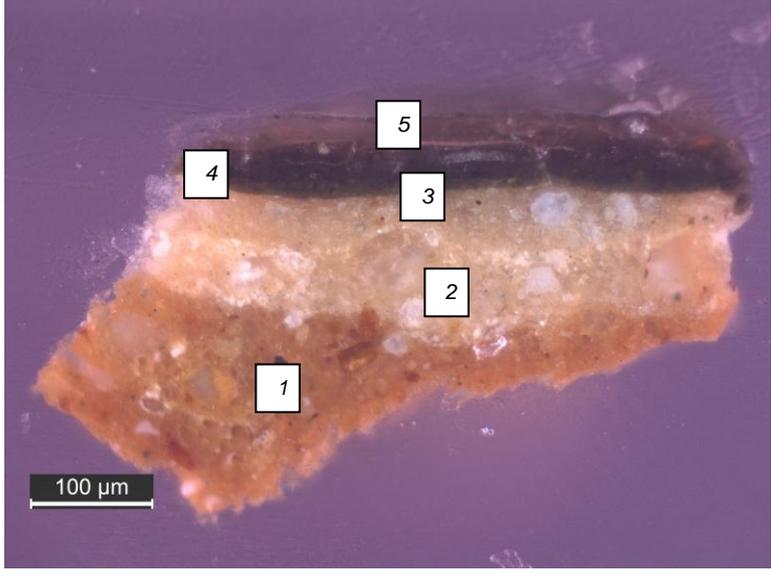
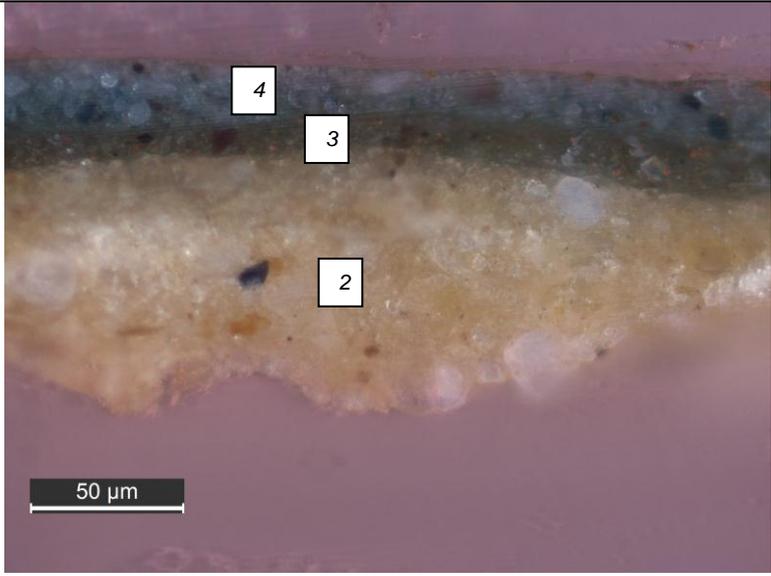
⁴³ C. Young, History of fabric supports,... p 128

The fiber identification tests have indicated 80 -92 % canvas samples to be hemp and 7- 20% to be linen. The 17th century French artists commonly used plain wave canvases and occasionally herringbone twill. A trend towards coarser hemp canvases has clearly been observed and had continued in the 18th the century. ⁴⁴

44K. Vanderlip Carbonnel , Astudy of French Painting Canvases, JAIC 1980, Volume 20, Number 1, Article 1, <http://cool.conservation-us.org/jaic/articles/jaic20-01-001.html>

5.2 Preparation layer

Color and location	Picture	Stratigraphic description
Black , incarnate surrounding	 <p>The figure consists of two micrographs showing the stratigraphic layers of a preparation layer. The top image shows a cross-section with layers 1-5 labeled. The bottom image shows a similar cross-section with layers 1-5 labeled. Both images include a 200 µm scale bar.</p>	<ol style="list-style-type: none"> 1. Canvas 2. Red-Brown ground 3. Light /White ground 4. Paint 5. Varnish

<p>Pinkish white, Incarnate area, shoulder</p>	 <p>50 µm</p>	<ol style="list-style-type: none"> 1. Red -brown ground 2. White/ ochre ground layer 3. Paint layer
<p>Black , black background , upper left edge</p>	 <p>100 µm</p>	<ol style="list-style-type: none"> 1. Red-brown ground 2. Whitish ground layer (possibly consistent of two layers) 3. Intermediate paint layer 4. Paint layer 5. Varnish
<p>Blue , landscape area (sky)</p>	 <p>50 µm</p>	<ol style="list-style-type: none"> 1. Reddish brown (polished away) 2. White /light ochre ground layer 3. Intermediate paint layer 4. Paint layer 5. Varnish (removed)

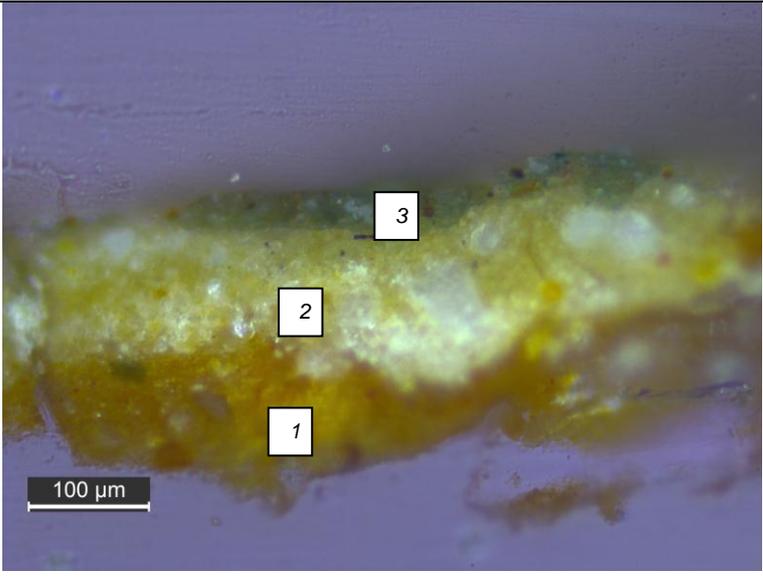
Green, plants , lamb figure surrounding		<ol style="list-style-type: none"> 1. Reddish brown ground layer 2. White / light ochre color ground layer 3. Green paint layer 4. Varnish (removed)
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Table 1 , Cross-section analysis via 250X magnification

Result interpretation

The observation of cross sections has indicated the presence of thin preparatory system containing two layers. The observation under 100-400 x magnification of five samples indicated the presence of the brown filler containing in the lower layer, this feature allows to make a presumption about the presence double ground layer preparation system. The first ground layer was possibly applied considering the economic and pragmatic reasons as to fill the interstices of the canvas and proved a uniform surface for the following coating containing more expensive pigments. The following light ground layer can be referred as a final ground that provided the painting with a basic color for painting. In the given painting, it clearly serves as a color base for the incarnate design which also proved by the cross-section taken from the area of Johns figure.

The cross-sections of blue, black exhibit an intermediate layer containing a coloring. Considering the fact that this layer has been found only in individual areas of paint while absent in the others, for instance incarnate, the layer can not be considered as a part of the preparation system. Thus this layer can be considered the first layer of paint applied semi-transparent on the initial stages of painting.

Originally the use light colored double grounds in the 17th century has spread from the Netherlands and Flanders to France, England and Scandinavia.⁴⁵ De Mayerne manuscript (1620-1644) describes ten double oil based grounds that employ a first reddish layer covered by a second lead white based layer. In one of the recipes, the lead-based upper layer is

⁴⁵M. Stols-Witlox, *Grounds, 1400–1900: Conservation of Easel Paintings*, Joice Hill Stoner, Rebecca Rushfield, Routledge, 2012, p 179

supplemented with charcoal black and a small amount of umber to assist the drying. De Mayerne recipes also include clay fillers. In a recipe of the „little painter“ bole is mixed with a smaller quantity of umber and ground in oil as the first layer for canvas, previously sized with animal glue. This layer is afterward coated with lead white based oil ground with additions of umber, yellow ocher or “burnt red”.⁴⁶ De la Fontaine (1679) describes a double ground consisting of a layer of umber and „brown red”, covered with a second ground containing lead white tinted with umber and a little carbon black.⁴⁷ Later, during the eighteenth century, differently colored top layers were used such as ochre, pinkish gray, light brown. The tendency to apply lighter grounds might have been related to the awareness of the dark ground effect in combination with the aging effect of oil paint; by becoming more transparent in result of aging processes the paint exposes the dark ground in the highlight areas changing the tonal balance between the objects.⁴⁸ This can be considered a reason by which the whitish layers of grounds have eventually spread in Southern of Europe in the first decades of the 18th century. In Italy, artists such as Guardi, Canaletto, Batoni, and Tiepolo were using double oil grounds with lead-white-based top layers. Tiepolo also used yellow ochre top layers and made smaller-sized paintings on single red earth grounds.⁴⁹

The exact reason for use of such grounds is not entirely clear. De Mayerne (1620-44) notes:

“if one wishes to save one could make the first layer of ocher before applying a lead white based ground layer”.⁵⁰

Thus a link to the economic reasons can be made. Cheaper materials could have been used to fill the intersites of the canvas and provide a more uniform surface. The final opaque priming layer was applied for the aesthetic reasons and served as a basic color for painting. The other reason may have consisted in the precaution measures taken when the primed canvases were bought from the colourmen. The suspicion for low quality of ground preparations had led the

⁴⁶Theodore De Mayerne „Pictoria, Sculptoria et quae subalternarum atrium” ,1620: Эрнст Бергер, История развития масляной живописи, Москва, Издательство Академии художеств СССР, 1961г. p 340-341, p 231 , p 242-243, p 345, p 342-343, p 358, p 407-408

⁴⁷J. H. de La Fontaine, , L'Académie de la peinture, Paris, 1679: M. Stols-Witlox, Historical recipes for preparatory layers for oil paintings in manuals, manuscripts and handbooks in North West Europe, 1550-1900: analysis and reconstructions, Amsterdam School for Culture and History (ASCH), 2014, p 115 <http://hdl.handle.net/11245/2.149676>

⁴⁸ Д. И. Киплик Техника живописи, Искусство: Москва 1950, p 276

⁴⁹ M. Stols-Witlox, Historical recipes for preparatory layers for oil paintings in manuals, manuscripts and handbooks in North West Europe, 1550-1900..., p 176

⁵⁰Theodore De Mayerne „Pictoria, Sculptoria et quae subalternarum atrium” (1620): Эрнст Бергер, История развития масляной живописи, Москва, Издательство Академии художеств СССР, 1961г. p 242-243

painters to apply a finishing coating themselves in order to reinsure the quality of the surface used for painting.⁵¹

5.3 Underdrawing and corrections

In general terms, the underdrawing is considered a structural basis of the painting. For technical research, the identification of the underdrawing is particularly valuable as it may provide the insight into the artist's original plot and eventually provide a link to the attribution of the painting, by making comparative stylistic analysis with drawings of the same painter. The author of the work Saint John the Baptist remains unknown and thus the present investigation can be used as a guide for the paint layer reintegration phase.

Starting from the 15th century the underdrawing can be encountered in two forms one is applied freehandedly and the other is applied via pounced drawing. According to Cennino Cennini, the work started by performing a drawing on a cartoon. The drawing was later transferred by the means of pounced drawing⁵² and outlined freehandedly with charcoal, lead pencil, dark color egg tempera or ink.⁵³ The evidence of such drawing method can be seen in the works of Northern European masters of the 15th and 16th century. One of most famous examples is the Ghent altar painted by van Eyck, where the slight tracing dots remain visible under IRR. Some of the 16th-century masters like Titian preferred working more freehandedly, starting from charcoal drawing directly on the ground surface and making further corrections during the painting process. The research of Titian's work have revealed that Titian used an opaque paint to cover imprecisions on the later stages of painting.⁵⁴

De Mayerne described a freehanded underdrawing preparation which employed charcoal, chalk, black oil paint or ink. He emphasized that painters preferred to remove most of the soft drawing material after its completion, in order to prevent spoiling the paint that was applied afterwards. This was usually done with a feather or by blowing.⁵⁵

⁵¹M. Stols-Witlox, *Grounds, 1400–1900: Conservation of Easel Paintings*, Joice Hill Stoner, Rebecca Rushfield, Routledge, 2012, p 176

⁵²The pounced drawing made of pricked holes is laid over a new working surface. A powder such as chalk, graphite or pastel is forced through the holes to leave an outline on the working surface below, thus transferring the image. [https://en.wikipedia.org/wiki/Pounce_\(art\)](https://en.wikipedia.org/wiki/Pounce_(art)), page was last modified on 12 March 2017, at 04:21.

⁵³C. Cennini, *El Libro dell' Arte*, around 1400 б Translated by Daniel V. Thompson, Jr. New York: Dover Publications, 1933, <http://www.noteaccess.com/Texts/Cennini/10M.htm>

⁵⁴National Gallery Technical Bulletin: Titian's Painting Technique before 1540, volume 34, Ashok Roy National Gallery Company London 2013, p 17-21

⁵⁵T. De Mayerne „Pictoria, Sculptoria et quae subalternarum atrium”, 1620 : Э. Бергер, "История развития масляной живописи", Ред. Л. Азарова, М. Ушкова, Москва, Издательство Академии художеств СССР, 1961, p 362-363

The IRR is a non-invasive method of studying a painting which allows to look beneath the visible layer of paint and examine the underdrawing along with any changes or *pentimenti* present in the work.⁵⁶ The long wave light produced by IRR lamp is able to penetrate through the layers of paint and reflect from the light colored grounds and at the same time being absorbed by the carbon-rich materials usually present in the underdrawing. When the long wave light is reflected into IRR camera it is recorded and allows to observe the underdrawing and corrections made in the preliminary stages of the painting process.⁵⁷

The IRR observation of „St John the Baptist“ has been performed with Osiris InGaAs Camera using 1600-1700 nm (nanometers). The observation of obtained image has indicated that no charcoal underdrawing is present under the paint. The initial outlining was presumably done freehandedly using a dark brown paint. The IRR picture allowed to view the correction made on the left foot, which is covered by the opaque lead white containing paint. Apart from that the outlines of the damaged areas of John`s incarnate became more traceable as well as overall composition became more clear.

⁵⁶ Introduction to Infrared Reflectography, Opus instruments ,
<https://www.opusinstruments.com/infrared-reflectography/introduction-to-irr/>

⁵⁷ Same



Figure 22. The IRR photo of painting „St. John the Baptist“ . After Varnish removal.

5.4 Pigment layer

Pigments

XRF examination has examined number of pigments present on the surface of the painting. The main issue of the present study consists in the identification of white blue and red pigments which can be considered the most specific and characteristic for the individual historical periods.

Sampling area and test code Nr	Color	16th and 17th cnetury pigments	XRF results (detected metals)	Interpretation:
Johns incarnate Shoulder , N 515	White	<ul style="list-style-type: none"> • Lead White • Znic white 	Pb, Fe	Lead White
Lamb incarnate, head N 516			Pb , Fe	Lead White
Johns incarnate, N 519			Fe , Pb , Hg Cu(?) , Ca(?)	Lead White , Vermilion red
Angel incarnate, N530			Fe , Pb , Ti(?), Cu (?)	Lead White , Titanium White ?
Bark backfground area, N526	Brown	<ul style="list-style-type: none"> • Van Dyck Brown (Fe O) • Brown (Fe O) 	Fe , Ca , Pb	Van Dyck Brown, Umber
Plants near the lamb incarnate (leaves) N527	Green	<ul style="list-style-type: none"> • Cooper resinate (Cu(C₁₉H₂₉COO)₂) • Verdigris (Cu(OH)₂) • Emerald green (Cu) • Green earth malachite (Cu) 	Fe , Pb , Cu , Ti(?) , Ca(?)	Unidentified. Presence of cooper may point to the presence of every single green piment mentioned in the paint.
Angel incarnate, N 517	Red	<ul style="list-style-type: none"> • Red ochre (Fe₂O₃) • Realgar sulfide (As₄S₄) • Red lead Pb (Pb₃O₄) • Vermilion HgS 	Pb, Hg , Fe, Ar , Ca, Cu	Vermilion
John`s icarnate, N 521			Pb, Fe, Mo, Ca(?), Cu(?)	Red ocher (?)/ Red lead (?)
John`s icarnate, cheek, N 522			Pb , Fe , Cu (?), Ca (?)	Red ocher (?)/ Red lead (?)

Landscape , Sky area, right and left sections, N 523, N524	Blue	<ul style="list-style-type: none"> • Cobalt ($\text{CoO} \cdot \text{Al}_2\text{O}_3$) • Ultramarine ($\text{SiO}_2:\text{Al}_2\text{O}_3$) • Azurite ($2\text{CuCO}_3$) • Smalt $\text{SiO}_2(65\%) + \text{K}_2\text{O}(15\%) + \text{Al}_2\text{O}_3(5\%) + \text{CoO}(10\%)$ • Prussian blue ($\text{C}_{18}\text{Fe}_7\text{N}_{18}$) 	Fe, Ca , Pb , Zn(?) Ti(?) Cu (?)	Unidentified. the presence of Cu can be represented by the small green pigment residue not intentionally mixed in the blue paint. The presence of Iron (Fe) may point to the presence of Prussian blue .
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Table 2 . XRF testing results , areas marked with (?) indicate uncertainty if the mentioned element is present. The elements of XRF result that are marked with red indicate the greatest amount of element consisted in the tested area(s) . For more details see Appendix III.

Historical and technical data

White

Lead white -(native mineral is cerusite) is a carbonate of lead which was in use since antiquity and was prepared from metallic lead and vinegar. It was the only white used in European easel paintings until the 19th century when its poisonous lead content restricted its manufacture and sale as an artist's pigment. Lead white is also the fastest drying of all of the whites because of the catalytic action of the lead pigment upon the oil. The high hiding power of the lead white became the reason why this paint became adopted for oil priming.⁵⁸

Blue

In general there are three blue pigments used until the beginning of the 18th mainly consisted of three pigments : ultramarine, azurite and smalt. In the beginning of 18th century two pigments were substituted with the artificial Prussian blue pigment.

Ultramarine blue- a complex sulfur-containing sodium aluminum silicate , one of the finest and most stable early blue pigments. Ultramarine is known since ancient times. The initial name of the pigment is known as lapis lazuli named by the stone from which the pigment

⁵⁸Pigments through the ages : Lead white , <http://www.webexhibits.org/pigments/indiv/overview/leadwhite.html>

was obtained. Starting from 6th century lapis lazuli was mined in the mountain valley of Kokcha, on the territory of Afghanistan.⁵⁹ Later in the middle ages it was transported to Europe possibly through Venice, where it obtained the name of ultramarine.⁶⁰ During the middle ages and in later periods ultramarine was considered the main blue pigment used for painting. Ultramarine was extremely expensive, exceeding the cost of gold. It seems that the use of this pigment was influenced by size of the painting, status of the painter and commission. During the late renaissance period and baroque ultramarine was widely used in Italy and less frequently in Northern Europe, where painters preferred azurite. In Spain both written evidence and examination of paintings pointed out that the use of ultramarine was occasional and has not been used as frequently as in Italy. Considering the high cost and economical reasons, ultramarine was often mixed with cheaper pigments like azurite or applied as a thin final glazing layer while the lower layer consisted of cheaper pigments.⁶¹

In 19th century ultramarine became produced artificially and became more available.

The identification of Ultramarine blue implies the use of ATR-FT-IR analytical technique.⁶²

Azurite - a deep blue pigment composed of mineral basic carbonate of copper. Comparing to ultramarine it has a lower color stability and after certain time period the color of the pigment shifts to green and darkens⁶³.

Azurite was employed as a painting pigment as early as the fourth Dynasty in Egypt, however, then it was not commonly used. During the Middle Ages, Renaissance and Baroque it became one of the most important pigments of easel painting, employed mostly as an under layer, an admixture or a cheaper substitute for ultramarine. One of the main sources of azurite located in Hungary. During the middle of the 17th century the part of the country was occupied by the Turks and the azurite supply to the other countries were cut off. The use of Azurite continued until the beginning of 18th century after which it was substituted with a more stable Prussian blue pigment.⁶⁴

⁵⁹ Pigments through ages, Ultramarine, <http://www.webexhibits.org/pigments/indiv/overview/ultramarine.html>

⁶⁰ Artists pigments: A Handbook of Their History and Characteristics, Ashok Roy, volume 2, ultramarine, p 38

⁶¹ M. P. Merrifield. Medieval and Renaissance Treatises on the Arts of Painting, cxi-cxiii

⁶² Pigments through the ages, Ultramarine, <http://www.webexhibits.org/pigments/indiv/technical/ultramarine.html>

⁶³ Pigments through ages, azurite, <http://www.webexhibits.org/pigments/indiv/technical/azurite.html>

⁶⁴ Artists pigments: A Handbook of Their History and Characteristics, Ashok Roy, volume 2, p 23

Azurite is easily detectable through XRF by the presence of copper (Cu).⁶⁵

Smalt - a ground blue potassium glass containing cobalt used from 15th to 18th centuries. Among the artists pigments it became wide spread in the 16th century as cheapest available blue pigment. It continued in use until the discovery of Prussian blue in the 18th century.⁶⁶

The general version of pigment's initial employment and production in Europe was originally related to the discovery made by Christian Schürer, a Bohemian glassmaker. However it seems that the pigment was known much earlier. Cobalt based blue pigment was used in Egypt since the 27th century BC, and later on in Persia. The blue colored cobalt glass was also known in mid 15th century in Venice, however the manufacturing recipe was kept in secret by glass makers.⁶⁷

Considering the issue of identification of the pigment it is possible to detect it using The ATR-FT-IR.⁶⁸

Prussian blue – Iron(III) chloride, also commonly known as Berlin Blue, Iron blue, Saxon blue, Antwerp blue.⁶⁹ Prussian blue is a stable pigment exhibiting a high resistance to atmospheric agents.⁷⁰

Prussian blue became one of the first artificially made pigments. Manufactured accidentally between 1704 and 1707 it was discovered by an alchemist Dippel and the colormaker Diesbach, both whom were recorded as working in Berlin. The initial recipe was kept in secret.⁷¹ The details of initial manufacturing method were first published in Philosophical transactions journal describing alkali calcined with bullock's blood dissolved and brought to boiling point and a solution of alumina and ferrous were added while boiling.⁷² The first written evidence mentioning this pigment is dated to 1710 in an anonymous paper in Latin. The employment of Prussian blue in easel painting on large scale practice is seen after the 1720s,

⁶⁵ Pigments through ages, azurite, <http://www.webexhibits.org/pigments/indiv/technical/azurite.html>

⁶⁶ Artists pigments: A Handbook of Their History and Characteristics, Ashok Roy, volume 2, p 114

⁶⁷ Ю.И. Гренберг, Технология станковой живописи, Издательство изобразительное искусство, 1982, p 157-158

⁶⁸ Pigments through ages, Smalt, <http://www.webexhibits.org/pigments/indiv/technical/smalt.html>

⁶⁹ Artists' Pigments: A Handbook of Their History and Characteristics, Volume 3, E. West Fitzhugh Washington: National Gallery of Art, 1986, p 192-193

⁷⁰ А. И. Винер, Материалы масляной живописи, по общей редакцией И. Грабаря, государственное издательство „Искусство“, Москва, 1950, p 302

⁷¹ <https://babel.hathitrust.org/cgi/pt?id=uc1.32106014957564;view=1up;seq=196....>, p 193

⁷² Artists' Pigments: A Handbook of Their History and Characteristics, Volume 3...., p 193

before this time the application of this pigment was occasional.⁷³ The known early application of Prussian blue for easel paintings has been dated to 1722, used by Andriaen van der Werf and in two paintings by Canaletto as well as at least one painting by Antoine Watteau. Kirby reported on the use of Prussian blue demonstrating occurrence by 1712 in Berlin and before 1721 in England.⁷⁴

Considering the initial dissemination of this pigment, Diesbach communicated the method to his pupil de Piere who began to manufacture it in Paris. The pigment immediately became popular not only in Europe but also in America where it was used as early as 1723 for interior painting. The study of European easel paintings studied by Kühn showed an increase in use of Prussian blue during the period of 1700-1800. The use of pigment continued in 19th and 20th century.⁷⁵

It is possible to detect this pigment using ATR-FT-IR whereas the XRF is less reliable.⁷⁶

Red

The main elements that may possibly indicate the type of red pigment use are Iron, Mercury and Lead. Considering the high iron and lead contents are present in every area examined these elements are most likely present in the layers located underneath the paint layer. The presence of Mercury on the other hand points directly to the presence of Vermilion.

Vermilion- also known under name cinnabar, a Mercury sulfide mineral (cinnabar) used from antiquity through to the present though only scarcely due to its toxicity. Made artificially from the 8th century (vermilion), it was the principle red in painting until the manufacture of its synthetic equivalent, cadmium red.⁷⁷

5.5 Varnish

The painting St, John the Baptist has been previously varnished at least two times. The cross-section sample taken from the upper right part of the painting has indicated single layer of varnish present, however the gross observation, UV and cleaning tests of the painting have indicated that the varnish coating consists of first fragmented varnish and the second continuous varnish coating. The first fragmented layer may possibly represent the original

⁷³Same

⁷⁴Pigment compendium: A Dictionary and Optical Microscopy of Historical Pigments , N. Eastaugh, V Walsh, Butterworth- Heinemann 2004 , p 314-315

⁷⁵Artists' Pigments: A Handbook of Their History and Characteristics, Volume 3,..., p 195

⁷⁶ Pigments through ages , Prussian blue , <http://www.webexhibits.org/pigments/indiv/technical/prussblue.html>

⁷⁷ <http://www.webexhibits.org/pigments/indiv/history/vermilion.html>

coating which was partially cleaned and afterwards masked with a second varnish. However considering the total overcleaning of the paint the lower layer of varnish is most likely another conservation varnish applied in the course previous intervention. The surface of both upper and lower varnishes exhibited a greenish-blue fluorescence which allowed to indicate that both coatings contained triterpenoid resin like dammar or mastic. The ATR-FT-IR spectroscopy analysis of cleaning swabs containing lower varnish residues have indicated that the lower varnish contains triterpenoid resin and a protein component which can be an admixture or a glue residue that that was left after facing application which employed during the lining process.



Figure 23. Photo of second fragmented varnish visible under UV Light

Historical context

Starting from the 15th and until the 20th century the choice of varnish for the easel painting varied between oil based and spirit based varnishes. This distinction is not clear cut as every type of varnish mentioned implied a small additions of either resin or oil to improve its properties in terms of durability and gloss.⁷⁸

The oil varnishes, thinned necessary for use, were possibly the most commonly used varnishes until the mid of the 16th century.⁷⁹ During the 17th century spirit varnishes were widely adopted for paintings throughout the Europe. Many varnishes of spirit and oil varnishes were mentioned in the manuscripts of De Mayerne and Palomino.⁸⁰ The writings of De Mayerne in particular, made the distinction between the oil based and spirit based

⁷⁸A. Phenix and J. Townsend, A brief survey of historical varnishes: Conservation of Easel Paintings, Joice Hill Stoner, Rebecca Rushfield, Routledge, 2012, p 253

⁷⁹A. Phenix and J. Townsend, A brief survey of historical varnishes,..., p 255

⁸⁰Э. Бергер, "История развития масляной живописи", Ред. Л. Азарова, М. Ушкова, Москва, Издательство Академии художеств СССР, 1961г.б, p 217, p 236

varnishes, indicating that the spirit varnishes were used for more delicate effects, while if the varnishes were made with oils (nut and linseed) the varnish will be “more beautiful and have more body. Amongst the resins for the spirit varnish preparation he mentioned: mastic, sandarac, gum juniper, gum anise, shellac, amber, and benzoin; for the dissolving media the oils of turpentine, spike lavender, and petroleum were mentioned. In 18th century is marked with the use of copal based spirit varnishes that were one of the most commonly used type during the century.⁸¹

5.6 Conclusion of material technical –research

The present part of the research remains incomplete and presents a number of questions that are unanswered. The first topical question of present research consists in the issue of presence and origin of titanium white in the structure of the painting. Titanium white is a titanium dioxide pigment, first became manufactured as a pigment in 1921 in America.⁸² In the present painting this pigment could have derived from several sources:

- it could have been applied together with a retouching paint
- originally used as a part of the paint
- is included as a natural impurity on one of the structural layers

The second objective is to identify the blue pigment. The XRF analysis has indicated iron in one of the structural layers of painting. The iron can possibly be the composite of Prussian blue pigment in the paint or earth pigment consisted in the ground layer.

In order to complete the present research the samples of picture layers were taken from white, red, green and blue paint areas. Using ATR-FT-IR, SEM and cross-sections observations it will be possible to confirm the presence of the titanium white pigment in the structure of the painting and indicate its exact location. The same analytical methods will be used to analyze the blue pigment present in the paint samples.

In addition to pigment issue the present research has also failed in identifying the support type used for the painting which can be either hemp or linen. The later issue will be similarly resolved by the means of SEM analysis.

⁸¹Theodore De Mayerne „Pictoria, Sculptoria et quae subalternarum atrium” , 1620 : Э. Бергер, "История развития масляной живописи", Ред. Л. Азарова, М. Ушкова, Москва, Издательство Академии художеств СССР, 1961г., p 296-297

⁸² Titanium white , History of Titanium white,
<http://www.webexhibits.org/pigments/indiv/history/titaniumwhite.html>

6. Project design

6.1 De- lining

Step 1 : detachment of Lining support

Remove the linoleum from the stretching frame. Criteria: as the paint is nailed from the front side and through the paint layer, the demounting must be done in a way that would not damage the paint layer.

The de-lining process will start from removing of linoleum support and lining adhesive. The rigidity of the linoleum support leads to restriction of the canvas movement and stress on the picture layer. The densities difference between original canvas and linoleum can lead to the subsequent detachment of the picture layer from the canvas. The consequences of the present lining type can be traced on the example of Jan de Ban painting "Cleopatra" which was lined using the same method. V.V Shulgin described the conservation process and has mentioned that original support exhibited deformation and a poor connection between the paint layer and support.⁸³

The most simplest method of de-lining is to remove it mechanically by dragging one of the lining support edges with intermediate tension, promoting the detachment by the means of dumb instrument..

Step 2 : Lining adhesive removal

The main objective of this procedure is to uncover the back side of the canvas in order to allow it to move freely. By removing the lining adhesive residue the original canvas will be allowed to „breath” and freely move under the influence of atmospheric agents. Leaving the lining adhesive in place, on the other hand, may produce tension centres which will eventually cause deformation of the support and hence threaten the stability of picture layer.

Options:

- Remove the lining adhesive using dry mechanical method. Comparing to chemical methods it is considered one of the safest. Regarding the present issue the sand paper Nr 150 and Nr 300 can be used to carefully remove the covering layer of resin and expose the threads.

⁸³ Extract from abstract composed by V. V. Shulgin : *Авторский холст картины ранее был дублирован на линолеум, имеющий грубую тканую основу... линолеум вызвал жесткую волнообразную деформацию вместе с авторским холстом, так что вся поверхность живописи была покрыта жестким кракелюром с приподнятыми краями.*

- Poultices have been used throughout the conservation practice for cleaning and moistening of the various surfaces. Traditionally they take form of adsorbents as their action generally can be defined as ability to adsorb another substance.⁸⁴ In general poultice consist of a retaining material such as gels, paper pulps, sponges and fabrics, and cleaning liquid that is the main cleaning component in the system. The working properties of most of the poultice cleaning systems depend on capillary action, and diffusion.⁸⁵ At the moment when poultice is placed on the object it begins its action by releasing the solvent into the structure of the substrate by the means of capillary forces; as the solvent breaks and dissolves the foreign material the solution is dragged back into the poultice by the means of same capillary force. The cleaning can be controlled by the means exposure time and capillary size which varies according to the vehicle. Poultices are successfully used for staining treatment on ceramics, textile and paper. Their cleaning action consists in the ability to work not only on the surface but also induce its cleaning action into the structure of fabric material in a gradual and highly controlled way thus allowing to extract the materials that are inaccessible for the cleaning solvents applied in free state.

6.2 Structural conservation: support

Considering the extent of structural material loss and the fact that the canvas has preserved fibre elasticity and strength, the present painting is by no means the issue of total lining. Considering the fact that original taking margins were lost in the course of previous intervention one of the tasks will be to reintegrate new margins in order to stretch the canvas on the wooden stretcher.

The second objective of the present procedure is stabilize and reintegrate the canvas structural losses in order to retain the continuity of the support as well as preventing further dissabilization in the loss areas. Patching or local application of canvas backing may satisfactory serve the aforementioned requirements. In general, two categories of materials employed in the patching and lining procedures can be considered:

Choice of fabric

⁸⁴Adsorbents, Farlex free dictionary, <http://www.thefreedictionary.com/>,

⁸⁵Emma A. Schmitt, Examination of the Working Properties of Agarose Gels for Textile Conservation, master thesis, School of Culture and Creative Arts, University of Glasgow, 2014, p16, Antwerp University: Natalie Saez Ortega

Patching and inlays are the means of the canvas loss reintegration process primarily related to the structural stability. The choice of the fabric has to correspond to the extent of damage present in the canvas, whether the damage is a puncture, tear, or a loss of certain part of the material.

On one hand, the choice of lining fabrics for patching is related to the compatibility with original canvas in terms of mechanical and visual properties. At the same time, this can be considered disadvantage as the backing canvas covering the original support from the back side is sensitive to moisture and by reacting with moisture it can counteract with the original support. Thus, in order to the improved structural reintegration of the canvas losses, it is preferable to choose the same type of canvas as the one employed for the original painting.

For tears, punctures and least damaged areas of the canvas, it is recommended to use polyester fabrics as a backing material. The advantage of the latter material consists in the low hygroscopicity and the minimal ability to interact the movement of the original canvas. The polyester fabrics present in the conservation studio at Estonian Academy of Arts are considerably thin and can only be used to support small tears and weakened part of the original canvas.⁸⁶

Adhesive:

The main factors to be considered for the choice of the patching and strip lining adhesive consists in the inertness of the material in relation to the original painting material and reversibility.⁸⁷

- Animal glue

A traditional material for of adhesive used for patching, thread by thread tear mending and lining. In free state application animal glue has a tendency to impregnate the canvas threads due to the property of low surface tension. The glue may eventually reach the preparation layer, and interact with it leading to visual alteration of the picture layer. In order to modify the flowability of glue, a wheat paste is added to the glue to act as a thickening agent which will restrain the flow of the glue and at the same time will act as plasticizing material. The

⁸⁶ Conservation of canvas paintings , consultations with M. Kallas , April 2017

⁸⁷ Е.В.Кудрявцев, Техника реставрации картин, 2002, <http://art-con.ru/node/105>

general limitation of the animal glue based adhesives consists in the ability contract and swell, deforming the original support together with the picture layer.⁸⁸

- BEVA 371

A complex synthetic resin and wax mixture, formulated as a stable adhesive capable of providing strong, reliable bonds. It was initially employed with impregnation application method, when both lining canvas and original support were covered and pressed together to form a stable bond. The later approach employed non-impregnating nap-bonds methods where the adhesive is applied to the lining support only. The one of the recent application employs a nap bond using BEVA 371 film commercially available in the form of very thin film. Patching as well as strip lining is proceeded by placing the Adhesive film between the original support and the canvas baking. The lining adhesive is afterwards activated by ironing through the backing fabric under 65-70C forcing the adhesive to active and form a stable nap bond between supportive and original canvases.⁸⁹ BEVA 371 has low melting point of 62–65o C and remain readily soluble in aromatic solvents.⁹⁰ Thus combination of reliable adhesion and improved reversibility is the prime reason why BEVA 371 has become the most widely used adhesive for patching, lining and strip lining.⁹¹

- Polyamide Textile Welding powder

This is a thermoplastic copolyamid resin with a melting point of approximately 90-100°C.⁹² The high tensile strength of this adhesive allows to produce a very stable butt- joints which makes it particularly preferable agent for tear mending and inlays. The tensile strength of polyamides allows to make inlays without backing (supporting canvas) application, performing a complete reintegration of the support loss.⁹³

Textile Welding Powder is a hot-melt adhesive. The easiest way of application is to stick a hot soldering needle into the powder and then apply the melted polyamide. Another method

⁸⁸ C. Tomkiewicz, M. Scharff, R. Levenson, Tear mending and other structural treatments of canvas paintings, before or instead of lining: Conservation of Easel Paintings, J. Hill Stoner, R. Rushfield, Routledge, 2012, p 384- 385

⁸⁹ Paul Ackroyd, The structural conservation of canvas paintings: changes in attitude and practice since the early 1970s, www.viks.sk/chk/revincon13.doc

⁹⁰ C. Tomkiewicz, M. Scharff, R. Levenson, Tear mending and other structural treatments of canvas paintings, before or instead of lining: Conservation of Easel Paintings, J. Hill Stoner, R. Rushfield, Routledge, 2012, p 385

⁹¹ P Ackroyd, The structural conservation of canvas paintings: changes in attitude and practice since the early 1970s, www.viks.sk/chk/revincon13.doc

⁹² Lascaux Polyamide Textile Welding Powder 5350, <http://www.talasonline.com/Lascaux-Welding-Powder>

⁹³ C. Tomkiewicz, M. Scharff, R. Levenson, Tear mending and other structural treatments of canvas paintings, before or instead of lining: Conservation of Easel Painting., p 385

consists of melting the polyamide powder with an iron between two sheets of silicone coated polyester film, in order to obtain a coat of approx. 1-2 mm thickness. After cooling, the polyamide coat is cut in very thin strips. These strips are then used together with the soldering needle to weld the threads.⁹⁴

One of the disadvantages of this material consists in the fact that it exhibits a lower reversibility grade than BEVA film. In general the reversibility of polyamides is not comprehensively studied and includes various opinions, most of which state that a high molecular weight material like polyamide textile is insoluble in low-moderate polarity solvents.⁹⁵

Painting Saint John the Baptist: structural conservation

The original canvas of painting Saint John the Baptist presents a single hole, tear and two areas where the threads are partially damaged and weakened. Considering the scale of damage presented by the tear and loss areas they should be stabilized with a natural canvas backing. Before the backing application, the hole present in the canvas should be treated with a fabric inlay to produce a better structural reintegration and at the same time visually mask the edges of the loss areas from the front side of the painting. BEVA adhesive film should be used for both inlay and fabric patch. In order to integrate the both inlay and backing the film should be placed between the inlayed original canvas and the backing fabric, and activated under 70o C. The only difficulty consists in presence of lining adhesive residues which may prevent the BEVA 371 film from forming a stable nap bond. The compatibility of BEVA 371 adhesive with the back side surface of the painting “Saint John the Baptist” film will be examined through a small margin test.

⁹⁴Lascaux Polyamide Textile Welding Powder 5350, <http://www.talasonline.com/Lascaux-Welding-Powder>

⁹⁵S. Prins, Reversibility of fusible polyamide, May 1, 2007, <http://cool.conservation-us.org/byform/ mailing-lists/cdl/2007/0503.html>

6.3 Cleaning

6.3.1 Theoretical framework

The idea of patina

Patina is an aspect of surface which bears the traces of time that the surface has endured. These traces of time may include external physical damage and natural deterioration of the material. The notion of patina lies between the two aspects of artwork representation namely historical and aesthetical. According to C. Brandi, the aesthetical aspect of the artwork answers its basic function as an image transmitting essence. Here the aesthetical representation of the artwork takes precedence over the material substance as it is not simply a collection of parts but a „work of art“. ⁹⁶As the artwork goes through a certain time passage it undergoes a material transition which inevitably affects the appearance of the object and thus will lead to the image alteration. For instance, the material transition can be referred to yellowing of oil paint medium, darkening of pigments and aging cracklier which altogether alter the initial image of the painting. From the standpoint of aesthetical representation of the artwork, this process carries a defective character, on the other hand, the transition of material is again inevitable and irreversible processes. An example of that can be seen in Baroque paintings, executed on the colored grounds. During the aging process, some of the thin layers of oil paint become more transparent making the underlying ground color translucent through the paint. This process disturbs the tonal relations of the colors, leading to the evident visual disharmony. ⁹⁷

According to P. Philippot patina is precisely the „normal“ effect induced by alterations as long as they do not disfigure the work. This concept is by no means negate the presence of patina, instead, it raises a critical domain and always implies an aesthetical judgment. Removal of patina would reduce the material data on the object and consequently would mean the ignorance of the fact that material has evolved in the certain time passage. This would be considered a scientific error and refusal to accept the aesthetic reality of the artwork. ⁹⁸ General question, however, is related to whether the effect of surface alteration can be accepted as a historical testimony or can be rejected as an element that distorts the aesthetical representation of the art object. In terms of conservation of painting "St John the Baptist", it

⁹⁶ C. Brandi, Theory of Restoration I: Historical and Philosophical Issues in the Conservation of Cultural Heritage, N.S. Price, N. Kirby Talley, Getty Conservation Institute 1996, p339

⁹⁷ P. Philippot, The idea of Patina and the cleaning of Paintings: Historical and Philosophical Issues in the Conservation of Cultural Heritage, N.S. Price, N. Kirby Talley, Getty Conservation Institute 1996, p 372-376

⁹⁸ Same

is related to the damage produced by previous defective cleaning procedures. The main question here whether the damage and alteration can be accepted as a historical testimony or not? Considering the Philipots's notion, patina is precisely the „natural“ and „normal“ effect of time on material. It can be presumed that the previous defective cleaning is less likely to be an element of patina but rather an independent element of painting which attenuates both the aesthetic and historical representations of the artwork. In other words the overcleaning damage prevents from seeing both aesthetic qualities and patina of the paint.

On a practical scale, the issue of patina finds numerous reflection in issues concerned with cleaning. One of the most common and frequently mentioned issues encountered by conservators consists in the varnish removal. It is the brilliance of varnish that fades with time, and this alteration combines with the alteration of underlying layers of paint to create what is called „patina“. Particularly when the paint layer has suffered some alterations, the alteration of varnish may either attenuate or contrast the effects of paint alterations. Thus raises the issue of evaluation of the effects that degraded varnish has induced on the appearance of the painting. In the case of painting “Saint John the Baptist”, it can be found that the “real” state of the paint surface is attenuated by the visual effects produced by the degraded varnish coatings. For this reason, the varnish has to be removed, in order to fully evaluate the current state of the paint layer.⁹⁹ Considering that the original state and image of the artwork can not be fully evaluated under the degraded varnish, it is important, during the cleaning process, to evaluate the role varnish plays as an element of patina. Thus the determination of the extent of cleaning or „how much should be removed and how much should be left behind, inevitably leads to the subjective appreciation of appearance of the surface. According to Philippot the objectivity of cleaning process can be regained through strict critical methodology and throughout awareness of every aspect of the cleaning problem. This can be achieved to a certain degree by considering two factors: assessment of alterations on a pure material level and the presence of the former coherence that is always present in the work, exposing the damage it bears.¹⁰⁰

In order to expose the „real state“ of the paint layer, it is required to proceed to and fro from the material to the image and vice versa, in course of which the critical diagnosis becomes more and more precise, that the conservator will be more able to evaluate the cleaning „level“.

⁹⁹P. Philippot, *The idea of Patina and the cleaning of Paintings: Historical and Philosophical Issues in the Conservation of Cultural Heritage*, N.S. Price, N. Kirby Talley, Getty Conservation Institute 1996, p 372-376

¹⁰⁰Same

From the critical point of view, such approach becomes the search for achievable equilibrium and original unity. As the partial cleaning is moved much further to the original paint surface the fragile areas of the paint might produce a medium migration which in its turn might affect the surface and subsequently affect the patina of this surface which will eventually produce the alteration of the „real“ image, causing the damage to both historical and aesthetical features of the paint .¹⁰¹

6.3.2 Technical cleaning

Historical context

Distinctively from modern practices and attitudes developed in the 20th century the early cleaning of oil paintings was mostly done routinely with little of respect to the original painting material. Starting from 13th and until the middle of the 18th century the easel painting conservation had been performed as part of the work in the artist's workshops, and done by the artists craftsmen. During the 18th century the profession of restorer emerged as a field independent from the artist's workshops. Apart from appearance of the professional restorers and respective attitudes for the painting treatment, the 18th century saw the appearance of the unprofessional practitioners known as „picture cleaners“. Criticism of latter has been reflected in the letters Julius Caesar Ibetson and Joshua Reynolds mentioning the incompetent and defective treatments that consisted in overcleaning and masking the damage by repainting.¹⁰² The cleaning has also been conducted by the painting owners. De Burtin described the pleasure owners would gain seeing their paintings unveiled “by their own hands”.¹⁰³

Prior to the 19th century the systematic approach of step-by –step cleaning has not yet been developed on the wide scale practice. Removal of superficial dirt, varnish and repainting were generally viewed as an issue of the single cleaning tool applied for all the dirt and layers simultaneously. One of the early signs of systematic approach has been reflected by Dossie,

¹⁰¹P. Philippot , The idea of Patina and the cleaning of Paintings: Historical and Philosophical Issues in the Conservation of Cultural Heritage, N.S. Price, N. Kirby Talley, Getty Conservation Institute 1996, p 372-376

¹⁰² J. Reynolds , comments on restoration (1783) :Issues in Conservation of Easel paintings, D. Bomford and M. Leonard, Getty conservation institute : Los Angeles , 2005, p 18-19 ;

J. C. Ibetson, Accidence , or Gamut of painting in Oil and Watercolor (1803): Issues in Conservation of Easel paintings, ...p 38-42

¹⁰³F.X De Burtin. *Traité théorique et pratique des connaissances qui sont nécessairesa tout amateur de tableaux*, Second edition. Valenciennes: Lemaitre, 1946M, via Stols-Witlox , *Historical Restoration Recipes: The Cleaning of oil Paintings 1600-1900*, 2011
https://www.academia.edu/19949929/Historical_restoration_recipes_the_cleaning_of_oil_paintings_1600-1900

stressing the individuality of each substance requiring an individual cleaning tool.¹⁰⁴ Courtin's comment (1830), "the state of the painting should determine the choice between procedures", was a first sign of a more methodical approach.¹⁰⁵ Almost simultaneously in 1829, Montaber described regulative measures for cleaning. These included the regulation of strength, cleaning agent concentrations and exposure time of the surface.¹⁰⁶ In general the early cleaning tool used during the period of 1600-1900 can be divided on three categories, mechanical, aqueous solutions and solvents.

- Mechanical cleaning included cloths, brushes, and steel instruments. Toothpicks were used to remove the varnish from the fissures and grooves. The report of Committee on National gallery in London mentioned powdering the varnish with fingers that was a popular method throughout the 19th century.¹⁰⁷
- Aqueous cleaning frequently used pure water mostly to remove the grime and dust. As the use of water alone was usually not sufficient to produce a desired cleaning effect, soaps and alkali were added to promote its cleaning action. Soap is a fatty acid salt produced from alkali and oil or fat. It possesses an amphiphile¹⁰⁸ character that allows breaking water/oil interface and emulsify greasy dirt and even varnishes during the cleaning process.¹⁰⁹ Various other historical recipes include use of Genoa and brown soaps, as well as mentioning their alkaline character leading to color loss.¹¹⁰ Among alkali one of the most frequently mentioned agent was lye prepared by boiling wood ashes in water.¹¹¹ Fresh or stale urine as an ammonia containing material was also frequently employed.¹¹²
- The solvent cleaning employed various cleaning liquids containing ethanol (wine spirit, brandy, alcohol, vodka) as the main as a main cleaning component.¹¹³ During

¹⁰⁴R Dossie, of *Mending and Cleaning of Pictures (1764)*: Issues in Conservation of Easel paintings, D. Bomford and M. Leonard, Getty conservation institute: Los Angeles, 2005, p 294-298

¹⁰⁵M. Courtin, *Encyclopédie moderne*, vol. 20, 1830 via Stols-Witlox, *Historical Restoration Recipes*

¹⁰⁶J.N.P. De Montabert., *Traité complet de la Peinture Vol. 8.* 1829. via Stols-Witlox, *Historical Restoration Recipes Cleaning of oil Paintings 1600-1900*,

https://www.academia.edu/19949929/Historical_restoration_recipes_the_cleaning_of_oil_paintings_1600-1900

¹⁰⁷Report of Select Comitee on National Gallery (1853): *Issues in Conservation of Easel paintings...* p 463

¹⁰⁸A substance consisting of molecules that poses both water and oil reactive parts.

¹⁰⁹R. Wolbers, *Cleaning Painted surfaces: Aqueous methods*, Archtype publications, 2000, p 27

¹¹⁰J. H. La Fontaine, de, *L'Académie de la peinture*, Paris, 1679: M. Stols-Witlox, *Historical Restoration Recipes: The Cleaning of oil Paintings 1600-1900*, 2011,

https://www.academia.edu/19949929/Historical_restoration_recipes_the_cleaning_of_oil_paintings_1600-1900

¹¹¹The use of lye was mentioned to loosen the color due to the strong alkaline properties. bases work directly through primary forces interaction, driving the organic materials to dissociate under the action of hydrolysis

¹¹²Stolz –Wotox, *Historical Restoration of Recipes: Cleaning of Oil Paintings, 1600-1900*

¹¹³Same

the 19th century later liquids were employed with various turpentine oil mixture to obtain the appropriate effect.¹¹⁴

The solvent cleaning method became the most common cleaning method for removal of varnish and grime during the 20th century.

a) Solvent cleaning

In general terms solvents are described as substances that are defined for their ability to dissolve a solute.¹¹⁵ Liquid organic solvents used in the artwork conservation field remain one of the most frequently used agents for varnish and repaint removal operations. Solvents can be classified on nonpolar aromatic and aliphatic hydrocarbons, alcohols, esters, ketones and nitrogen containing solvents. Their working principle is based on their ability overcome the intermolecular forces of other materials by the means their own secondary bonds. This mechanism is comprehensively described as “like dissolves like”.¹¹⁶ In other words in order to make a solution the solvent must first overcome the intermolecular interactions of the other substance with its own secondary interactions in order to find its way between and around the solid material and put it into solution. This is best accomplished when the intermolecular attractions between the molecules of the solvent and solute are relevant. In case if these forces between the solvent and solute will sufficiently differ, the mixing will result in immiscibility.¹¹⁷ A fine example of intermolecular, or secondary bonding differences can be observed between water and mineral oil, as water predominantly consists of strong hydrogen bonding interactions while oil molecules consist of predominantly weaker interactions such as London or Dispersion forces.¹¹⁸

I. Scientific background

The attraction forces between the molecules that are responsible for the cohesion of material are generally known as Van der Waals forces (after the name of the scientist who first described them).¹¹⁹ Molecule is composed of a positively charged atoms in the centre, while the outer surface is covered by a dispersed cloud of negatively charged electrons. If these

¹¹⁴Same

¹¹⁵Solvents, Encyclopedia Britannica, <https://www.britannica.com/science/solvent-chemistry>, last updated: 2-7-2011

¹¹⁶Conservation Unit Museums and Galleries Commission, The Science For Conservators Series: Volume 2: Cleaning, Routledge, 1992, p 61-62

¹¹⁷J. Burke, Solubility Parameters: Theory and Application, The American Institute for Conservation, Book and Paper Group Annual, 1984, <http://cool.conservation-us.org/coolaic/sg/bpg/annual/v03/bp03-04.html>

¹¹⁸Same

¹¹⁹Same

positive and negative charges balance out the molecule as a whole is neutral. If the distribution of the electron cloud is uneven small local charge imbalances are created: the parts of the molecule with a greater electron density will be negatively charged while the other imbalanced part will be positively charged. The molecule as a whole, while still neutral, will have the properties of a small magnet, with equal but opposite poles called dipoles. A single molecule, because of its structure, can have several dipoles at once, some strong and some weak, some which cancel out, and some which reinforce each other. The sum of all the dipoles is known as the dipole moment of the molecule. Molecules that have permanent dipole moments are said to be polar, whereas molecules in where all the dipoles cancel out are said to be none-polar. Molecular polarity is at the heart of intermolecular attractions. The strength with which the molecules cling together, and therefore the cohesive energy density and the solubility parameter of the substances, is directly related to the strength of molecular dipoles.¹²⁰ These dipoles interactions can be defined on three types:

- Dispersion or London forces

The dispersion forces are none polar type of intermolecular interaction. The mechanism of dispersion forces action can be described by shift in the outer electron layer of the none-polar molecule. During this shift the more positively charged electrons are exposed and the temporary dipole is produced. This type of forces is very weak and mostly occurs among the none-polar molecules where the distribution of the charge is even.¹²¹

- Polar Forces

Other kind of molecular interactions occur due to uneven distribution of charged particles in the molecule. Some elements attract electrons more vigorously than others, a dipole moment occurs when electrons are unequally shared between atoms in a molecule. In general there are three types of intermolecular bondings defined as polar. The first type called Keesom interactions exhibits an intermolecular attraction when the polar molecules arrange themselves head to tail, positive charge to negative charge. These dipole interactions are temperature dependent. As the temperature rises the increased motion of the molecule causes bond breakdown.¹²² The second type of polar interaction, called Debye forces, occurs when a non-polar molecule in the presence of polar molecule produce a shift in the outer electron

¹²⁰ J. Burke, Solubility Parameters: Theory and Application, The American Institute for Conservation, Book and Paper Group Annual, 1984, <http://cool.conservation-us.org/coolaic/sg/bpg/annual/v03/bp03-04.html>

¹²¹ Same

¹²² Same

layer producing a temporary dipole. The later interaction is similar to dispersion forces, however here the attraction force is considerably higher. The third type represents the strongest kind of polar interaction known as Hydrogen bonding.¹²³

- Hydrogen Bonding

Hydrogen bonding forces occur between molecules where a hydrogen atom is bonded to a strongly electronegative atom, O, N, or F. The oxygen or nitrogen atom attracts the hydrogen electron cloud so strongly that very powerful dipole forces result within the molecule. Hydrogen bonding explains why water is a liquid rather than a gas at room temperature. Although water is a small, lightweight molecule, the hydrogen dipole is attracted to an adjacent oxygen dipole. Hydrogen bonding is important in alcohols, in addition to water.¹²⁴

II. Application and working action

The working action of the solvents and cleaning liquids can be generally described by two interrelated processes: the capillary flow and diffusion. Capillary action is a physical process related to the permeability of the substrate and the surface tension of the solvent. Capillary sorption can be simply explained as the movement of the liquid in the structure of material.¹²⁵ The surface tension of organic solvents is lower than of an oil substrate, allowing it to efficiently penetrate into the structure of the treated material. The diffusion on the other hand is a process following the capillary suction, representing an interaction between the solvent and substrate on an intermolecular level. The effect of later processes is best described by the swelling that a single solvent or a solvent blend can induce on the surface of the paint film. If swollen to a significant degree due to sorption of solvent, the binding power of the oil medium is reduced and the pigment is vulnerable to removal, for example, by the mechanical action of the cleaning swab. The main principle in cleaning is concerned with ability to remove degraded covering material from the surface of painting while leaving the underlying oil paint unaffected. For this reason a series of safety margin tests have to be undertaken to

¹²³ Same

¹²⁴J.Burke, Solubility Parameters: Theory and Application, The American Institute for Conservation, Book and Paper Group Annual , 1984, <http://cool.conservation-us.org/coolaic/sg/bpg/annual/v03/bp03-04.html>

¹²⁵ A Phenix , Ken Sutherland , Cleaning of paintings effects of organic solvents on oil paint films : Sutherland, K., 'The extraction of soluble components from an oil paint film by a varnish solution' Studies in'Conservation 45, 2000, pp. 54-62. www.viks.sk/chk/revincon10.doc

study and measure the swelling properties of the organic solvents on the oil paint surfaces , in order to develop a cleaning system that would satisfactory answer the mentioned criteria.¹²⁶

III. Solvent parameterization and swelling effects on oil paint films

This critical approach to solvent cleaning requires empirical data on both solvents and solutes in their ability to overcome each other.¹²⁷ The simplest parameter referring to the cohesive properties of materials is Hildebrandt value (δ) that describes the net energy required to dissociate intermolecular interactions of the certain material. This energy can be measured by various means. One of the simplest method is to boil out the material, and measure the amount of energy spent to brake the secondary forces. The measuring units for Hildebrandt parameter indication are expressed in SI and δ .¹²⁸ The oil Paint swelling tests conducted by Stollow indicated variation in the degree of swelling caused by organic solvents in relation to their Hildebrand solubility parameter δ . Maximum swelling was found to correspond roughly to the solubility parameter region 8.8 – 10. This region included butanone (methyl ethyl ketone), cyclohexanone, 2-ethoxyethanol (cellosolve) and a number of chlorinated solvent. Aromatic solvents (benzene, toluene, xylene) also showed significant swelling behavior. Solvents far removed from this region - with δ values under 8 (cal/cm^3)^{1/2} (various mineral spirits and aliphatic hydrocarbons) or over 13 (cal/cm^3)^{1/2} (methanol, water) - caused very little swelling. Although absolute swelling values varied according to the age of the paint film, the overall pattern and the „peak” swelling region were generally the same. However, a slight shift to higher polarity solvents was discerned for Stollow's oldest film (27 years old).¹²⁹

¹²⁶D. Stulik, D. Miller, H. Khanjian, Solvent Gels for the Cleaning of Works of Art: The Residue Question , Valerie Dorge, Getty Conservation Institute Publications, 2004, p 54-57

¹²⁷John Burke, Solubility Parameters: Theory and Application, Part 2 - The Hildebrand Solubility Parameter, The Oakland Museum of California, August 1984, www.viks.sk/chk/revincon10

¹²⁸Same

¹²⁹A. Phenix and K. Sutherland , The cleaning of paintings: effects of organic solvents on oil paint films, Reviews in Conservation, IIC , Volume 2, 2001 p.47-60, www.viks.sk/chk/revincon10.doc

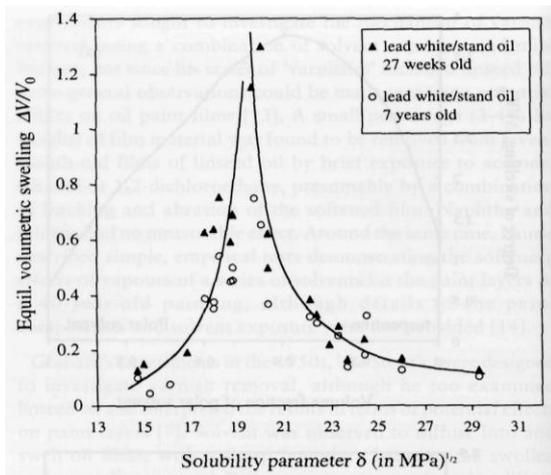


Figure 24. Stollow's oil paint swelling scale.

Stolow has also pointed out to the importance of individual diffusion rates of the solvents, by comparing the times taken for swelling to reach completion. The solvents with low molecular weight such as acetone and benzene exhibited a more rapid swelling than more viscous solvents such as iso-butyl.¹³⁰

Graham's experiments held in 1950¹³¹ studied the effect of binary mixtures on paint films. The swelling effect of certain binary mixtures was found to be greater than that expected, assuming a linear relationship between the fractional composition of the solvents and the degree of swelling. This finding by Graham cast doubt on the then common practice of restriction of more active solvents like ethanol with less active solvents like turpentine, since the swelling action of the resultant solvent mixture may actually be greater than either of the solvents alone. The very high swelling powers found by Graham of mixtures of an alcohol (ethanol) and a chlorinated solvent (chloroform) are consistent with what is known of lipid solubility in the biological field.¹³¹

IV Teas solubility chart

The Teas diagram is the most commonly used graph for conservation expressing the solubility parameters of the solvents and polymers. In this diagram the solubility parameters are determined by the relative amounts of three component forces that build up a total solubility value.¹³² The Teas diagram layout represents a triangular form consisted of three scales that

¹³⁰ A. Phenix and K. Sutherland : The cleaning of paintings: effects of organic solvents on oil paint films, www.viks.sk/chk/revincon10.doc, Original source: A. Phenix and K. Sutherland : The cleaning of paintings: effects of organic solvents on oil paint films, *Reviews in Conservation*, Volume 2, IIC : 2001 p.47-60

¹³¹ Same

¹³² John Burke, *Solubility Parameters: Theory and Application*, The American Institute for Conservation, Book and Paper Group Annual, 1984, <http://cool.conservation-us.org/coolaic/sg/bpg/annual/v03/bp03-04.html>

describe the solvent “power” on the basis of dispersion forces (f_d), polarity (f_p), and hydrogen bonding (f_h).¹³³ Zero point end of every scale is the upper limit of the other one. Independently of the position of the liquid or material on the diagram the total of its parameters will inevitably be 100. Knowing the solubility parameters of solvents it is possible to mark their positions on the graph and classify them according to their swelling and dissolving effect on the paint and varnish surfaces.¹³⁴

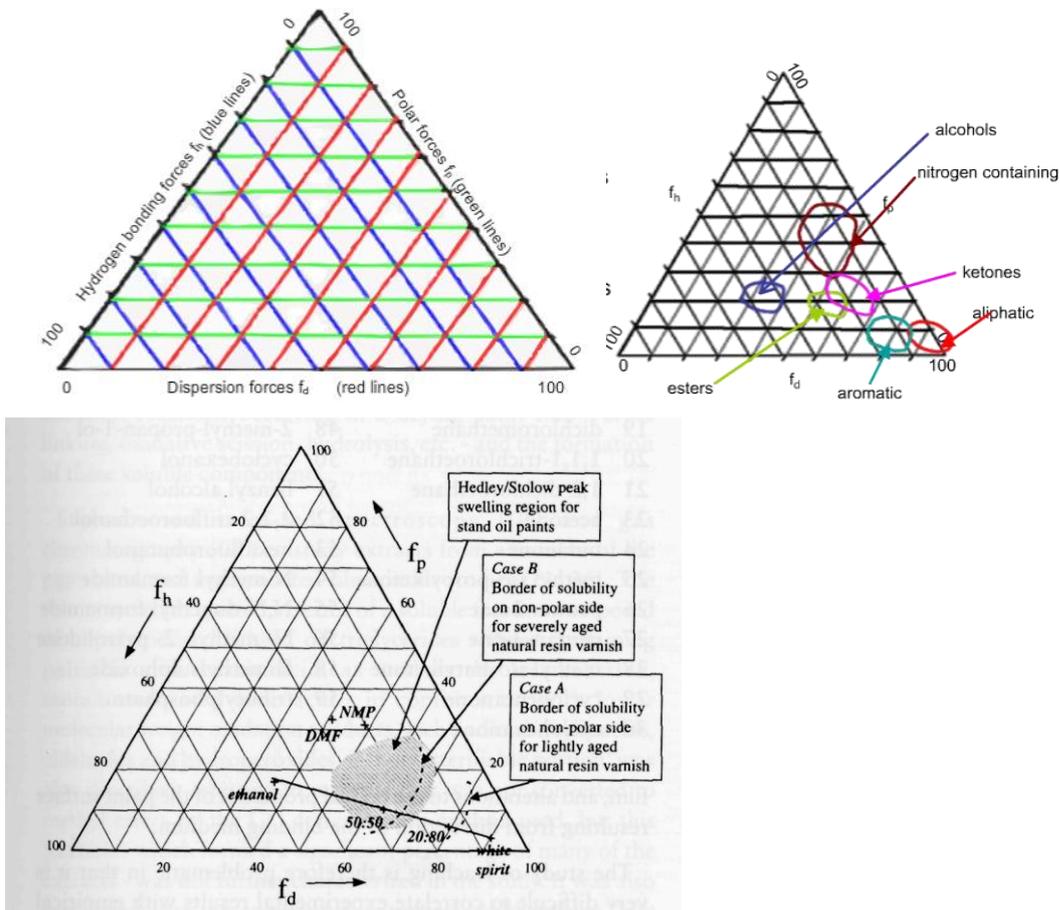


Figure 25-27.. Graphical depiction of the Hedly-Stollow solubility region.

Using data collected by Stollow and Graham, Hedley in 1980 used the Teas fractional solubility parameter chart, identifying for oil paint a '*peak swelling region*', which represented a nominal zone of solvent power associated with increased risk during the varnish removal. For cleaning situation where a natural resin varnish (moderately oxidized) was to be removed from the oil paint substrate, the conservator could effectively use the Teas chart as a guide to map the respective solubility and swelling regions of varnish and paint and to locate regions where the two do not coincide. The tool for finding a nonpolar boundary for the varnish

¹³³Christopher McGlinchey, Boundaries of Teas solubility Concept, WAAC Newsletter, Volume 22, Numer 2, May 2002, <http://cool.conservaion-us.org/waac/wn/wn24/wn24-2/wn24-205.html>

¹³⁴John Burke, Solubility Parameters: Theory and Application, ..., 1984

removal is represented by solvent binary or ternary mixtures that are efficient for varnish removal and at the same time safer for the oil paint.¹³⁵ The high swelling capacity of binary mixtures was explained by the fact that at proportions these mixture fall into the peak swelling region producing a high swelling effect that was described by Graham. The behavior of the solvent blend was predicted using a mathematical and geometrical method. For a mathematical way of solvent blend parameters calculation, each force fraction of the solvent is multiplied on fraction of the amount of the same solvent given in the solvent mix. The same calculation is done with the other solvents consistent and after that, the calculated parameters of the solvents in the blend are summed. The geometrical way of solubility point placement can be done using simply a ruler and a pencil. The distance between the positions of two solvents are connected with the line where the total centimeter value is divided proportionally to the percentages of the solvents in the blend.¹³⁶

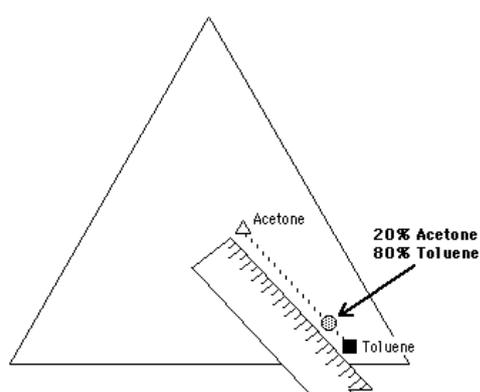


Figure 28. Geometrical calculation of the solvent blend of acetone 20 % and Toluene 80%

The risk increases proportionally to the ageing of varnish, as it becomes more polar thus requiring a more polar solvent or solvent mixture with a higher active solvent proportion to dissolve it. The other concern regarding oxidized varnishes and solvent mixtures is related to the redeposition of the insoluble material. Normally to dissolve a varnish an amount of solvent or solvent mixture added is sufficient to remove the bulk material in the coating while leaving some highly oxidized parts of the varnish or other material(oil) behind. The application of the highly volatile solvent, for instance acetone and isopropanol, separately or in mixture, leads to redeposition of the insoluble material on the surface of the painting in

¹³⁵ Same

¹³⁶ John Burke, Solubility Parameters: Theory and Application, The American Institute for Conservation, Book and Paper Group Annual , 1984

form of hazy whitish material. The solution to this problem has been reflected in Keck¹³⁷ mixtures incorporating diacetone alcohol along with acetone and mineral spirits. The diacetone alcohol remains on the surface longer allowing re-form and redissolve the residual material.¹³⁸

V. Reevaluation of Hedley- Stollow solubility region and Teas trinary chart

The swelling region proposed by Hedley and the use of Teas diagram as solubility prediction tool presents certain misconceptions. One of most evident features indicates that solvent mixtures will have the higher swelling power than the each of the solvents individually. This has been related to the retention of the more active component of the solvent blend responsible for the diffusion into the treated material. The other feature immediately evident is that the swelling region indicated by Hedley does not include strong solvents such as n, n,-dymethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP) which are known to have high swelling effects on oil paint films.¹³⁹

A part inconsistency of swelling effects of solvents and solvent blends , Teas trinary system has a lack of theoretical back ground:

- The hydrogen bonding character is not specified¹⁴⁰
- The Hildebrand value or the overall magnitude of the cohesive energy has been lost
- It only applies to neutral solvents, no information on response of substances to acidic/alkali conditions.
- Teas tends to distinguish solvents according to magnitude of dispersion forces. In other words the more polar the solvent the lesser dispersion force value.¹⁴¹

One of the recent studies describing the solvents swelling effects on oil paint films has been preformed by Alan Phenix. Phenix indicated a wide range of solvents and solvent blends outside the Hedley-Stollow peak solubility region that caused high degree of the oil paint film

¹³⁷ The solvent mixtures usually have codified names usually including names of the conservators that proposed them and a number. Example Keck 1, Keck 2, named after Sheldon Keck , a director of Conservation Center of the Institute of Fine Arts at New York University, who proposed the present solvent blend

¹³⁸ D. Stulik, D. Miller, H. Khanjian, Solvent Gels for the Cleaning of Works of Art: The Residue Question, Edited by Valerie Dorge, Getty Conservation Institute 2004, p 66-68

¹³⁹ A. Phenix and K. Sutherland : The cleaning of paintings: effects of organic solvents on oil paint films, www.viks.sk/chk/revincon10.doc, Original source: A. Phenix and K. Sutherland : The cleaning of paintings: effects of organic solvents on oil paint films, Reviews in Conservation, , Volume 2, IIC : 2001 p.47-60

¹⁴⁰ A. Phenix, Solvent Abuse: Some observations on the safe use of solvents in the cleaning of painted and decorated surfaces, <http://www.buildingconservation.com/articles/solvent/solvent.htm>

¹⁴¹ C. Stavroudis and S. Blank , Solvents & Sensibility, WAAC Newsletter Volume 11, Number 2, May 1989, pp.2-10, <http://cool.conservation-us.org/waac/wn11/wn11-2/wn11-202.html>

swelling, namely aromatic hydrocarbons such as xylene. Phoenix classified the solvents by swelling power: Low-Sweilling, Low moderate, High Moderate , High-swelling. Beside the swelling power Phoenix also included rate of swelling as another parameter of solvent classification.¹⁴²

The key finding consisted in a linear relation in terms of swelling ability of the solvents. The maximum or equilibrium degree of swelling $\Delta A_{max} \%$ ¹⁴³ increase in the following sequence: *iso*-octane, white spirit (17% aromatics), turpentine, xylene, and toluene, a pattern reflective of increasing polarity and solvent power. The research outcome has pointed out that aliphatic alcohols (methanol, ethanol, propan-1- ol, etc.), aliphatic acyclic ketones (acetone, butanone, etc.), and the lower aliphatic esters (*n*-butyl acetate, ethyl propanoate, etc.) generally fall within the class of low-moderate swelling power, which to certain degree justifies the use of these solvents for cleaning operations on oil paintings. However it must not be forgotten that oil paints may still be very sensitive to the solvents of low-moderate swelling category .¹⁴⁴

Eventually Phenix has indicated a relation between oil paint and solvents that are appreciably more complex than the single zone of high swelling suggested by Hedley. This was reflected by Phenix in Teas solubility chart (figure 1.).¹⁴⁵

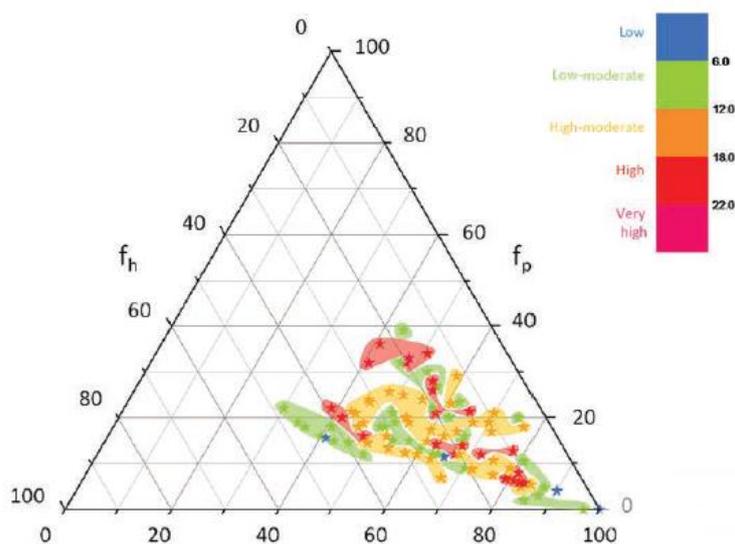


Figure 29 . Reevaluation of Hedly-Stollow peak swelling region

¹⁴² Alan Phenix, Effects of Organic Solvents on Artists Oil Paint Films: Swelling: New Insights into the Cleaning of Paintings Proceedings from the Cleaning: International Conference Universidad Polit cnica de Valencia and Museum Conservation Institute M. F. Mecklenburg, A. E. Charola, and R. J. Koestler, smithsonian contributions to museum conservation , number 3, p69-76

¹⁴³Is a reflection of the magnitude of solvent activity on the paint. It is used independently of the swelling rate parameter and describes the response of oil paint on individual solvents or solvent blends

¹⁴⁴Alan Phenix, Effects of Organic Solvents on Artists Oil Paint Films.....p 72-73

¹⁴⁵Same.

VI. Leaching

Leaching is a process of extraction of the soluble fractions of the oil paint media by solvents in the course of cleaning and as a process accompanied with swelling of the paint films. Erhardt and Tsang analyses of solvent extracts from a range of oil paint films, of different age and pigmentation indicated the major low molecular weight components extracted from the paint films were the saturated fatty acids, palmitic and stearic, and amounts of monounsaturated and dicarboxylic acids. These components are responsible for the plasticizing properties of the paint and their extraction leads to the embitterment of the paint. The extraction of these components is also accompanied with visual alteration of the paint surface. The aforementioned effects produced by the solvents are considered the main limitation of the solvent cleaning. Leaching is contentious, because - in contrast to swelling - it is less immediately tangible during the solvent application process. The reason consists in the fact that it occurs on a purely intermolecular level.¹⁴⁶

The quantitative measurements of material extractable from a range of reference paint samples, as well as older samples from paintings, were made by Sutherland and Shibayama indicated a number of factors contributing to leaching. The quantities of the extractible material were found to be related to solvent swelling effect, pigment type, medium saturation and drying time. Earth paints including raw sienna and burnt umber are more responsive to highly polar solvents and the amount of extracted material is larger than for the lead white based pigments. This difference is related to strength of the paint film contributed by total amount of cross linking in the dry paint film.¹⁴⁷

Regarding the solvent strength in relation to the leaching, acetone and ethanol were generally found to extract the greatest quantities of material from the younger paint films. Dichloromethane - was found to have a pronounced leaching effect on the older thirteenth to nineteenth-century paint samples. The latter result was explained by specific solvent interactions of the dichloromethane with free fatty acids, which form an increasing proportion of the extractable material in older paint films. Analysis of lead white pigmented films of different ages, from 3 to 65 years, showed decreasing proportions of acetone-extractable material with age, suggesting that ongoing chemical changes over extended ageing periods

¹⁴⁶Alan Phenix, Ken Sutherland, Cleaning of paintings effects of organic solvents on oil paint films : Sutherland, K., 'The extraction of soluble components from an oil paint film by a varnish solution' *Studies in Conservation* 45, 2000, pp. 54-62, www.viks.sk/chk/revincon10.doc

¹⁴⁷ Same

had produced a gradual stabilization ,either from increased cross-linking, or strong non-covalent interactions such as ionic bonds in these paint films.¹⁴⁸

A part from solvent cleaning the leaching may also be contributed by the number of additional factors. Components of solvent-extractable phase of oil paint, such as free fatty acids, may be lost by efflorescence and volatilization during the ageing process, or possibly even by sorption into the ground layer. The application of a solvent-based varnish to an oil paint film can also result in a similar extraction of soluble fractions as it is found with exposure of the paint films to free solvent. This was revealed after GS measuring the quantities of fatty acids in varnish samples removed mechanically. ¹⁴⁹

Regarding the solvent effects on oil films on a practical scale , the problem of leaching and swelling becomes an issue of partial and total cleaning . Stollow and Ruhemann presumed that the cleaning procedure must be consistent of the single through cleaning rather than a number of semi-cleaning insitings. Ruhemann suggested the use of acetone as a strong and highly volatile solvent as to reduce the solvent exposure time of the surface and efficiently remove the coatings . Other opinions , suggest thinning instead of total cleaning as to avoid putting solvent in contact with the color layer since its binder would become impoverished. This stand point is valid in the sense that mechanical exposure to the swabbing action is reduced to minimum. However the experiments carried out by Stollow have indicated that due to rapidity with which the solvent penetrates through varnish, the paint exposure is the same as in the uncoated varnishes. ¹⁵⁰

In contrast to laboratory experiments carried out on a test paint films , the investigation carried out at National Gallery, London, in the 1990s employed samples taken from the actual paintings of old masters in the course of solvent cleaning and were analyzed by gas chromatography mass spectrometry and scanning electron microscopy to investigate possible changes in the organic composition and physical structure of the paint layers. The comparative analyses did not provide evidence for alterations as a result of cleaning in the cases studied. Similar approach was taken by Sutherland to investigate possible leaching of paintings dating from 17th to 19th century paintings. Thus the results may indicate that the

¹⁴⁸Alan Phenix , Ken Sutherland , Cleaning of paintings effects of organic solvents on oil paint films : Sutherland, K., 'The extraction of soluble components from an oil paint film by a varnish solution' Studies in Conservation 45, 2000, pp. 54-62. www.viks.sk/chk/revincon10.doc

¹⁴⁹Same

¹⁵⁰Ken Sutherland ,Solvent Leaching Effects on Aged Oil Paints, <https://repository.si.edu/bitstream/handle/10088/20488/10.Sutherland.SCMC3.Mecklenburg.Web.pdf?sequence=1>

paint films of significant age (hundreds of years old) exposed to solvent in practical situations, leaching likely occurs at very low levels.¹⁵¹

b) Solvent gels

The issue of volatility and capillarity effect of solvents and cleaning solutions for paintings has been long recognized with the introduction of the organic solvents into the conservation/restoration field in the beginning of the 20th century. The first form of restraining mediums for organic solvents were wax pastes. The limitation of this cleaning approach consisted in wax residue issue and need of sufficient amounts of organic solvent in order to clear the surface of the paint after cleaning. Other thickening agents consisted of cellulosic products, like methyl cellulose, ethyl cellulose, hydroxyl methyl cellulose and sodium carboxymethyl cellulose and carboxy methyl cellulose. In the middle of the 1980s R. Wolbers introduced a new set of the solvent gels for cleaning of artworks which included polyacrylate thickened gels .¹⁵²

In broad terms gel is a water-based formulation thickened with a polymer or other high molecular weight material.¹⁵³ In a solvent gel system the active cleaning component is represented by organic solvent while the other component comprising the gel play mostly supportive role, non the less obtaining cleaning properties on their own. Thickening of solvent carries a number of advantages contributing to a more selective and controlled cleaning process:

- it allows to increase retention time of the solvent ,
- increase the action time and improve the dissolving action of the weaker or less polar solvent; restrain the capillary flow to prevent the uncontrolled sorption of the cleaning liquid into the substrate, reducing swelling and leaching effect;
- provide dispersion aid¹⁵⁴ for the insoluble materials , for instance, highly oxidized or cross-linked materials consisting in the varnish coating;

¹⁵¹Ken Sutherland ,Solvent Leaching Effects on Aged Oil Paints,
<https://repository.si.edu/bitstream/handle/10088/20488/10.Sutherland.SCMC3.Mecklenburg.Web.pdf?sequence=1>

¹⁵²D. Stulik, D. Miller, H. Khanjian, Solvent Gels for the Cleaning of Works of Art: The Residue Question ,
Valerie Dorge, Getty Conservation Institute Publications, 2004, p 5

¹⁵³Same

¹⁵⁴Dispersion aid is in other fords a tool for holding dissolved material in a stable dispersion and preventing dissolved material from redepositing back onto the cleaned surface . For gel clening the dispersion aid is ensured by the physical density of gel and a slight detergency effect . Source : R Wolbers , Cleaning Paintied surfaces: Aqueous methods ,Archetype Publications, 2000, p 64-65

- reduce evaporation rate and exposure of the user to fumes of toxic solvents such as xylene.
- In terms of handling and application, gels support the cleaning procedures on a vertical and other complex surfaces avoiding dripping, which is usually expected in free solvent applications.¹⁵⁵

All of the mentioned gel properties can be seen in contrast with the working action of the free solvent. The usual strategy of the solvent cleaning employs solvent blends of low and high polarity solvents which through mixing attain a required solubility parameter that allows to dissolve the varnish coating or other materials covering the surface. The limitation of this strategy becomes evident as the more complicated materials are encountered- for example a coating with a substantial drying oil content that requires high hydrogen bonding aspect and a higher dipole moment to solvate it. By incorporating a solvent that is capable of disrupting the drying oil component in the varnish, gives a very narrow margin for safety related to the oil paint beneath. Thus the main criterion for cleaning is to remove the varnish coating without incorporation strong solvents that are capable of affecting the material underneath. Instead of ultimate dissolving of the oleo resinous varnish, solvent gels use another cleaning strategy that employs less polar solvents where the dipolar moment allows to swell the coating and disperse it with the dispersion aid provided by the gel and mechanical work of swab. Dispersion aid in this sense is represented by the gel „scaffolding“ containing detergent that is capable of picking up the disrupted varnish (and subsequently drying oil) material and stably hold it in the gel matrix similarly to the way it holds the solvents. This cleaning strategy allows to prevent redeposited material on the surface of the painting, however the clearance of the surface following the varnish removal represents a limitation consisted in application of the polar solvents to remove the gel residues.¹⁵⁶

Regarding the choice of thickener, polyacrylic acids are considered as a one of the most appropriate types of gelation agents for the solvent gel preparation due to their compatibility with organic solvent and ability to produce a highly viscous gel at very low concentrations of

¹⁵⁵ D. Stulik, D. Miller, H. Khanjian, *Solvent Gels for the Cleaning of Works of Art: The Residue Question ...*, p 6

¹⁵⁶ D. Stulik, D. Miller, H. Khanjian, *Solvent Gels for the Cleaning of Works of Art: The Residue Question*, Valerie Dorge, Getty Conservation Institute Publications, 2004, p14-17 and *New Methods in the Cleaning of Paintings*, A video Course with Richard Wolbers, recorded in 1991, <https://udcapture.udel.edu/misc/cleaningpaintings/>

dry polymer. Commercially polyacrylate polymers are available in form of Carbopol and Pemulene polyacrylic acids.

I. Carbopol gels

Carbopol was the first from this class employed in for the various types of decorative surface cleaning.¹⁵⁷ Carbopol resins are long-chain acrylic acid polymers cross-linked with a polyalkenyl polyether (carboxy polymethylene), with pH of 2.5-3.0 in a 1% water dispersion.¹⁵⁸ In dry state it represents a whitish powder which consist of coiled long chained molecules.

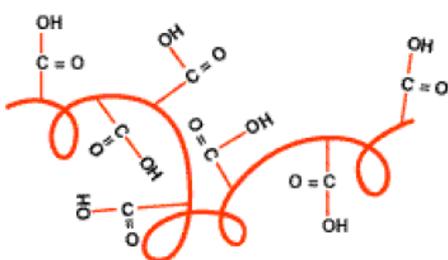


Figure 30. Coiled Carbopol resin molecule

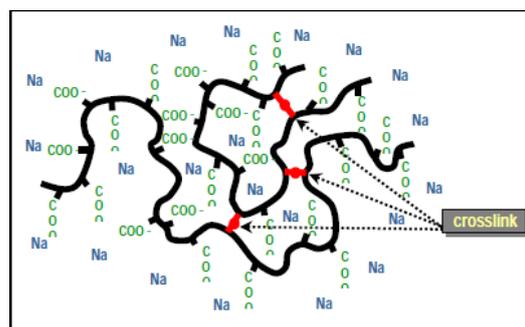


Figure 31. Uncoiled Carbopol Molecule

The thickening of the carbopol polyacrylic acid chain can be described by two simultaneous actions: on one hand the polyacrylic chain is entwined with itself, either by the mean of hydrogen bonding or physical entangling, and on the other hand part of its acid groups are attracted into the water or organic solvent. In order to make solvent gel the solubility of the polyacrylic acid polymer has to be modified. This can be done by neutralizing the acidic groups on the polymer with a basic material like amine, which will serve as bridging material between the solvent and polymer.¹⁵⁹ The addition of water into this system is required to complex the amine with acid groups, since the transfer of a hydrogen ion is required for the association of acid and base.¹⁶⁰ Carbopols can well be soluble in solvents if they are complexed with aliphatic amines:

¹⁵⁷ R. Wolbers and C. Stavroudis, Aqueous methods for the cleaning of paintings, s, Conservation of Easel Painting, Joyce Hill Stoner, Rebecca Rushfield, 2012, p 512

¹⁵⁸ T. Cuerteis, An Investigation on the Use of Solvent Gels for Removal of Wax-based Coating from Wall Paintings, Conservation of Wall Painting Department, Courtauld Institute of Art, 1991, p 13-19
http://www.tcassociates.co.uk/downloads/cuerteis_gels.pdf

¹⁵⁹ New Methods in the Cleaning of Paintings, A video Course with Richard Wolbers, recorded in 1991,
<https://udcapture.udel.edu/misc/cleaningpaintings/>

¹⁶⁰ R. Wolbers, Cleaning Painted surfaces: Aqueous methods, Archetype Publications, 2000, p 76-79; T. Cuerteis, An Investigation on the Use of Solvent Gels for Removal of Wax-based Coating from Wall Paintings, Conservation of Wall Painting Department, Courtauld Institute of Art, 1991, p 13-19

- The Ethomeen C-25 is an insoluble cocoamine (polyoxyethylene(15)cocoamine) most suitable for the oxygen containing polar solvents such as isopropanol, ethanol, acetone and bezylalcohol.
- The Ethomeen C-12, (Cocobis(2-hydroxyethyl)amine) implies the use of non-polar solvent such as Aliphatic and aromatic hydrocarbons.
- Armeen® 2C (dicocoamine) is used for the least polar solvents like non-polar hydrocarbon solvents : Shellsol T and Shellsol D40.¹⁶¹

During the initial stage of preparation, amine and polyacrylic acid are mixed together to form a lump free paste which is then dispersed in the solvent, and the water is gradually added until the acid and base combined forming a transparent viscous gel. Despite the fact the main active component of the gel formulation is represented by solvent, it remains a water thickened formulation. The amount of water is increasingly small and exists in a purely coordinated state. In other words the water does not exist in the gel in a separate phase but only as a part of polymer structure.¹⁶²

Carbopol exhibits as a low electrolyte tolerance and can only be stable at pH 6 to 10. This means that if the gel is applied on a surface where pH is above 10 it will lose its gelling properties.¹⁶³

The surface application of the solvent gel implies regular swabbing or using gel as a compress. Following the latter application method, the gel is applied with a small brush, massaged on the surface to induce the cleaning action and left for the required time interval to allow the varnish to soften. Then the swollen varnish is disrupted with a cotton swab and removed together with the gel residues. As it is impossible to remove all the gel from the surface just in one swabbing procedure, the surface is afterwards cleared with a rinsing solvent.¹⁶⁴ The principle of residue removal implies the use of appropriate rinsing liquid that would be capable of removing all of the residual material from the surface of the paint. Carbopol gel residues mainly consist of a polymer and a surfactant. The simplest way to remove the residues is to use the same solvent employed in the gel formulation. However for more polar solvent gel formulation it is not necessary to use the same solvent such as

¹⁶¹R. Wolbers and C. Stavroudis, *The Cleaning of Paintings : Handbook for Critical Cleaning: Applications, Processes, and Controls*, Second Edition, Barbara Kanegsberg, Ed Kanegsberg, CRC Press, 2011, p 408

¹⁶²R. Wolbers, *Cleaning of Painted Surfaces : Aqueous Methods*, Archetype publications, 2000, p 71-74

¹⁶³T. Cuerteis, *An Investigation on the Use of Solvent Gels for Removal of Wax-based Coating from Wall Paintings*, Wall Paintings, Conservation of Wall Painting Department, Courtauld Institute of Art, 1991, p 13-19, http://www.tcassociates.co.uk/downloads/cuerteis_gels.pdf

¹⁶⁴R. Wolbers and C. Stavroudis, *Aqueous methods for the Cleaning of Paintings: Conservation of Easel Painting*, J. Hill Stoner, R. Rushfield, Routledge : London and New York, 2012, p 509-513

ethanol or acetone. A lower polarity solvent can also be employed which will minimally affect the substrate. The surface rinsing procedure can be considered as one of the main limitations of the solvent gel cleaning as the final treatment of the surface leads to the exposure of the paint surface to the free solvent.¹⁶⁵

The carbopol gels can be considered incompatible for the irregular and uneven surfaces as part of the gel remains trapped in cavities in form of whitish scum.



Figure 32. The example of residue left after carbopol cleaning.

Photo : Mihhail Stashko

II. Clearance and residue issue

Considering the application of solvent gel cleaning formulation the main limitation of their application has been indicated during the studies performed in the 1990s. Clearance has been generally considered as a limitation of the Carbopol solvent gel cleaning procedures as solvent gel rinsing required a considerable amount of solvent to remove the residue from the surface of the painting. This operation again raises the issue of abrasion, swelling, and leaching of the oil paint films.¹⁶⁶

Apart from effects of free solvents applied on the last steps of gel cleaning the other problem was related to the possibility of remaining residues and their long term effects on the oil paint films. All of these issues were addressed in 1990 during the research conducted by Getty Conservation Institute. The presence and amounts of solvent gels were indicated

¹⁶⁵D. Stulik, D. Miller, H. Khanjian, *Solvent Gels for the Cleaning of Works of Art: The Residue Question*, Edited by Valerie Dorge, Getty Conservation Institute 2004, p 14-15

¹⁶⁶Same

through the radiolabelling method. The testing performed on a 100 years old naturally aged sacrificial painting and new reference paint films.¹⁶⁷

The cleaning tests indicated that residues always remain on the surface independently of application and rinsing technique. The remaining residues consisted of polymer residues, surfactant and solvent impurities. Surfactants as the largest part of the gel residues was particularly addressed with the long-term stability issue in relation to the underlying paint film.¹⁶⁸

The next phase of the study has investigated aging characteristics of five nonionic surfactants including Ethomeens C12 and C25. The aging of each surfactant and underlying paint surfaces was examined over the aging period of 72 hours under FTIR lamp and GC-MS in order to follow the process of degradation and nature of degradation products. After 72 hours of intensive light exposure, nonionic surfactants have rapidly degraded to volatile products and disappeared from the surface. The tested surfactants appeared to degrade independently of oil paint to which they were applied and had no detectable effect on both new and 100-year-old oil paint films.¹⁶⁹

Study of other residue components indicated that (Carbopol) becomes more stable during the aging process by forming internal crosslinking, thus remaining neutral to the paint material. Similarly to the other components, the solvent residues degraded independently from oil paint.¹⁷⁰

By the end of the investigation made by Getty Conservation Institute, the issue of residue effect on the original painting material remained open. Considering Carbopol gel cleaning Ethomeen was indicated to be the component that on aging remains active for a certain period of time, the exact effect of this process in the oil paint film has not yet been fully studied.¹⁷¹

¹⁶⁷ Same

¹⁶⁸ D. Stulik, D. Miller, H. Khanjian, Solvent Gels for the Cleaning of Works of Art: The Residue Question, Edited by Valerie Dorge, Getty Conservation Institute 2004, p 35-53

¹⁶⁹ D. Stulik, D. Miller, H. Khanjian, N. Khandekar, Solvent gel cleaning for Works of Art, The residue Question,, p 87-98

¹⁷⁰ D. Stulik, D. Miller, H. Khanjian, N. Khandekar, Solvent gel cleaning for Works of Art, The residue Question, ... p 135-136

¹⁷¹ D. Stulik, D. Miller, H. Khanjian, N. Khandekar, Solvent Gel Cleaning for Works of Art...., p 140

c) Rigid gels

Following the work of Richard Wolbers the aqueous rigid gels introduced in the conservation field is one of the conservation cleaning tools that in general terms pose a specter of benefits considering the surface cleaning procedures.¹⁷² Given their hydrophilic nature and the particular type of interaction with water, rigid gels can be identified as hydrocolloids or substances that in certain conditions take on structures capable of holding and trapping the molecules of water within which they are impinged.¹⁷³ When loaded with cleaning liquid and applied to a porous surface, the gel can gradually release the liquid, which is a physical process termed syneresis.¹⁷⁴ This occurs as the internal structure of the gel contracts, tightening the pores within the gel. The restriction of the pores results in water being forced from the gel.¹⁷⁵ Mentioning the absorbive properties of the gel it can in the same manner absorb the solvents water or pH modified solutions. This property was taken into advantage by the conservation specialists to treat the difficult surfaces where dirt or other foreign material is trapped both on the surface and in the structure of the material. Considering both syneresis and adsorption properties of the aqueous rigid gels are capable of producing a washing effect. At first the gel releases the cleaning solvent into the structure of the treated material, dissolves the dirt or other unoriginal material. The dissolved material is then dragged back into the gel. As a solvent gel it contains a sufficient advantage over the polyacrylate solvent gels namely rigid gels do not require a surface rinsing procedure after treatment. The cleaning effect produced by the gel can be regulated by the means of surface contact time and the concentration of dry product used for gel preparation.¹⁷⁶

In present, there are three products available for rigid gel preparation: Agar, Agarose. Agar is a gum derived from the cell walls of a species of red algae of the *Gelidium* or *Gracilaria*

¹⁷²Emma A. Schmitt. An examination of the Working Properties of Agarose Gels or Textile Conservation, School of Culture and Creative Arts, University Of Glasgow, August 21, 2014 , Antwerp University: Natalie Saez Ortega

¹⁷³Emma A. Schmitt. An examination of the Working Properties of Agarose Gels or Textile Conservation, School of Culture and Creative Arts, University Of Glasgow, August 21, 2014 , p14 Antwerp University: Natalie Saez Ortega

¹⁷⁴P. Cremonesi, Rigid Gels and Enzyme Cleaning, New Insights into the Cleaning of Paintings Proceedings from the Cleaning 2010 International Conference Universidad Politécnica de Valencia and Museum Conservation Institute Edited by M. F. Mecklenburg, A. E. Charola, and R. J. Koestler, Smithsonian School Press Washington D.C. 2013

¹⁷⁵Emma A. Schmitt. An examination of the Working Properties of Agarose Gels or Textile Conservation, School of Culture and Creative Arts, University Of Glasgow, August 21, 2014 , p14 Antwerp University: Natalie Saez Ortega

¹⁷⁶Aqueous Cleaning Systems, introductory lecture by Natalie Saez Ortega , University of Atwerp, May 2016

families. It is composed of two polysaccharides: 70% of agarose and 30 % of agaropectin.¹⁷⁷ The agarose is the main component responsible for the gelation properties of the agar gel, thus in purified form, it represents a higher quality gel, having a more uniform capillary structure distribution than Agar. The uniformity of the pores(capillaries) provide gel with a more even moisture release and better interaction with the treated material.¹⁷⁸ Such factors as retention and diffusion rates related to the working action of Agar gel are directly related to the porosity and pore size in the gel. The fine pores of the gel produce a low retention and a slow diffusion of the cleaning liquid, while large pore size produces the exactly opposite effect. The pore size is in turn regulated through concentrations of the dry gel product in water solution. The overall percentage range can be accounted for 1% - 5% v/v of dry gel powder in water. The largest pore size is attained at 1-2% concentration. By increasing the concentration to 6 % will produce a more rigid gel with a very fine porous structure.¹⁷⁹

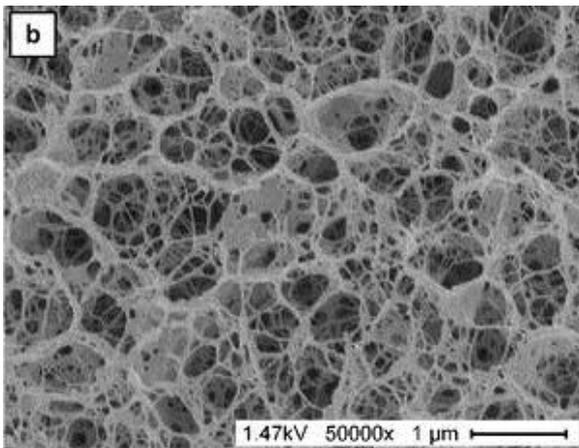


Figure 33. 2% Agarose

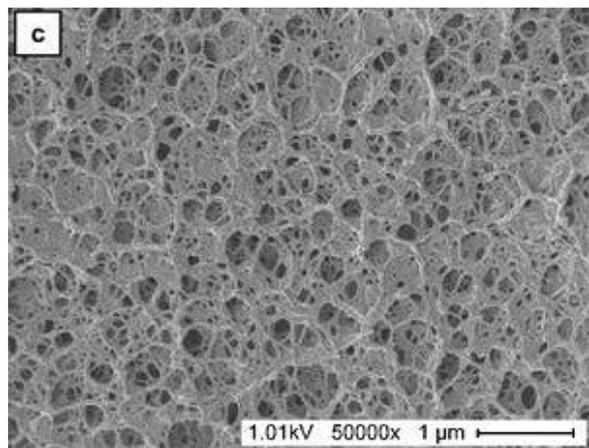


Figure 34. 6% Aggarose

Considering the preparation process, gelation mechanism of agarose, according to Lonza, involves „shift” from a random coil in solution to a double helix in the initial stages of gelation, and then to bundles of double helices in the final stage.¹⁸⁰

¹⁷⁷ Cindy Lee Scott, The Use of Agar as a Solvent Gel In Objects Conservation , AIC Objects Specialty Group Postprints, Vol. 19, 2012 <http://resources.conservation-us.org/osg-postprints/wp-content/uploads/sites/8/2014/12/osg019-04.pdf>

¹⁷⁸ Aqueous Cleaning Systems, introductory lecture by Natalie Saez Ortega , University of Atwerp, May 2016

¹⁷⁹ Aqueous Cleaning Systems, introductory lecture by Natalie Saez Ortega , University of Atwerp, May 2016

¹⁸⁰ Cindy Lee Scott, The Use of Agar as a Solvent Gel In Objects Conservation , AIC Objects Specialty Group Postprints, Vol. 19, 2012, <http://resources.conservation-us.org/osg-postprints/wp-content/uploads/sites/8/2014/12/osg019-04.pdf>

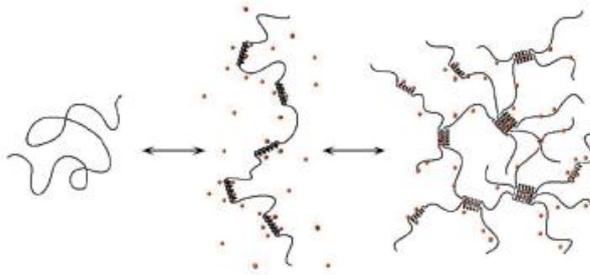


Figure 35 . Illustration of coil –helix transition

The preparation of agar gels starts from the mixing of dry product in water, producing a sol¹⁸¹. The sol is then heated in a microwave under 80 -85 degrees Celsius, which allows to melt the powder into the water. As sol is heated in the microwave it is important to control the heating process, checking the mixture every 20 or 30 second during heating process until the suspension starts to boil. The liquid is afterwards pored into a silicone tray and left to cool down and form a rigid gel. The gelling process is reversible and can be repeated several times without loosing the working properties of the gel.¹⁸²

The application and working action of the gel is determined by the ability of the gel to properly wet onto the surface. The latter feature has been indicated during the introductory course and cleaning workshop held at Antwerp University. The cleaning test was done on a varnished oil painting prepared on MDF board. The varnish of the painting has been fire damaged and was decided to be removed. The painting was treated with a 3% agarose gel loaded with isopropanol solvent. The gel was placed on the surface of the painting for 18 minutes. During the working action of the gel, it was noticed that isopropanol solvent started to accumulate on the borders of the testing areas. After the gel was removed the surface exhibited an aureole of destructured varnish. The center of the cleaning area has been slightly crazed which allowed presuming that the gel has not attained a proper contact with the surface due to the low permeability of varnish. In general, more testing is required to study the efficiency of agar gels on easel paintings; however, it is likely to presume that this method is

¹⁸¹Sol is a colloidal dispersion containing small solid particles dispersed in a liquid environment, for example ink.

¹⁸²Aqueous Cleaning Systems, introductory lecture by Natalie Saez Ortega, University of Atwerp, May 2016

mostly compatible with more permeable (porous) surfaces like textiles and wall paintings.

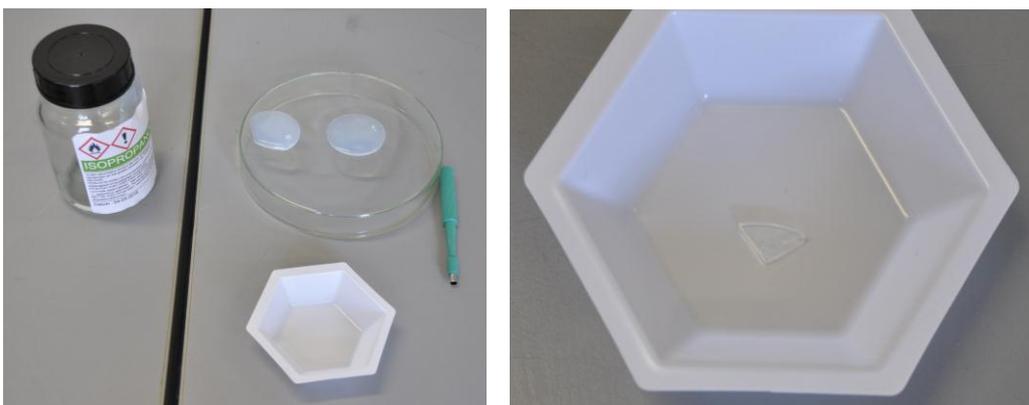


Figure 36 and 37. to prepare the solvent gel agarose was imbedded into isopropanol for 5 minutes and afterwards transferred to the painting. Photo : Mihhail Staško



Figure 38 and 39. Cleaning process, after 18 minutes of working time. Photo : Mihhail Staško

d) Tissue gel cleaning

Pointing out the main limitations of solvent and solvent gel cleaning, specialist in the conservation field has been concerned with idea of development of method that would answer the curtail requirements of surface cleaning including solvent capillarity flow and diffusion control and at the same time would be effective to remove the degraded varnish and dirt materials while leaving the oil substrate unaffected in short and long term perspective.¹⁸³

One of the innovative methods pursuing the mentioned criteria has been recently introduced in Estonia through the work of SRAL conservation institute. Harnessing the advantages of using a gelled solvent and minimizing the disadvantages of gel clearance is an underpinning concept for SRAL's tissue gel technique. The tissues impregnated with cellulose ether gelled

¹⁸³ Gwendoline R. Fife, Jos Van Och, Bascha Stabik, Nada Miedema, Kate Seymour, René Hoppenbrouwers, A package deal: the development of tissue gel composite cleaning at SRAL, 2011, <https://nigulistemuuseum.ekm.ee/wp-content/uploads/sites/6/2016/05/G.R.-Fife-A-package-deal.pdf>

organic solvents are applied to the varnished paint surface to swell, dissolve, and absorb the non-original coatings.¹⁸⁴

The solvent (or mixture of choice) is selected according to the regular safety margin tests performed using swabs and free solvent. The chosen solvent is then gelled by adding 2 to 4 percent by weight of cellulose ether, typically Klucel G (hydroxypropyl cellulose). The gel is used to impregnate a specific tissue, small sections of which are then tested on the painting to indicate the optimum length of contact time for dissolution of the degraded covering material, or desired “cleaning level”. In general, the gel impregnated tissue is applied to the surface for the average of 60 seconds, during which time it may, or may not, be covered with a Melinex insulation foil to further reduce solvent evaporation from the system. During this working period, the tissue remains semi-transparent and wet, allowing some monitoring of the cleaning process as the discolored varnish residues (and sometimes also the old retouching and overpaints) can be seen dissolving into the tissue gel composite. After this working period, a second dry absorbent tissue is placed directly above the first tissue and gently pressed using a sponge roller or metal spoon to absorb the non-original materials and gel. The pack of tissues and absorbed materials is then lifted from the cleaned painting surface and remaining residues are rolled with a dry swab.¹⁸⁵

Considering the residue issue, the ageing tests performed on Klucel G have indicated relatively stable, and although any residues left on the paint surface may undergo some yellowing, it critically maintains its solubility behavior and is inert with regards to any chemical effect it may have on the original paint surface.¹⁸⁶ The visual impact of Klucel G of residues after cleaning is also minimal whereas other cellulose ethers such as methyl cellulose might slightly alter the surface, giving it an extra glance.¹⁸⁷

Cleaning in context of painting “Saint John the Baptist”

The degraded varnish layers covering the painting “Saint John the Baptist” contain large amounts of oxidized groups produced during the aging process will most likely respond to the action of alcohol solvents. The fragmented first layer of varnish, however, presents a

¹⁸⁴ Same

¹⁸⁵ Gwendoline R. Fife, Jos Van Och, Bascha Stabik, Nada Miedema, Kate Seymour, René Hoppenbrouwers, A package deal: the development of tissue gel composite cleaning at SRAL, 2011, <https://nigulistemuuseum.ekm.ee/wp-content/uploads/sites/6/2016/05/G.R.-Fife-A-package-deal.pdf>

¹⁸⁶ Feller, R.L., and M. Wilt. 1990. Evaluation of cellulose ethers for conservation. Getty Publications http://www.getty.edu/conservation/publications/pdf_publications/ethers.pdf, mentioned in G. R. Fife, J. Van Och, B. Stabik, A package deal: the development of tissue gel composite cleaning at SRAL, 2011,

¹⁸⁷ Issues of paint surface stabilization using cellulose ethers, consultations with conservator Caroline de Wilde, Antwerp University, 10 march 2016.

cleaning difficulty in a sense that it contains material other than soft resin varnish. It can be presumed that the protein component can resist the solvent cleaning. For this reason, it is reasonable to prolong the action of the solvent and accompany it with a detergency effect. Carbopol solvent gels answer this requirement and should be employed. During cleaning action, the solvent will dissolve the bulk material (resin) while the immiscible part (protein) will be dragged into the gel by the means of detergency effect.¹⁸⁸

Considering the second varnish is considerably dark and blached it is difficult to determine when the substrate contains retouching, dirt or fragile parts of original paint. In this sense, it is also advisable to use the solvent gel as a more controlled and gradual system that will slow down the cleaning action of the solvent in order to attain a more accurate observation of the cleaning process. The cleaning will start with series of safety margin cleaning tests to find the safest and most efficient cleaning tool.

¹⁸⁸ Detergency effect will provided by ethomeen C25 that will surround the protein and form a molecular „trap“ that will allow to drag it into the gel

6.4 Reintegration of paint losses

The development of conservation attitudes in Italy

During the late 19th century the state of conservation theory exhibited a deviation in attitude and practical approach. In the 1930s the conservation of the artworks distinctively from conservation of architecture was still the matter of arts and crafts. One of the main representatives of this attitude were Count Secco -Suardo and his followers. The general concept of conservation was to restore the “true style ” of damaged artworks. This implied a complete reintegrative retouching and overpainting extending outside the loss areas. Initially, this standpoint emerged from ideas of Violet le Duc and was subscribed by Giovanni Secco – Suardo as well as by most specialists of that time including famous restorers and academic painters like Gaetano Bianchi and Giuseppe Molteni. In 1850-53 Bianchi uncovered Giotto’s wall paintings in the Bardi chapel and in Santa Croce, in Florence and made additions to and over painted the fragments in a neo –medieval painting style. His work was greatly admired up to 1920 but was strongly criticized afterward.¹⁸⁹

On the other hand, there existed an archeological restoration approach which was related to the work of Giovanni Batista Cavalcaselle. From the standpoint of Cavacaselle, the artwork like mural, painting, or mosaic was, first of all, a historical document, where cognitive value took precedence, frequently at the expense of the aesthetical appreciation of the artwork. The “true state” or the condition of authenticity implied acceptance of a number of material alterations including damage and patina. Basing on this new concept the restoration process implied minimal intervention and carried mostly a preservative character. Under guidance and supervision of Cavalcaselle in 1858-1861 the same Gaetano Bianchi , by restoring the wall paintings of Piero de La Francesca in the choir of Franciscan church in Arezzo, made no extensive additions to the original painting and restricted the intervention to filling the losses with plaster which was afterwards toned with a “neutral” toning. These “neutral” filling were afterwards overpainted during the following restoration of the chapel in 1960 by Leonetto Tintori with an addition of another “neutral filling”.¹⁹⁰

The aesthetical and historical theoretical bifurcations of the 19th century were eventually balanced out in the essays of Cesare Brandi, who was appointed the head of a newly

¹⁸⁹ Ursula Schädler-Saub. *Teoria e metodologia del restauro . Italian contributions to consevation in theory and practice: Conservation and preservation: Interactions between Theory and practice , In memoriam Alois Reigl (1858-1905) M. S. Falser , W. Lipp, A. Tomszewski, Vienna ,Austria, 23-27 April 2008 , p 81-82*

¹⁹⁰ Same

established *Instituto Centrale Del Restauro* in Rome on 1939. The publication of “*Teoria del Restauro*” emerged from Brandi’s essays published in 1963.¹⁹¹

Based on Gestalt philosophy the focal point of Brandi’s theory was the distinction of artwork from the regular craftsmanship objects. The main difference according to Brandi consisted in the fact that artwork is not the collection of parts serving a certain function but an “artwork”. The material of the artwork, in this sense, plays only a secondary role while the image takes precedence. Basing on this difference restoration is “*a methodological moment in which the work of art is appreciated in its material form and historical and aesthetical duality, with a view to transmitting it to the future* “. ¹⁹² By describing relations between material and the image Brandi stated that „*only the material can be restored*”. This statement means that the material form of work of art must necessarily take precedence because it represents a transmitter of the image and thus guarantees its perception within human consciousness. But the physical medium to which the transition is entrusted does not accompany it, on contrary it coextensive with it. Thus it is not a question of material on one hand and the image on the other.¹⁹³

The second axiom of Brandi states: „*Restoration must aim to reestablish the potential unity of the work of art without producing and artistic and historical forgery and without erasing every trace of passage of time left on the work of art.*“ ¹⁹⁴

Apart from image transmitter the material substance of art work is a witness of time passage and exists in two time moments simultaneously. In first the object exists in the past, at the moment of completion, and the second exists in the historical present. In terms of Brandian theory, the restoration is a process that legitimates the historical passage of the object. On a practical scale, such “time passage” elements can be represented by external alterations and natural ageing effects of material, which are legitimate as long as they do not take precedence over the aesthetic requirements of the artwork. If one to remove the evidence of time passage by making the appearance of 17th-century painting look as new, or vice versa, a historical forgery will be produced.¹⁹⁵

Considering the aesthetical requirement, connected to the issue of reconstruction and past additions. From historical requirements, addition is legitimate as an element of material history, as long as it does not go in conflict with the aesthetical component of the art work.

¹⁹¹ C. Brandi , *Theory of Restoration I: Historical and Philosophical Issues in the Conservation of Cultural Heritage*, N.S. Price , N. Kirby Talley, Getty Conservation Institute 1996 p339-342

¹⁹² *Same*

¹⁹³ *Same*

¹⁹⁴ *Same*

¹⁹⁵ *Same*

A reconstruction, on the other hand, seeks to reshape the work art, intervening with the creative processes that had originally taken place. By doing so the reconstruction merges the present and past moments and apart from producing an aesthetical forgery it also eliminates the evidence of time passage of the object, and by doing so it additionally produces a historical forgery.¹⁹⁶

6.4.1 Reintegration of losses in context of C. Brandi „Teoria del Restauro“

Considering the Brandian principle that the artwork transmits the image through the material, the artwork can not be understood as a collection of parts but rather as a holistic entity where the potential unity exists in its every piece and the object as a damaged entity continues to exist. For Brandi lacuna is not merely a structural loss but an independent element in the painting, which not only „disturbs the figurative pattern“ of the painting but also creates a certain boundary between the image and itself. Inside this twofold relation, the lacunae exists as a foreground element and the painting itself is pushed to the background. From this perspective the main issue - as stated by Brandi- consists not in „what is lost but what is inserted inappropriately“. The visual impact on the appreciation of the artwork becomes the main aspect of lacunae. The inappropriate insertion can be referred both to the empty space of loss and inappropriately inserted retouching.¹⁹⁷

Following the Brandi concept, Paolo Moras and Laura and Paul Philippot stated that retouching is a matter of critical interpretation, justifiable as long as it helps to see the potential unity within the fragments of the art object. This implies that „intervention should stop where the hypothesis begins“, thus reintegration as a general procedure should be limited to treating the loss in such a way that instead of coming forward as an independent element of painting, lacuna should be neutralized and become the part of the background. In addition, the historical requirement implies that the retouching should remain distinguishable from the original work, as an evidence of critical interpretation, although remaining integrated with the formal tonality of the work .¹⁹⁸

¹⁹⁶C. Brandi , Theory of Restoration I: Historical and Philosophical Issues in the Conservation of Cultural Heritage, N.S. Price , N. Kirby Talley, Getty Conservation Institute 1996, p339-342

¹⁹⁷ Same

¹⁹⁸ P Mora , L mora , P Philippot, Problems of Presentation , Historical and Philosophical issues in conservation of cultural heritage , The gettu conservation institute , Loss Angeles 1996., p 343-354 .

Methodology

Considering the painting presents losses of different types it is important that reintegration be adapted while respecting the both historical and aesthetical requirement of the painting. To avoid resorting to hypotheses and restore maximum presence and unity of painting the retouching should proceed within a coherent system. To attain this purpose it is generally advisable to proceed progressively starting from the paint wear and abrasions which represent a minor disturbance of the painting and proceed forward to the state where larger losses can be assessed. Then it is important to determine which of the losses can be reconstructed and which not. The latter should be consequently treated in such a way that the restored image is disturbed as little as possible. The reconstruction of limited losses is justified by the potential unity of the surrounding paint remains visible and does not imply a „subjective moment“ in the course of reconstruction. For areas of larger paint losses located both outside and in the important figurative parts of the painting, it is particularly advisable to use *Tratteggio* technique.¹⁹⁹ According to Moras and Philippot reconstruction in *tratteggio* consists “*in transposing the modeling and drawing of a painting into a system of hatchings based on the principle of the division of tones.*”²⁰⁰ The two main purposes of *tratteggio* consists in differentiating the retouching area from the original painting and preventing conservator from personal expression. The latter is achieved by restraining the retouching process to pure mechanical work and preventing the restorer from imitating the lines or brushstrokes of the original source. It is, however, important for the restorer, to achieve the most complete and rigorous reintegration by working through this „filter“.²⁰¹

In application to painting „Saint John the Baptist“ the numerous small areas of damage and losses located in the dark areas of paint can be reintegrated using a complete reintegration method as the potential unity in these areas still remain visible. In the large structural loss area located in the lower left section of the painting the potential unity of the fragment of the main layer is lost and requires another retouching technique, in order to avoid a subjective reintegration. *Tratteggio* in this sense satisfactorily answers the aesthetic criterion and avoids a subjective interpretation of the fragment.

Maimeri Varnish retouching colors

¹⁹⁹ P. Mora, L. Mora, P. Philippot, *Problems of Presentation, Historical and Philosophical issues in conservation of cultural heritage*, Getty Conservation Institute, Los Angeles 1996., p. 343-354.

²⁰⁰ Same

²⁰¹ Same

According to Maimeri Gruppo, the Varnish Colors are a mixture of pure, authentic, lightfast pigments mixed with mastic resin and refined hydrocarbon solvents. Mastic is a triterpenoid resin derived from the sap of a tree, *Pistacia Lentiscus*. According to research conducted by CCI revealed that the solvent was likely a-pinene on a-pinene. However, in 2000 Safety Data Sheet stated that Maimeri colors contained naphtha benzene.²⁰²

Maimeri Varnish Colors are initially soluble in a range of solvents including low aromatic mineral spirits, xylene, toluene, isopropanol, 1-methoxy 2-propanol. During the application, the process the gloss of the retouching can be modified by the means of admixtures including fast evaporating solvent and a similar triterpenoid varnish. The solvent admixture such as toluene allows producing a more mat appearance of retouch, while the addition of resin produces a more saturated and glossy appearance of the paint.²⁰³

The main issue of aging of this type of retouching consists of yellowing of mastic media in the paint.²⁰⁴

²⁰² *Charlotte Seifen Ameringer : Maimeri Restauro Varnish Colours: Painting Conservation Catalog Volume III: Inpainting, Catherine A. Metzger, The Paintings Specialty Group of the American Institute for Conservation, p 193-197*

²⁰³ *Same*

²⁰⁴ *Same*

6.5 Varnishing

6.5.1 General considerations for choice of varnish

Historical

The varnishes are frequently mentioned in the 17th and 18th century historical treatises and are known for their role as a unifying and color saturation media intentionally applied by the painters on the final stage of making of the painting.²⁰⁵ The varnishes used for the surface coating application were generally spirit or oil based and included a number of soft and hard resins as. The first attempt to reestablish the „final appearance” of the painting was done by Sir Charles Eastlake. Historical varnish reconstructions made by Eastlake had led him to a conclusion that originally historical varnishes had warm dark unifying tone. The conclusion of this research has led to the use of oleoresinous varnishes or pigment containing, tinted varnishes to provide the painting with “original” unifying dark tone. The opposite the aesthetical requirements related to the application of the varnish are reflected in Paolo Palomino`s description.²⁰⁶

*When it has been varnished by someone who does not know how it should be done, and especially if the varnish is clouded (as happens with balsam varnish), or if it has been washed with water, which tends to leave the whole canvas the colour of ashes; or if the varnish is very heavy and brilliant, preventing the picture being enjoyed, although to those who know little this seems the greatest perfection. It should, of course, be the contrary, that it [the colour] be saturated but not reflect light.*²⁰⁷

In contrast to Eastlake`s conclusion, it may be pointed out that clearness and a visual uniformity provided by the saturation effect of are the crucial varnish application requirements that were originally followed by the previous artist of 17th and 18th century.

The more recent research was done in 1994. Dr. Carlyle, using several historic recipes, had mixed up a number of varnish solutions as close to the original recipes as was possible in this modern age. She pointed out that over the years resin sources have changed, in some cases

²⁰⁵ Э. Бергер. История развития техники масляной живописи. М. Издательство Академии Художеств СССР, перевод А. Н. Лужецкой, под редакцией А. А. Рыбникова, 1961, р 205-210, р 296 -305

²⁰⁶ Alan Phenix and Joyce Townsend , A brief survey of historical varnishes, Conservation of Easel Paintings Joice Hill Stoner , Rebecca Rushfield ,2012 , p259

²⁰⁷ Same

quite dramatically, thus even her varnishes may not have had the same exact working properties, appearance, coloration as those originally used.²⁰⁸

Aesthetical

Considering the previous interventions taken place on the surface of the painting it is important to consider the structural as well as aesthetical alteration of the paint film. For „John the Baptist“ this issue is related to the paint binding media erosion resulted from rough cleaning interventions. Applying a new varnish will render the colors with saturation and will allow to certain extent recover the lighting effect of the picture and distinguish details that were not visible, due to the poor preservation state of the paint.²⁰⁹

Technical : isolation

Considering the paint layer has suffered a total overcleaning damage the conservation process will include a numerous retouching to retrieve the coherence of paint material. Thus an isolative coating will be applied to isolate original material and increase the reversibility of the retouching paint. In order to further integrate the retouching layer, a final coating is most likely will be applied. Considering the long-term preservation issue, both of the varnish coatings will protect the surface of the painting “Saint John the Baptist” from airborne dirt, abrasions, stains, and vandalism, as well as reduce the atmospheric agent influence, thus buffering the aging processes of the paint.²¹⁰

6.5.2 Choice of resin

Dammar varnish

Dammar varnish-a triterpinoid resin extracted from plants Dipterocarpoideae subfamily of the Dipterocarpaceae family. It was first described as a painting varnish by an apothecary Freidrich Lucanus in 1828. It is a low molecular weight resin with a high refractive index of 1.539. Dammar exhibits superior visual properties as a painting and conservation varnish. For conservation use, the liquid dammar varnishes can be found in various forms and gloss grades.²¹¹

²⁰⁸ Varnishes: Authenticity and Permanence, September 19-20, 1994, Ottawa, Conference Reviews, Column Editor: Mary Piper Houg, WAAC Newsletter, Volume 17, Number 1, Jan 1995, p.28

²⁰⁹ W. H. Samet Selecting a varnish, Historical considerations, submiettied 1996, Surface Coatings, Painting conservation catalogue, Volume 1, Wendy Samet, AIC, 1998, p 6

²¹⁰ W. H. Samet Selecting a varnish, Historical considerations, submiettied 1996...., p 2

²¹¹ L. Mrez –Le, Low molecular weight varnishes, Dammar varnish, submiettied 1996, Surface Coatings, Painting conservation catalogue, Volume 1, Wendy Samet, AIC, 1998, 63-69

On preparation, stage dammar is well soluble in aromatic and aliphatic hydrocarbons. On aging, they become more insoluble and require alcohols for de-varnishing.²¹²

Historically this varnish was prized for its visual properties durability and yellowing resistance superior to mastic resin. However as a triterpinoid resin Dammar exhibits a high yellowing capacity than the low molecular weight synthetic resins such as Arkon® P-90, Laropal R-80 and Regalrez® 1094.²¹³ The testing done to examine the ageing properties of dammar has indicated that after the 15 years the dammar exhibit a trace of yellowing while Laropal R-80 and Regalrez® 1094 exhibited none.²¹⁴

Rene de la Rie stated that because of this properties both mastic and dammar varnishes are inappropriate for conservation application as they present a long term stability issue.²¹⁵ He pointed out that historically the use of natural resin varnishes has led to what he called „varnishing cycle“ or continuous cycle of cleaning and varnishing which in turn had affected the paintings in terms of both structural and visual stability.²¹⁶ However the solution to this problem has been reflected in the research „Varnishign and Authenticity“ in Quebec . Both mastic and dammar varnishes supplemented with Tinuvin 292 (3% v/v of dry resin) have exhibited resistance to yellowing after 15 years of natural light aging.²¹⁷

Laropal K-80

Laropal® K80 is a polycyclohexanone condensation. It is a transparent low molecular weight ketone resin introduced in 1979 by BASF. It refractive index 1.529 with the gloss parameters similar to dammar varnish. Commercially its available in form of transparent resin lumps which can be dissolved in Stoddard Solvent/Shell Sol® 340 HT, Shell Mineral Spirits 145, Petroleum Benzine, Turpentine, Shell Cydo Sol® 100/Shell CydoSol® 53. The resin can be brushed effectively in mineral spirit solutions between 10% and 30% (v/w)²¹⁸ Same percentage or lower (10-15%) solutions can be used for airbrush applications. Possessing a high glass transition temperature 50.8 this varnish can efficiently protect the painting from the external mechanical factors . However due to its brittleness it rapidly

²¹²Same

²¹⁴ M. O'Malley , Review of Samples from the 1994 CCI Workshop “Varnishes: Authenticity and Permanence” after 15 Years of Natural Ageing, p 4-6 https://www.cac-accr.ca/files/pdf/Vol35_doc1.pdf

²¹⁵Varnishes: Authenticity and Permanence, Conference Reviews, editor :M.Piper Hough, WAAC Newsletter Volume 17, Number 1, Jan 1995, p.28, <http://cool.conservation-us.org/waac/wn/wn17/wn17-1/wn17-107.html>

²¹⁶Same

²¹⁷ M. O'Malley , Review of Samples from the 1994 CCI Workshop “Varnishes: Authenticity and Permanence” after 15 Years of Natural Ageing, https://www.cac-accr.ca/files/pdf/Vol35_doc1.pdf

²¹⁸ Volume to weight

looses structural stability and starts to cleavage. On ageing the Laropal ® K80 yellows and looses initial solubility parameters and can be only removed with alcohols.²¹⁹

6.5.3 Application tools

Brushing

Brushing is a traditional method of varnish application. It is most often used for intermediate varnish application or on the surfaces where no retouching is present. The later precaution is essential as the solvent sensible retouching might be disrupted in the course of brushing action. For brushing the painting has to be placed in a horizontal position as to avoid dripping and irregular spread of the varnish on the surface of the paint. The varnish can be applied in strips placed precisely one next to another in order to produce a maximally uniform coating.²²⁰ Other method implies a simple criss-cross application which is usually applied for small format works.²²¹ The essential requirement for brush application varnishing consist in controlled delivering of varnish onto the surface of the painting and requires skill and more or less precise amount of varnish carried on a brush. Brush dimmed in the varnish has to contain small amount of varnish as to avoid producing an excessively thick coating.²²²

Rubbing

The other method consists in varnish application by the means of silk cloth or nylon stocking. Both of these materials tend to release smaller quantities of varnish and evenly cover the surface via gradual circular motion on the surface of the painting. The dry silk cloth can also be used for leveling the varnish coating, however it must be remembered that leveling of varnish using this method most often leads to additional sorption of the varnish into the paint layer and thus must be limited.²²³

²¹⁹R. Barath-Cox , Low Molecular Weight Varnishes , Ketone Resin Varnishes , Laropal K80, submited 1996, Surface Coatings , Painting conservation catalogue, Volume 1, Wendy Samet, AIC , 1998 , the source is available from author of the present thesis.

²²⁰Recommendations of Malle -Reet Heidelberg during the restoration of painting “ The Rapids” on may 2014.

²²¹K. Nicolaus The restoration of paintings , 2007, p 322-323

²²²same

²²³M. von der Goltz, Varnishing application techniques:Conservation of Easel Paintings , Joice Hill Stoner , Rebecca Rushfield , p 636-637

Spraying

This method implies the varnish application through spraying using a spraying gun. This method allows to produce thinner and more uniform varnish coating than the one produced by brush or cloth. The other advantage of spray application is that it requires smaller amounts of varnish to produce an even coating.²²⁴

Varnishes can be applied using either low or high pressure methods. The low pressure guns, usually aerosols, have operating pressure about 0.2-0.9 bars. They use little air but the varnish vapor they produce is not as fine as high pressure method and may provide a higher risk of dripping during the application process. By adjusting the spray gun above the low pressure value allows to produce finer vapor and more uniform varnish coating using smaller amounts of varnish. Distinctively from brushing, the spray gun application permits working on the difficult surface, for instance weathered and highly permeable paint films or sensitive and mechanically unstable surfaces.²²⁵

Varnishing of painting „Saint John the Baptist”

Considering the cleaning that previously took place on the present paint surface, it can be presumed that the surface of the painting is very permeable, making the traditional brushing and rubbing applications difficult due to the fact that these application methods will carry larger amounts varnish, most of which will sink into the structure of the painting and producing an irregular coating.

Considering the aesthetical requirements of the painting, the shades and the half tones of the painting has to be saturated in order to provide the dark passages of paint with their former depth and saturation. For this reason it is advisable to use a high refractive index glossy varnish such as dammar. During the conservation process the varnishing will proceed with testing, using both traditional and spray application methods in order to determine the optimal treatment method.

²²⁴ K. Nicolaus, *The restoration of paintings*, 2007, p 322-323

²²⁵ Same

7. Conservation process

De-mounting

Before the intervention the fragile areas of the paint layer were temporarily stabilized from the front side of the painting using filter paper patches applied with 3% sturgeon glue aqueous solution. The patches were first placed on the surface of the painting and afterwards glued from the frontside using animal glue. The treated areas included lower right edge, and two large areas of structural losses located in the left section of the painting.

The canvas together with the lining support was demounted from the stretcher. The nails were slightly lifted from canvas with a screw driver and gently plugged out using crossbar. By the end of this procedure all of the nails were removed and the painting was transferred by four people onto the working table face down.

De-lining

The linoleum removal initially proceeded with a test observation to determine the behaviour of the adhesive during the attempt to detach the lining support. The test proved that the lining adhesive has sufficiently brittle with age and is very responsive to mechanical action produced by carefully lifting the linoleum support and promoting detachment with dumb flat instrument like spatula. The total detachment of linoleum was done by slightly lifting the linoleum and promoting the detachment by inserting hand between linoleum and original support.

The exposed backside of the original canvas was covered by an uneven layer of reddish-brown resin that in some areas had been removed almost completely, while in other areas exhibited larger accumulations. The unremoved portion of lining adhesive was sanded down to the original support. The sanding proceeded using sand paper of 150 and 320 grit. Areas with the largest accumulations of resin (lining adhesive) were treated with coarser 150 grit sandpaper until the lumps and irregularities on the surface were eliminated; the remaining resin was sanded using more fine 320 grit sand paper to expose the canvas threads. Connecting seam was the only area remained unsanded. The decision to preserve the resin covering of the seam was made to ensure the connection stability between two canvas pieces in the long term perspective.

By the end of this this treatment the backside of original canvas has been sufficiently exposed to allow the canvas to partially regain its elasticity. For the safety and inaccessibility reasons part of the lignin adhesive remained in the structure of the canvas fibers.

Support structural conservation

The procedure started with a margin test . A small piece of BEVA and supporting fabric were placed on a surface of the canvas and ironed at a temperature around 70C . The margin test showed that the nap bond produced by BEVA film has achieved a satisfactory adhesion with the original canvas despite the presence of adhesive residues.

The patches and taking margins were cut from the linen fabric of the same weave and density. A part from patching a single inlay was made from the same fabric in order to level the loss area and hide the edges visible from the front side of the painting .

The linen canvas margins of 15x 157 and 15x 123 cm were placed on the canvas . The width of overlapping strip between original and the lignin canvas has been accounted on 4-4.5 cm. The exact number of the strip can not be given as the edges of the canvas are considerably irregular. The application proceeded according to the following steps :

1. A double layer BEVA 371 film were placed on the surface of the canvas with the tacky side (containing the BEVA 371 adhesive) downwards .
2. The margins of the film were ironed in small areas located close to the edges of at a temperature of about 70-80o C in order to fix the adhesive films in place
3. The adhesive was covered with a supporting fabric and thoroughly ironed under 70 -75o with sufficient pressure application.

This method allowed to provide a stable nap bond between the original and supporting canvas.

The next step was to mount the canvas on a new stretching frame using a staple gun and a stretching pieler. The painting was laid face down on the floor paved with paper sheet to avoid dirtying or damaging the surface of the paint. The stretcher was placed on the backside of the painting in a concentrated position where it matched the position of original canvas and at the same time following the thread directions. The mounting proceeded with an initial stapling of margins ,which allowed to temporarily stabilize stretcher and original canvas in a fixed position. The stretching of each side of the canvas was done with a stretching pieler and staple gun; by gradually stapling each side of the canvas starting from

the centre and moving towards the edges the canvas was stabilized on the wooden wedge stretcher support.

Cleaning

Before the cleaning has been undertaken, the paper patches applied from the front side on the earlier stages of intervention process were removed after slightly moistening the filter paper with distilled water.

Step 1: safety margins test

The cleaning procedure of the painting „St. John the Baptist” began with a safety margin test. The safety margin test is a procedure done on in the least visible area of painting, that allows to predict several cleaning factors to be considered during the cleaning. These include: response of the varnish to various cleaning solvents , amount of covering material to be removed , sensitivity of paint and measuring the „cleaning level” or how far the cleaning should be carried out .²²⁶

The surface chosen for the testing located in the lower left edge of the painting. Additional small cleaning tests were made on the St. John`s incarnate (forearm), lamb incarnate area and on left angel`s incarnate.

The test solvents used for the procedure were sorted according to their swelling strength, starting from weakest, like water and gradually proceeding towards the strongest such as acetone. The chosen agents included: distilled water, saliva, triammonium citrate, ethanol, acetone, benzyl alcohol gel and Acetone/Ethanol 50: 50 gel. Both solvents and gels were applied using cotton swab(s). The testing results were observed via gross observation and stereo microscope.

²²⁶ D. Stulik, D. Miller, H. Khanjian, N. Khandekar, Solvent Gels for the Cleaning of Works of Art: The Residue Question, Edited by Valerie Dorge; 2004, p 66-68

Testing area	Margin test	Margin test	Margin test	Margin test	Margin test + angel incarnate	Margin test + Green elements Lamb incarnate
Question/ solvent	Distilled water	Saliva	Triamonium citrate 2%	Triamonium citrate 3%	Ethanol	Acetone
Number of swabs used	1	1	1	1	3	3
Was the upper varnish removed?	No	No	No	No	Yes	Yes
Was the lower layer of varnish removed ?	No	No	No	No	Partially	Slightly
Was the surface dirt removed?	Partially	Yes	Yes	Yes	Yes	Yes
Was there any sign of the pigment loss?	No	No	No	No	No	No
Was there any visible alteration of the surface?	No	No	No	No	No	No
Was there any paint removed by mechanical action of the swab ?	No	No	No	No	No	No

Table 3 . Evaluation table for free solvents.

Teas area	Margin test	Margin test ,
Question/ solvent	Ethanol/acetone gel	Benzyl alcohol gel
Number of cleaning swabs	6	5
Was the upper varnish removed?	No	No
Was the lower layer of varnish removed?	(There was no lower varnish in the tested area)	(There was no lower varnish in the tested area)
Was the surface dirt removed?	Partially	Yes
Was there any sign of the pigment loss?	No	No
Was there any visible alteration of the surface?	No	No
Was there any paint removed by mechanical action of the swab ?	Uncertain , the swab exhibited a tint that reminded of pigment.	No

Table 4 .Solvent gel evaluation table

Result interpretation and conclusion

Cleaning liquids including triammonium and saliva had only removed the surface dirt and exhibited no effect on the varnish. Other cleaning agents including acetone, ethanol and solvent gels had successfully removed the superficial dirt from the surface, as well as dissolved the degraded upper varnish coating. The lower varnish was occasionally encountered during the cleaning tests. It was found that the lower varnish satisfactory responds on the action of ethanol although an additional mechanical „ work“ is required to remove it.

Considering the effects on the original paint paint surface , the observation of the swabs under the light microscope has indicated that some pigmented material was removed by acetone-ethanol gel test. This material could possibly be a retouching or the original paint.

The attempt to indicate the presence of retouching layers on the surface of the painting has failed due to the soiled and degraded dark varnish covering.

The removal of the varnish layer required 2-3 swabs of free solvent and 5-6 of solvent gel.

The gel cleaning required extra 2-3 swabs to clear the surface from the gel residues.

The exposed surface of the paint was expectedly blanched due to the oil medium erosion. The later aspect of the surface was most certainly produced earlier, in result of strong cleaning agent application during the previous intervention.

The major difficulty of the present cleaning consisted in lack of control over the cleaning process. The upper varnish material together with the dirt exhibited a dark brown colour which was similar to the colour of original paint. In order to avoid possible damage in the dark paint areas it was decided to remove only the part of the varnish with a controlled system like benzyl alcohol solvent gel.

Step 2 : removal of the upper varnish layer (Background, lamb incarnate)

The cleaning of the upper varnish layer began with benzyl alcohol gel.

Recipe:

1. 2g Carbopol 980/940
2. 20 ml Ethomeen c 25
3. 100 ml benzyl alcohol
4. 15ml water

Clearance : isopropanol/white spirit 50:50²²⁷

During the cleaning with benzyl alcohol gel, the larger part of the upper varnish layer was removed. The observation under the UV light has indicated a considerable amount of varnish still present on the surface of the painting, confirming that the paint surface was not fully exposed. The additional light microscope observation of the swabs indicated no evident traces of pigment present on the swabs. It is also important to mention that the varnish coating was thicker in the background areas and thinner in the incarnate areas. In addition the Carbopol gel cleaning presented handling difficulties, as it required a considerable amounts of rinsing solvent to clear the surface of the painting, which increased the risk of paint surface exposure to the solvent action.

²²⁷ N. Unmney, S. Rivers, Conservation of furniture, Norbert S. Baer, Butterworth-Heinemann 2003, p 556

By the end of this cleaning phase upper layer and small part of lower layer of varnish was removed from the background and lamb incarnate areas. The exposed surface exhibited two features:

- Randomly spread fragments of the first varnish, which were most prominently visible in the lighter parts of the painting
- Numerous paint losses in both upper and lower part of the painting. The presumption that the paint damage was produced by the present cleaning was dismissed, as the damage pattern exposed in the lower part of the painting²²⁸ had the same character as the damage present in the upper section of the paint surface, which was readable through the varnish before the cleaning was undertaken. In addition the UV light observation indicated a considerable amount of varnish present in the damaged areas thus confirming that a thin layer of varnish still remaining on the surface of the painting.

Step 3: St John`s and an angel`s incarnate cleaning

Following previous strategy, the upper varnish layer was carefully removed with benzyl alcohol gel. In the course of cleaning a thin red and brown layers of paint were found underneath the varnish layer. The color and tonal dissonance between these layer and original paint surface allowed to conclude that the present layers represented retouching applied in the course of previous intervention. Considering the evident visual disharmony of these materials with the surrounding paint they were removed together with the varnish.

- The exposed lower layer of varnish exhibited a minimal response to the benzyl alcohol gel. Pointing out the limitation of Carbopol gels, consisted in the free solvent application by the end of the cleaning process it was decided to remove the lower varnish using free ethanol only. Considering the possible instability of the darker areas of the incarnate it was decided to completely remove the varnish layer in the highlights areas while leaving the darker parts partially covered. The cleaning of lower varnish layer was done using small swabs (about 5-10mm in length). Every fragment of varnish was removed separately to avoid damaging the surrounding less covered areas of paint areas. The lower solubility of varnish could have consisted in the presence of protein material in the painting which on ageing crosslinks and is harder to dissolve. The other reason could

²²⁸Before the cleaning the lower part of the varnish was heavily crazed, preventing the observation of the paint surface underneath the varnish layer.

have consisted in the ion migration from the lead white paint layer that formed a stronger ionic bonds with the varnish layer.



Figure 40. The final stage of Step 3 . The surface on the lower right part of the painting was saturated with dammar resin varnish prepared 1:1 proportion using *Nevskaya palitra* liquid dammar varnish and white spirit.

Step 4: Varnish removal

The previous cleaning phases have removed most of the old degraded varnish material from the surface of paint, however leaving considerable amounts of varnish residues behind. It was especially prominent in the St. John and angel incarnates. The next step was to conduct a selective cleaning, in order to remove most prominent distortions (especially evident in the incarnate areas) and achieve a more „uniform“ appearance of the surface.

The difficulty of residues removal consisted in the fact that most of them were left after the less soluble first varnish layer, requiring ethanol and much cleaning effort to dissolve it. To provide a minimal exposure of the surface to ethanol the alternative supporting tools were used.

Tissue gel cleaning

By the time this cleaning phase had been preformed, a new cleaning method was introduced through the series of lectures and ckening workshops held in Niguliste Museum. Course instructor Gwendoline Fife a member of SRAL conservation

The tissue gel cleaning starts from preparing a solvent gel from 2 % Klucel G gel (hydroxypropyl cellulose) admxtured and a cleaning solvent; in this case 2% was added to ethanol. The gel is used to impregnate a specific tissue, small sections of which are then tested on the painting to indicate the optimum length of contact time for dissolution of the degraded, non-original covering material, and finding a desired “cleaning level”. For John the Baptist the gel impregnated pad was held on the surface for 60 to 80 seconds under the Melinex foil to reduce the evaporation rate of the solvent and promote the cleaning action. During this working period the tissue remains semi-transparent and wet, allowing some monitoring of the cleaning process as the discolored varnish residues (and sometimes also the old retouching and overpaints) can be seen dissolving into the tissue-gel composite. After this working period, a second dry absorbent tissue was placed directly above the first tissue and gently pressed using a metal spoon to absorb the non-original materials and gel. The pack of tissues and absorbed materials are then lifted from the cleaned painting surface. The Lager part of the lower varnish did not come off together with the tissue gel and was removed by cotton swab loaded with isopropanol.²²⁹



Figure41. Before treatment



Figure42. The example of tissue gel clenined surface

²²⁹ Gwendoline R. Fife, Jos Van Och, Bascha Stabik, Nada Miedema, Kate Seymour, René Hoppenbrouwers, A package deal: the development of tissue gel composite cleaning at SRAL, 2011, <https://nigulistemuuseum.ekm.ee/wp-content/.../sites/.../G.R.-Fife-A-package-deal.pdf>



Figure 43. Description of the tissue gel cleaning process

Cyclomethicone methicone cleaning

Some of the remaining varnish residues removed by a combined method including semi-permeable cyclomethicone solvent barrier that was used to restrain the cleaning action of the ethanol solvent.

“Cyclomethicone.” also known as D4, is high molecular weight, volatile cyclic siloxane.²³⁰ It is a high molecular weight silicone based solvent that is immiscible with water. It has a very low surface tension and can be easily spread over low surface energy surface like oil paint and varnish. Cyclomethicone evaporates slowly, a working property that lends well to use it as a masking agent.²³¹ In other words it creates a semi-permeable liquid film that can be used to restrain the solvents contacting with surface of the paint in the similar way as Japanese paper is used to restrains the sorption of the cleaning solvent into the structure of wall painting during the cleaning.²³² The restriction of the diffusion rate allows to remove gradually without disrupting the underlying layers. For the present painting the

²³⁰ R Wolber , ckening Workshop ,video recording , Icon Book & Paper Group chanel , Youtube.

com

²³¹ M. Sullivan, S. Brogdon-Grantham, and K. Taira , Conservation New Approaches to Cleaning Works of Art on Paper and Photographs, Winterthur/University of Delaware Program in Art, 2014

http://cool.conservation-us.org/anagpic/2014pdf/anagpic2014_sullivan_etal_paper.pdf

²³² Cleaning of Wall Paintings, recommendations of Sarah de Smet , Artesis Hogeschool Antwerp, 2012

Cyclomethicone was spread over the surface with a dripper and the pure ethanol was used to clean the surface through the liquid mask formed on the surface of the painting. By the end of this procedure, the remaining parts of the varnish were further thinned in the dark paint areas and allowed to achieve a more uniform appearance of the surface.

Step 4: Mechanical removal of stains and varnish residues from the incarnate areas

After the incarnate areas had attained a certain degree of visual uniformity, the only issue was the presence of small stains and hardly soluble small varnish residues, which disturbed the appearance of highlights of figures. Both of these materials were removed using a combined cleaning method. At first they were slightly softened with ethanol and afterwards removed by the means of scalpel. During the cleaning process it was discovered that part of the stains present in the painting have merged with the paint surface and thus removing them would damage the underlying paint.

Removing of old restoration materials

The white water soluble putty filled in the tears located in the lower left section of the painting was removed by a combined method including moistening and dry mechanical removal. The surface of the putty was moistened through the application of water gel prepared with 4% of Klucel G which was applied as a poultice, from the front side of the painting and was left to swell the putty for 20 minutes. After this time the putty has been removed with palette knife.

Intermediate varnish application

After the cleaning process it was attempted to apply the intermediate varnish by the means of varnish impregnated piece of fabric (piece of nylon stockings). The varnish solution was prepared using „*Nevskaya Palitra*” liquid dammar varnish and artist grade white spirit in proportion 1:1. The varnish coating produced by this application method has been proved unsatisfactory as most of the varnish has sorbed into the substrate and generally produced a very uneven, patchy appearance of the surface. The coating was afterwards removed from the surface using artist’s grade white spirit.

During the second varnish application, low pressure spraying equipment was used and the mixture was adjusted to 1:3 proportion of same dammar varnish and artist grade white spirit. This application method produced a considerably more uniform coating; however, the

produced varnish vapor was too dense. This feature produced difficulties with application control uneven varnish layer, larger amounts of varnish applied on the surface and dripping. The excessively thick areas of varnish coating and dripping were thinned with a piece of nylon stockings dimmed in artist grade white spirit and a second varnish coating was applied by the means of high pressure spraying equipment with the same varnish (1:3). The surface produced by last varnishing attempt allowed to achieve a uniform appearance of the paint surface.



Figure 44. The intermediate varnish application

By the end of this intervention phase the paint surface was covered with a uniform varnish coating which allowed to reveal some of the landscape elements located behind the figure of Saint John, bring forward the heavily damaged plant elements located in the lower part of the painting and making figurative elements considerably more readable. The varnishing of painting Saint John the Baptist allowed to ones again evaluate the preservation state of the painting. It seems that the right leg of Saint John has been over cleaned to the state when the first line of the figure along with corrections became visible have become visible. On the other hand the observation of the figures after the varnishing has confirmed the possibility of recovering their “potential unity”.

On the other hand the present varnishing has produced a thick varnish layer, which exhibits a higher tendency to age and greater structural instability. None the less a highly permeable and large format painting like “Saint John the Baptist”, does not allow to achieve a uniform surface by applying a thin layer of varnish, thus the present thickness of the varnish is fully justified by the surface requirements of the painting.



Figure 45. Photo of painting “Saint John the Baptist” after varnishing

Filling putty

The structural losses of paint and preparation layer were filled with white putty prepared from the following materials: sturgeon glue 5% in distilled water, white chalk, honey, “*Nevskaya Palitra*” linseed oil .

The preparation procedure included following steps:

1. A small portion of 5 % hot sturgeon glue was poured on the hand palm

The hand palm is precisely used to keep the glue warm. The warm glue exhibits an improved penetration and gluing ability.

2. The glue was mixed a eye measured amount of chalk to produce a thick flexible paste
3. The Glue-chalk paste was added with a small portion of honey , used as plasticizing agent
4. A drop of linseed oil is added to improve the mechanical strength of putty

The putty was applied into the structural loss areas with palette knife and polished down to the level of original paint surface using palette knife. The excess of the putty on surrounding surface was slightly moistened and removed mechanically.

Retouching

In general the retouching process followed the methodology provided through the work of Laura and Paulo Mora and Paul Philippot . The first step was to lower the tone of smaller paint losses, abrasions and paint wearing in dark incarnate surrounding areas in order to render the damaged figurative elements more readable, and clarify the tonal relations between light and dark parts of the painting. The first layer of retouching was made very transparent with neutral color to tone down the contrast between losses and original paint. This allowed to read the position of shades, half tone and outlines of figures. As the shades and half tints outside the incarnate areas were “neutralized” it became possible to make colour precisions with an additional glazing layer to fully reintegrate small paint losses. The larger structural losses located in right part of the painting were reintegrated with *tratteggio* retouching technique. The surface of the putty was isolated with a varnish to seal the porous surface of the painting.

Before the retouching the surface of the putty has been sealed with dammar varnish to prevent the sorption of retouching media into the ground layer.

Normally tratteggio is applied with water colour. Tratteggio starts with placing vertical blue lines of about one cm in length at regular intervals equal to the width of one line. Intervals are then filled with red lines and the rest with yellow lines. Then, one by one, these lines are covered with a transparent glazing of fourth colour that eventually creates a tonal base. The colour reintegration was done by applying a final layer of hatching with Maimeri Restauro Varnish Colours that gave the saturation to the previous layers and at the same time corrected the colour of retouching. Each layer of hatching should be weak in intensity, the desired intensity of the whole is being obtained by superposition of glazes of transparent lines rather than by strength of colour which would cause the retouching to lack the vibration indispensable for the required effect.²³³



Figure 45-47. Tratteggio in progress (unfinished)

The incarnate areas were retouched last. The full reintegration performed in the incarnate areas consisted in neutralizing small loss areas locating in the important figurative areas like John's legs, chest and face. To aid the reintegration of the numerous small losses on John's legs the life model example was used as a guide for recognising the location of shades and half-tints of the figure.

²³³ P. Mora, L. Mora, P. Philippot, Problems of Presentation: Historical and Philosophical issues in conservation of cultural heritage, The Getty conservation institute, Los Angeles 1996, p 343-354

Final varnishing

The conservation procedure concluded with the application of final varnish consisted of Matt Dammar varnish purchased through Kremer. The final varnish coating allowed to reduce the excessive surface glance produced by the previous varnish and additionally reintegrate retouching with the surrounding paint. The mixture prepared consisted of 1 part of Matt Dammar varnish (Kremer) and 3 parts of artist grade White Spirit.

8. Conclusion

The present project has provided the possibility to study an extreme case of painting conservation presenting both practical and theoretical challenges.

One of the main issue stated in the begging of the present research was addressed to the possibility recuperation of the artwork in terms of aesthetical representation. During the initial observation, it was indicated that the painting is covered by the two layers of degraded varnish. Following the notion of patina provided through the theoretical framework of C. Brandi and P. Philippot it has been found that the varnish exists on a painting as an independent element that both disfigures the image of the painting and prevents the evaluation of the paint material condition. For this reason, it has come to the decision to uncover the paint layer from the degraded varnish. During the elaboration of the varnish removal strategy and subsequent cleaning process, it was possible to study various cleaning strategies in terms of their historical development, application, and issues related to long-term effects on oil paint. Bu studying the traditional solvent cleaning system study, it has been found that the commonly used Teas solubility chart can be by no means used as a critical tool for the cleaning but serve only as an illustrative material of solvents and polymer solubility properties. The previous studies of solvents in general, has recognized two general problems: swelling and leaching. Basing on this two limitations of the solvent cleaning R. Wolbers has developed a water based solvent gel cleaning systems carrying the advantage of restraining the flow of the solvent and reducing the risk of swelling and leaching of oil paint film. The preparation and working mechanism of the gels have shown that it is possible to increase the solvent activity on the surface and accompany it with detergency effect, which considerably increases the cleaning effect of solvents. However, for cleaning of painting "Saint John the Baptist", it has been found that despite the use of considerably highly polar solvent gel formulation like benzyl alcohol gel some of the varnish coating parts remained insoluble and responded only to pure ethanol solvent cleaning. The limitation of the gel cleaning consisted in the fact that every solvent gel cleaning requires a considerable amount of solvent to rinse the gel residues from the surface of the painting which again leads to the problems related to free solvent application. An additional problem consists in the fact that every time the polyacrylate gel cleaning is preformed, a small portion of residues is always left behind. On ageing process the residues contain an active component effects of which are not yet fully studied. This issue can be resolved by a cleaning method elaborated by SRAL conservation institute. It implies the use the tissue composite impregnated with cellulose ether gel. The

advantage of the cellulose ester gels consists in the fact that even if they are retained on the surface of the painting they exist only as a physical residue, remaining chemically inert to the original painting material and having the least visual impact on the surface of the painting. The last cleaning tool studied during the present project consisted of application of masking agent such as Cyclomethicone solvent, which allowed to successfully restrain the action of the pure ethanol solvent and safely remove the varnish in the sensitive areas of paint.

By the end of the cleaning procedures, the overcleaning damage of the paint layer that was attenuated by the dark varnish layer has now been brought forward. In addition, to overcleaning damage of the paint layer was sufficiently blanched due to the oil media migration that had taken place in the course of the previous cleaning. Both of these problems required varnish application that on one hand served as an isolation layer for retouching and on the other hand saturated the blanched surface of the painting. The varnishing procedure for painting Saint John the Baptist was again challenging because the surface of the paint was considerably permeable. This allowed to study different varnish application methods as well as try them on practice. The methods studied were: brushing, rubbing and low- and high-pressure spraying methods. By the end of this conservation phase, the high-pressure spray varnishing has provided the most even coating. Other methods, especially rubbing and brushing have provided the least satisfactory results.

During the conservation process of the painting "Saint John the Baptist", it has been found that despite the fragmented state of the paint layer, its potential unity can still be brought forward. Thus one of the most important phases of the present treatment has consisted in retouching. The extreme condition of the paint surface implied a variety of retouching possibilities. The key finding was that *tratteggio* is the most appropriate choice of reintegration technique for a partially ruined painting like "Saint John the Baptist". This technique was applied to the most prominent paint loss areas present in the left section of the painting. Considering the large scale of damage on the left. section of the painting the complete reintegration would most likely be aesthetically incompatible and would bring the loss area forward instead of pushing it backward. Distinctly from complete reintegration the use of *tratteggio* implies respect to historical passage of the art object and at the same time answering the aesthetical requiems of the painting by completely reintegrating the loss area when the painting is viewed at a longer distance and remaining easily recognizable at a close distance.

The smaller damage area where the potential unity still remained readable were reintegrated by a complete retouching. The finishing procedure consisted of application of final varnish coating which additionally reintegrated the retouches.

The secondary aspect of the present conservation works consisted in the structural conservation, during which the painting has been de-lined and cleaned from the reverse side and stabilized with a standard method of strip lining and patching using BEVA 371 adhesive.

By the end of the practical conservation phase, the painting was structurally stabilized and the visual coherence of picture layer recovered. Considering the damage that the painting has suffered during the previous cleaning, the former visual properties of the painting can not be recovered completely and some fragments remain in their raw material state. Visually these fragments were neutralized with retouching and continue to exist in the painting as a part of the background, without disturbing the important figurative elements of painting.

The other part of the project included a technical examination of original material in order to attain a link to the origin of the painting. The technical research framework provided a possibility to study painting materials employed in the present painting using a number of analytical techniques and interpret the results through 16th, 17th and 18th century historical resources on painting materials and techniques.

The analytical techniques employed during the examinations of painting Saint John the Baptist included XRF, cross-sections and stereo microscope observation of the canvas fibers. The examination of the preparation systems through series of cross-section tests has indicated a light colored double ground layer system that can be either referred to the Dutch preparation systems of the 17th century or popular 18th-century preparation that was widely spread across the Europe. The most important finding of XRF analysis consisted in the presence of titanium white, which raised a number of questions related to the origin of the painting. The examination of blue pigment which was expected to give a sufficient data on the painting's origin has indicated the presence of iron in either paint or ground structure and can be either Prussian blue or yellow ochre consisting in the ground layer. The observation of the canvas fibers has also failed to indicate the type of fabric used for the painting. Considering the fact that the present technical research may not provide a link to the origin of the painting, an additional study is required. The missing data on pigments and canvas fibers will be obtained through an additional investigation conducted using cross-section series, SEM, and ART-FT-IR.

The additional research has also been made to study of conservation methods and materials employed for the painting „Saint John the Baptist“ during the previous interventions. Using

ATR-FT-IR analytical technique it was possible to indicate the natural resin lining adhesive used to line the original canvas on the linoleum support. The only example of the similar lining support used for painting conservation has been mentioned by Rostov-on –Don State art museum restorer V. V Shulgin, describing the treatment of the XVII century oil painting that was previously lined on a linoleum support. Thus it can be presume that the lining of John the Baptist has originally taken place in Russia, where the painting has been stored until 1955. Considering the cleaning method that produced the damage of the paint layer it is most likely to presume that a very strong polar solvent or highly caustic aqueous solution was used.

Resüme

Antud tekst kirjeldab maali “Ristija Johannes” uurimist, koserveerimist ja restaureerimist. Tekst koosneb üheksast peatükist: sissejuhatus, objekti kirjeldus, (maali)ajaloo kirjeldus, koserveerimiseelne seisukord ja varasemate koserveerimistööde kirjeldus, koserveerimisprojekti kirjeldamine ja praktiline koserveerimine. Magistritöö lõpeb kokkuvõttega ja sisaldab nelja lisandit.

„Ristija Johannese“ maali koserveerimine

Uuritava maali näol on tegemist õlimaaliga tekstiilalusel, mis on tõenäoliselt valmistatud 18. sajandi alguses. „Ristija Johannese” maal saabus Eestisse 1955. aastal endise Eesti Vabariigi saatkonna hoonest Moskvas. Kuni 2015. aastani oli maal hoiul Eesti Kunstimuuseumi Tallinna filiaali hoidlas. 2015. aastal jõudis maal uurimiseks ja koserveerimiseks Eesti Kunstiakadeemia muinsuskaitse ja koserveerimise osakonda, mistõttu saigi kõnealune maal käesoleva magistritöö uurimisteemaks.

Saabumise ja esmakordse läbivaatuse hetkeks oli maali seisukord halb. Maali autorilõuend oli äralõigatud ning töö oli dubleeritud linoleumile. Töö esikülg oli saanud varasemate koserveerimistööde käigus läbiviidud puhastamisel tugevalt kahjustada ning oli kohati täielikult hävinenud ja kaetud kahest kihist koosneva vana oksüdeerunud lakikihiga. Käesoleva magistritöö käigus läbi viidud koserveerimistööde põhieemärgiks oli leida erinevaid metodoloogilisi lahendusi maali värvikihi taastamise ning maalialuse koserveerimisega seotud praktilistele küsimustele.

Tehnilised uuringud

Arvestades maalikihi väga halba seisukorda, ei olnud maali täieliku stiililise analüüsi teostamine võimalik. Küll aga oli maali päritolu puudutavat teavet võimalik koguda materjalide tehnoloogiliste uuringute tulemustel saadud informatsiooni analüüsimisel ning erinevate ajalooliste allikate interpreteerimise abil.

Tehnoloogilise uuringu käigus uuriti maali alust, krundikihti, värvikihte ja lakikihte. Kuna nii lina- kui ka kanepikiud on visuaalselt väga sarnased, tehti maalilõuendi niidiproovide analüüsimisel steromikroskoobiga kindlaks, et lõuendi näol võib olla tegemist nii lina- kui ka kanepikiust lõuendiga.

Ettevalmistuskihi uuringute käigus liimistuskkihti ei tuvastanud. Krundikihist võetud proovidest valatud mikrolihvide vaatlemisel täheldati, et maal oli teostatud heledale

kahekihilisele krundile. Antud ettevalmistuskiht oli laialdaselt kasutusel 17. sajandi Põhja-Euroopas ja Prantsusmaal ning sajand hiljem ka Lõuna-Euroopas.

Värvikihi analüüs teostati röntgenfluoressentsmeetodil, kasutades portatiivset XRF aparati. Analüüsimise käigus tuvastati ühes maalikihis vähene kogus titaani, mis suure tõenäosusega viitab titaanvalge olemasolule värvikihis.

Kuna titaanvalget hakati kasutama alles 20. sajandil, siis tekitas antud tulemus mitmeid küsimusi seoses maali päritoluga.

Taeva piirkonnas esineva sinise värvikihi analüüsimine osutas raua sisaldusele, mis võib tähendada nii Preisi sinise olemasolu värvikihis kui ka kollase ookri esinemist krundi alumises kihis.

Laki uurimine UV-lambi all võimaldas leida kaks lakikihti, mõlemad koosnesid kas mastiks- või dammarlakist. Kõige pealne lakikiht osutus väga tugevalt fragmenteerituks. Lakikihi kõige alumise kihi täiendavate uuringute käigus ATR-FT-IR spektroskoopia teel tuvastati lisandina ka proteiinset ainet.

Konserveerimisprojekti ülesehitus ja conserveerimise protsess

Kõige olulisem tekstiosa, Konserveerimisprojekti ülesehitus, seisneb struktuursete ja esteetiliste meetodite otsingutest “Ristija Johannese” maali conserveerimiseks, mis oli töö praktilise osa aluseks. See sisaldab maali lahtidubleerimist ning tagakülje puhastust, lõuendi servade dubleerimist, maalipinna puhastust, kadude retušeerimist ning maalikihi katmist uue lakikihiga.

Struktuurse maali conserveerimise ajal oli autorilõuend lahtidubleeritud ning tagakülje puhastatud smirgelpaberiga. Maali tagaküljele asetati paranduslapid kasutades BEVA 371 adhesiivkilet ning lõuendi äärised dubleeriti. Kuna maali vana alusraam oli väiksemate mõõtudega kui autorilõuend, asendati see uue alusraamiga.

Põhiprobleem maali conserveerimisel seisnes selle kujutise terviklikkuse taastamises, mistõttu oli peatähelepanu sellel tekstiosal pühendatud puhastusele ja retušeerimisele.

Teoreetilistest tugimõistetest kõige mahukam koht on paatina ja lakuuni terminitel, mis mõlemad lähtuvad C. Brandi teoreetilistest hoiakutest. Vastavalt C. Brandi ja tema järgijale P. Philippot’le on paatina materjali vananemise ja kulumise „normaalseks“ efektiks, mis peegeldab maali ajaloolist väärtust. Philippot’ järgi on paatina maali normaalse seisundi osaks seni, kuni see ei hakka kahjustama maali esteetilist terviklikkust. „Ristija Johannese” maali puhul oli paatina probleem seotud põhiliselt vana lakikihiga, mis moonutas maali esteetilisi

omadusi ning varjas värvikihi füüsilist seisukorda. Tuginedes eelkirjutatule võeti vastu otsus vananenud lakikiht eemaldada.

Esteetiliste küsimustega paralleelselt puudutas konserveerimisprojekti ülesehituse sektsioon ka küsimuse tehnilist poolt, kirjeldades lahustigeelide ja koegeelide puhastamismeetodit maali lakikatte eemaldamisel. Käesoleva töö raames teostatud maalipinna puhastamise käigus eemaldati degradeerunud ja tumenud lakk sammhaaval, katsetades kõiki ülalmainitud meetodeid.

Enne retušeeringute teostamist isoleeriti maali originaalvärvikiht lakikihiga. Laki pealekandmisel kasutati vedelat dammarlakki „Nevskaya Palitra“. Arvestades seda, et maalipind oli väga poorne (läbilaskev), otsustati lakikihi pealekandmiseks kasutada spetsiaalset pihustit, mis võimaldas saavutada ühtlase lakikihi ja läike. Seejärel täideti maalikihi kaod krundiga.

Vastavalt C. Brandi õpetusele eemaldatakse kaod värvikihis nõ neutralisatsioonimeetodiga. Tuginedes C. Brandi teoreetilisele hoiakule töötasid Paolo ja Laura Mora välja retušeerimistehnika, mida tuntakse nime all „tratteggio“- Antud tehnika teeb võimalikuks maalikihis olevate kadude visuaalse integreerimise, jättes samal ajal retušeeritud koha siiski eristatavaks. Ristija Johannese maali retušeerimise käigus neutraliseeriti värvikihi kahjustused ja kaod, mis rikkusid maali terviklikkust.

„Ristija Johannese” maali retušeerimisetapi käigus neutraliseeriti kõik värvikihi kahjustused ja kaod, taastades seeläbi maali visuaalse terviklikkuse ja vaadeldavuse.

Konserveerimistöde lõpp-etapis kanti peale lõplik lakikiht, mis aitas täiendavalt veelgi enam visuaalselt ühtlustada retušeeritud piirkondi kogu ülejäänud maalipinnaga.

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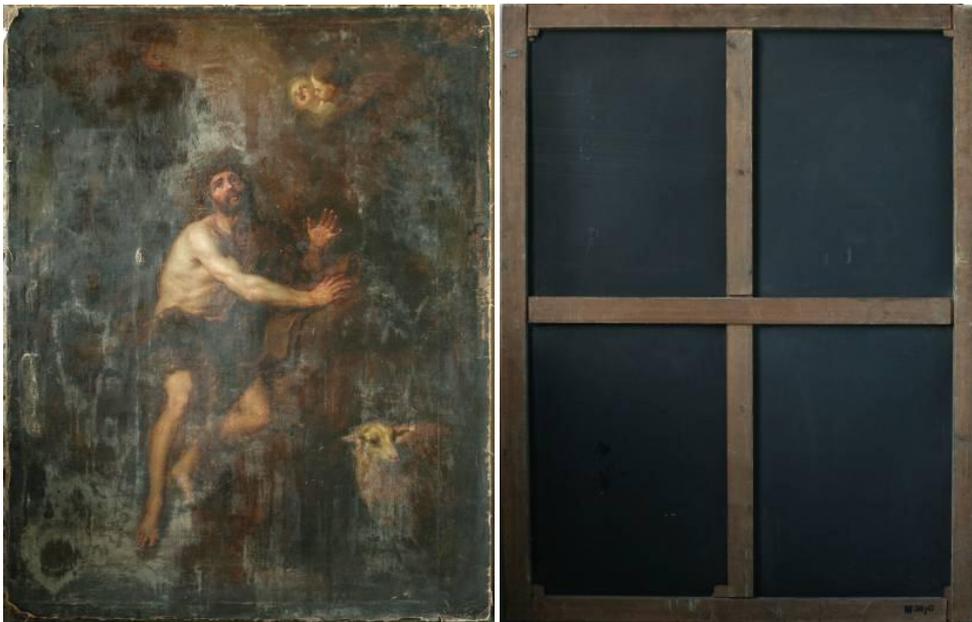
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Appendix I : Registration form

Inv. nr.	VM 731
	Maal



Conservator: Mihhail Staško

Object	Painting “ Saint John the Baptist
Author , Artistic school	Unknown
Dating	18 century (?)
Material	Oil paint , canvas
Technique	Oil painting
Size	147, 8 x113

Beginning of working period	March 2015	Deadline	29.05. 2017
Work finished	29.05.2017	Returned to the owner	

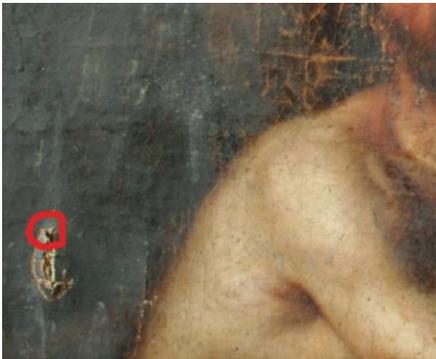
Back ground	Starting from an unknown period the painting has been stored in a depository of a Estonian Embassy in Moscow . In 1954 it has been decided to transfer . By the 19 The painting was brought to Estonian Art Museum in 1955. The painting has been stored in the depository of
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	Estonian art museum until march 2015 when it has been brought to Estonian Academy of arts for examination and conservation. ²³⁴
Historical reference	The painting is most likely referrers to the 18 th century. Considering the poor preservation state of the paint layer the attribution of the painting remains uncertain.
Data on previous interventions	The painting has been removed from the taking margins and lined on a linoleum support. The structural losses of paint layer and canvas were filled with putty and the paint layer has previously undergone a cleaning procedure.

Technical research

Analyzed material	Sampling description	Result and interpretation
<p>Lining</p> 	<p><u>Research Issue :</u></p> <p>The original canvas was lined on with a brownish adhesive on a multilayered lining support , which consisted of linoleum, and intermediate coarse fabric.</p> <p><u>The research objective:</u></p> <p>Determine the lining type used for the present painting . The possible methods can include :</p> <ul style="list-style-type: none"> • Wax-resin • Pure resin • Resin with admixture of oil • Animal glue (less likely) <p><u>Analytical methods::</u></p> <ul style="list-style-type: none"> • Stereo microscope observation • ATR-RF-IR 	<p>The lining adhesive consist of a pure natural resin without admixtures of wax or oil. An additional interpretation is required to determine the exact type of resin . For detailed information see appendix II</p>

²³⁴ Record on 1955. Document in Archives of Estonian Art Museum of Estonia

<p>Canvas</p> 	<p><u>Research Issue :</u></p> <p>The present canvas consist of two pieced of canvases</p> <p><u>Research objective:</u></p> <ul style="list-style-type: none"> • To examine the canvas whether it consist of a single material or several fabric types • Identify the type of material(s) used <p><u>Analytical tool</u></p> <ul style="list-style-type: none"> • Dry twist method • Leica Stereo microscope observation 	<p><u>Canvas</u></p> <p>The observation of fibers under 150-400X magnification has indicated that the present canvas consists of either flax or hemp. In order to make a precision the study requires an additional examination using SEM analysis..</p>
<p>Preparation layer</p>  	<p><u>Research Objective:</u></p> <p>Identify the preparation system used for the present painting</p> <p><u>Analytical tool:</u></p> <ul style="list-style-type: none"> • Cross-section • Stereo microscope Leica 	<p>It has been found that the painting includes a light coloured double ground preparation system , consisted of a brown first ground and the final light coloured ground. The observation of number of cross-section has not indicated the presence of sizing layer .</p> <p>The double ground has been first developed in the second half of the 16 century and became widely used during the 17th and 18th century. The light -colored grounds are more characteristic for 18th century paintings.</p>
<p>Paint layer</p>	<p><u>Research issue:</u></p> <p>Basing on the superficial</p>	<p>The XRF analysis has indicated the presence of very small amount</p>

	<p>stylistic analysis the present painting can be related to the beginning of the 18th century. Considering the brown and yellow pigments most likely contain earth pigments , the particular interest of the present research is related to white , blue and red .</p> <p><u>Research objective:</u></p> <ul style="list-style-type: none"> • Pigment identification <p><u>Analytical tool:</u></p> <ul style="list-style-type: none"> • XRF gun (X-ray fluorescence) 	<p>Titanium white in green, blue red and white areas. The red pigment consist of red lead</p>
<p>Varnish</p> 	<p><u>Research objective:</u></p> <p>Identify the varnish type used for the present painting . The possibilities may include</p> <ul style="list-style-type: none"> • Natural soft resin varnish like dammar and mastic • Oleo resinous varnish <p><u>Analytical tool:</u></p> <ul style="list-style-type: none"> • UV lamp • Solubility tests • Cross-section • ART-FT-IR 	<p>Both solubility tests and UV observation have indicated a double layer of varnish : first fragmented coating and the second continuous. Both varnishes contain natural resin. The examination of cleaning swabs with ATR-FT-IR analysis has indicated the presence a protein admixture consisting in the first layer of varnish.</p>

Category	Oil painting on canvas
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General description	The painting depicts a wilderness life scene of Saint John the Baptist. The centre of the composition is occupied by the man's figure, surrounded by a lamb figure on the right, and by three angel figures in the upper section of the painting. All five figures are counterposed on dark background, that depicts a landscape, which includes sky, rocks and green elements. The Man figure is holding a manuscript in the right hand.
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Material	Structural description	Preservation state
Stretcher	A wooden wedge stretcher	Exhibits a satisfactory state of preservation
Support	Consists of three layers: linoleum, coarse fabric and original canvas. The lining support together with the original canvas are nailed to the wooden support from the front side of the painting. The original canvas represents itself a plain wave canvas. Thread count per square centimetre 16 x 14,5.	The painting's support exhibits a hole and a tear running through every layer of support and visible both from the front and back side of the canvas
Preparation layer	A double layer ground layer systems, consisting of the first brown layer and the final light coloured ground layer. The sizing layer has not been found.	The preparation layer exhibits a satisfactory adhesion to both original support and paint layer.
Paint layer	The oil paint was applied thinly	The paint layer has been totally overcleaned, exposing the bare ground surface in various parts of the painting 

Retouching	Not visible under the varnish	-
Varnish	The varnish is composed of two layers both consisting of soft resin varnish like dammar and mastic . The first layer is fragmented and a part from natural resin contains an admixture of protein material.	The varnish is considerably crazed and in some areas entirely deconstructed , obscuring large parts of the paint surface. 

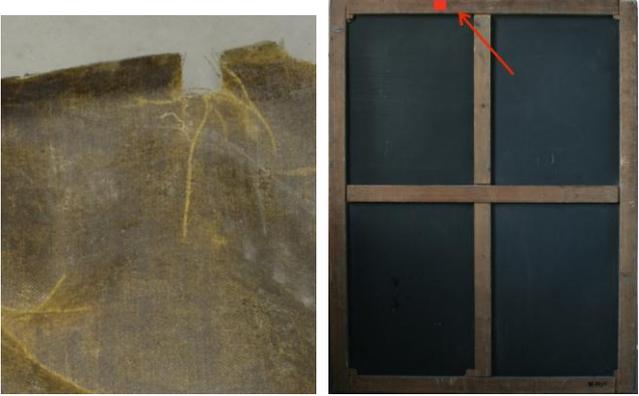
Project objective	Stabilize the canvas on the new stretching frame. Neutralize the damage of the picture layer and bring forward the potential unity of the work.
Treatment proposal	<ol style="list-style-type: none"> 1. Photographic documentation 2. De-mounting 3. De-lining 4. Strip lining and patching 5. Cleaning (front side) 6. Removing old fillings 7. Intermediate varnish application 8. Retouching 9. Final varnishing

Conservation process	Materials employed during the work
De-mounting	Screwdriver, small crowbar
De-lining	Palette knife
Strip lining and patching	BEVA371 , linen fabric strips
Cleaning	bezyalcholo gel, ethanol , Cyclomethicone, scalpel
Intermediate varnish application	„Nevskaya Palitra“ liquid dammar varnish
Retouching	Marmeri retouching colors, Winsor & Newton , watercolor

Final varnishing	Matt Dammar Varnish mat
Conclusion and final remarks	The painting has been structurally stabilized and esthetically regained its unity. It is recommended to store the painting under 20oC and 55% RH

Appendix II: ATR-FT-IR examination

PROTOCOL

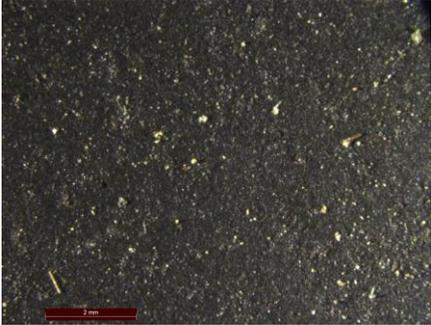
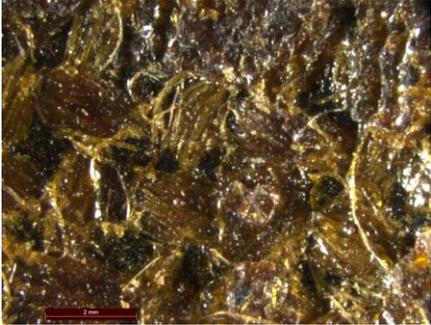
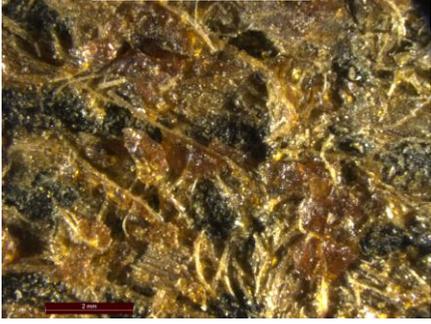
Execurtor name :	Mihhail Staško
Object :	Painting „Saint John the Baptist“
Sampling areas :	 <p>Lining support</p>  <p>Varnish sampling area</p>
Description of testing sample:	<ol style="list-style-type: none">1) Linoleum support covered by a coarse fabric and lining adhesive2) A cotton swab containing brownish-red resin removed from the painting . The samples were taken from the incarnate of the „Saint John the Baptist“ with pure ethanol solvent.

<p>Study objective :</p>	<ol style="list-style-type: none"> 1. Objective of the present analysis is to identify the lining adhesive employed for lining of painting „Saint John the Baptist „. The solubility tests made prior to the present research have indicated that the lining adhesive is insoluble in water but responds to the cleaning action of alcohols (ethanol, isopropanol). Considering the results of solubility tests the lining adhesive is most likely contains natural resin and thus the main questions are: <ol style="list-style-type: none"> 1. Does the lining adhesive consistS of pure resin? 2. Is the lining adhesive used is wax-resin type? 3. Are there other admixtures used? For instance oil? 2. To Identify the first layer of varnish. Considering the the first fragmented layer of varnish is less soluble than the second varnis , the main questions is whether it contains of pure resin or includes admixtures of oil or other materials.
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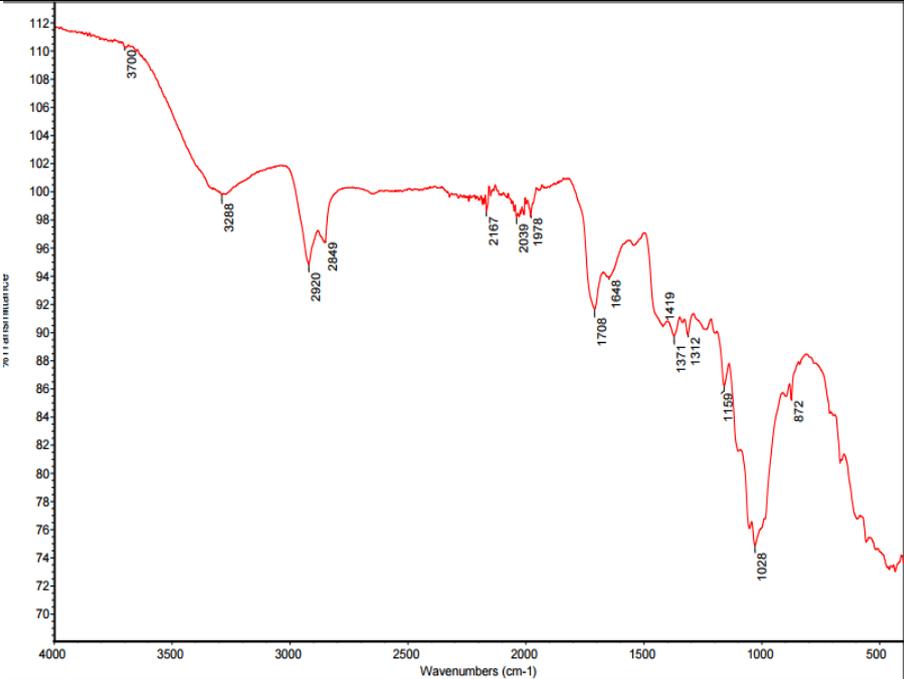
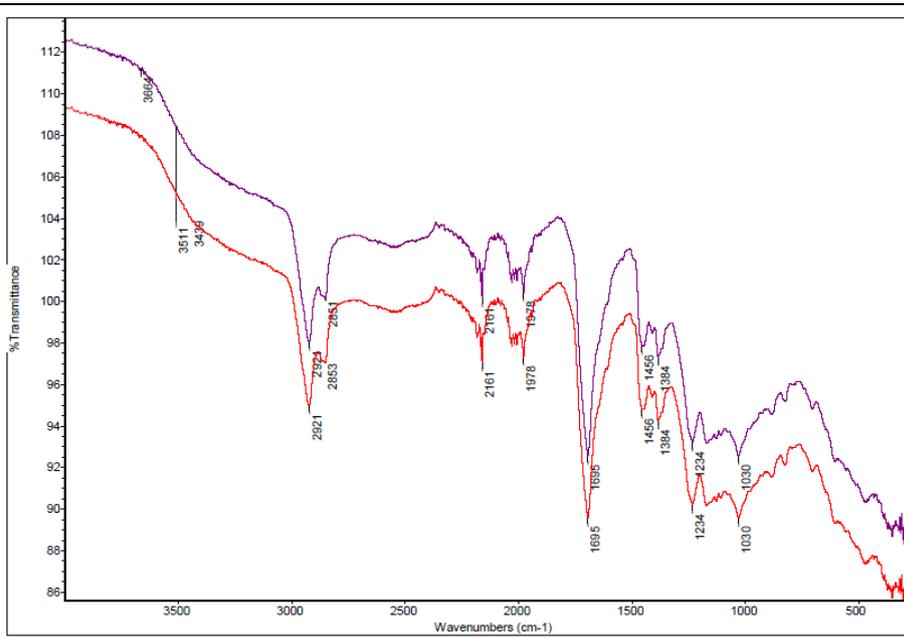
Working proposal

1. Collecting samples from the painting
2. Sample observation via Leica M165 FC optical steromicroscope
3. ATR-FT-IR spectrometer measuring (Nicolet 6700 FT-IR spectromeeter with Smart Orbit analyzer)
4. Result interpretation

Experimental part and interpretation

Analytical tool	Analysis description	Interpretation
Stereo Microscope	 <p data-bbox="624 846 770 907"><i>Backside of the test</i></p>	Back side: black linoleum
	 <p data-bbox="624 1283 786 1344"><i>Test sample front side</i></p>	<p data-bbox="1002 1025 1425 1097">(Front side) The sample consists of three layers :</p>
	 <p data-bbox="624 1720 786 1780"><i>Test sample front side</i></p>	<ol data-bbox="1050 1216 1409 1653" style="list-style-type: none"> 1. Black areas: linoleum support 2. Yellow threads: coarse fabric 3. Glassy orange material: lining adhesive

ATR-FT-IR spectrometer analysys

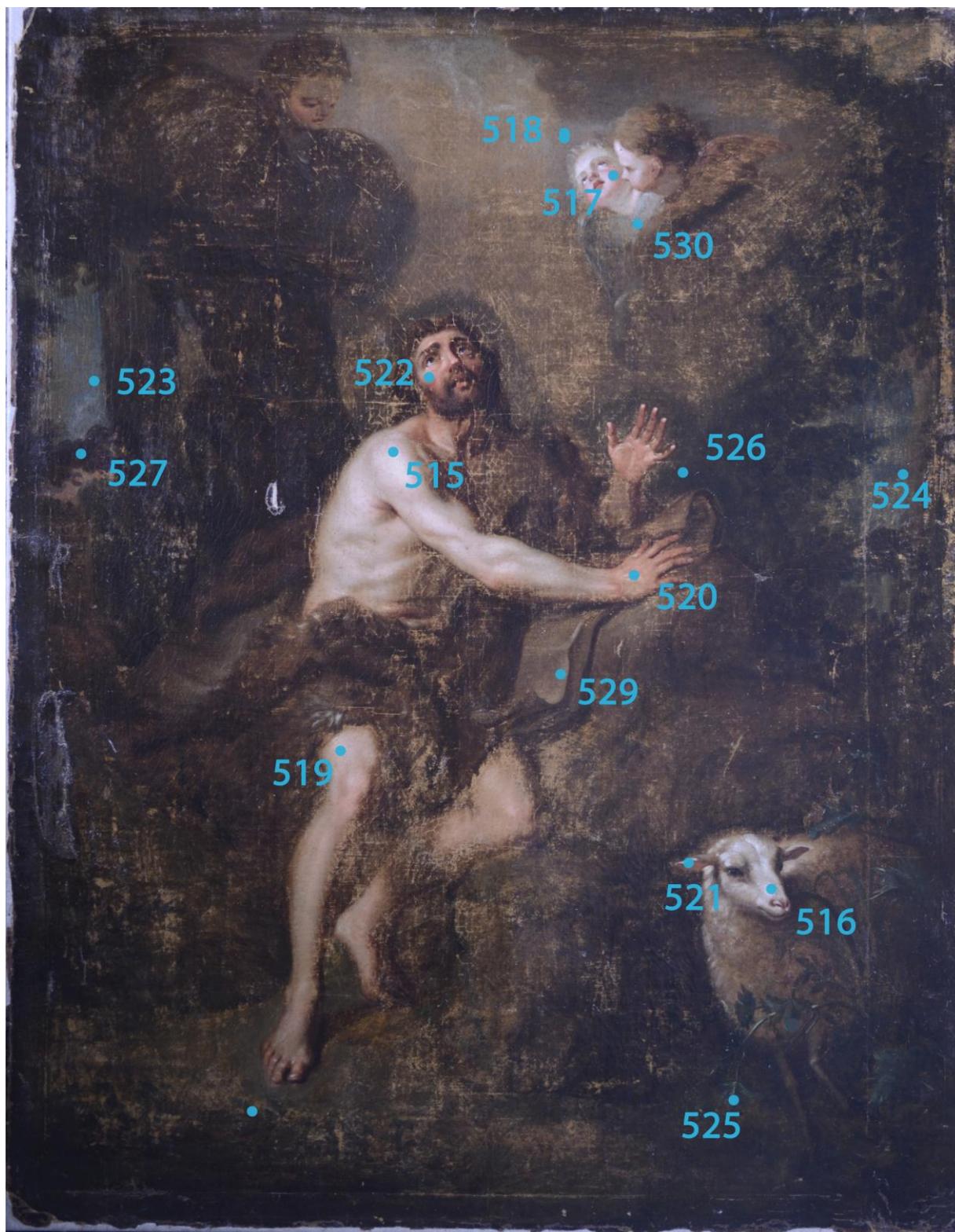
ATR-FR-IR results	Interpretation
 <p>ATR-FT-IR spectrum showing % Transmittance vs Wavenumbers (cm-1). The y-axis ranges from 70 to 112, and the x-axis ranges from 4000 to 500. Key peaks are labeled at 3700, 3288, 2920, 2849, 2167, 2039, 1878, 1708, 1648, 1419, 1371, 1312, 1156, 1028, and 872 cm-1.</p>	<p>The examination has indicated no presence of oil medium. The varnish is most likely consists of triterpenoid resin like dammar with an admixture of protein material. The latter component is yet to be identified.</p>
 <p>ATR-FT-IR spectrum showing % Transmittance vs Wavenumbers (cm-1). The y-axis ranges from 86 to 112, and the x-axis ranges from 3500 to 500. Key peaks are labeled at 3694, 3511, 3426, 2921, 2853, 2843, 2161, 2131, 1978, 1843, 1695, 1456, 1384, 1384, 1234, 1030, and 1030 cm-1.</p>	<p>Adhesive most likely contains natural resin reminding of colophony. Analysis has not indicated presence of wax or oil which allows to conclude that the present adhesive consist of natural resin only.</p>

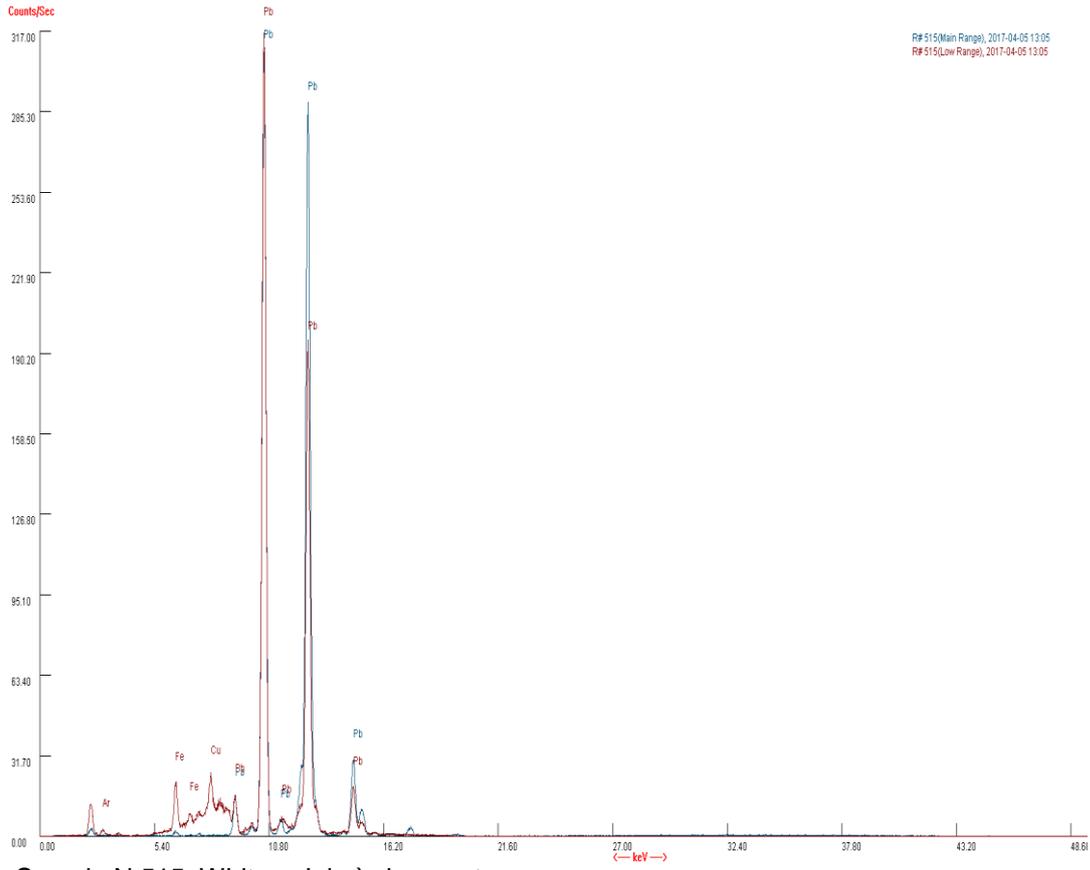
Testing results and conclusive remarks

Material composition:	<p>In the course of the present research it has been found that the lining adhesive used for the present painting consists of pure natural resin , which allows to conclude that the present lining type is different from the one used for painting „Cleopatra“ by Jan de Ban .²³⁵</p> <p>The least soluble varnish layer examination has indicated two components consisting in the coating, namely protein component and natural soft resin varnish like dammar and mastic. The presence of aged protein component in the varnish could have modified the solubility of the coating which on ageing became more insoluble than the pure mastic or dammar varnish.</p>
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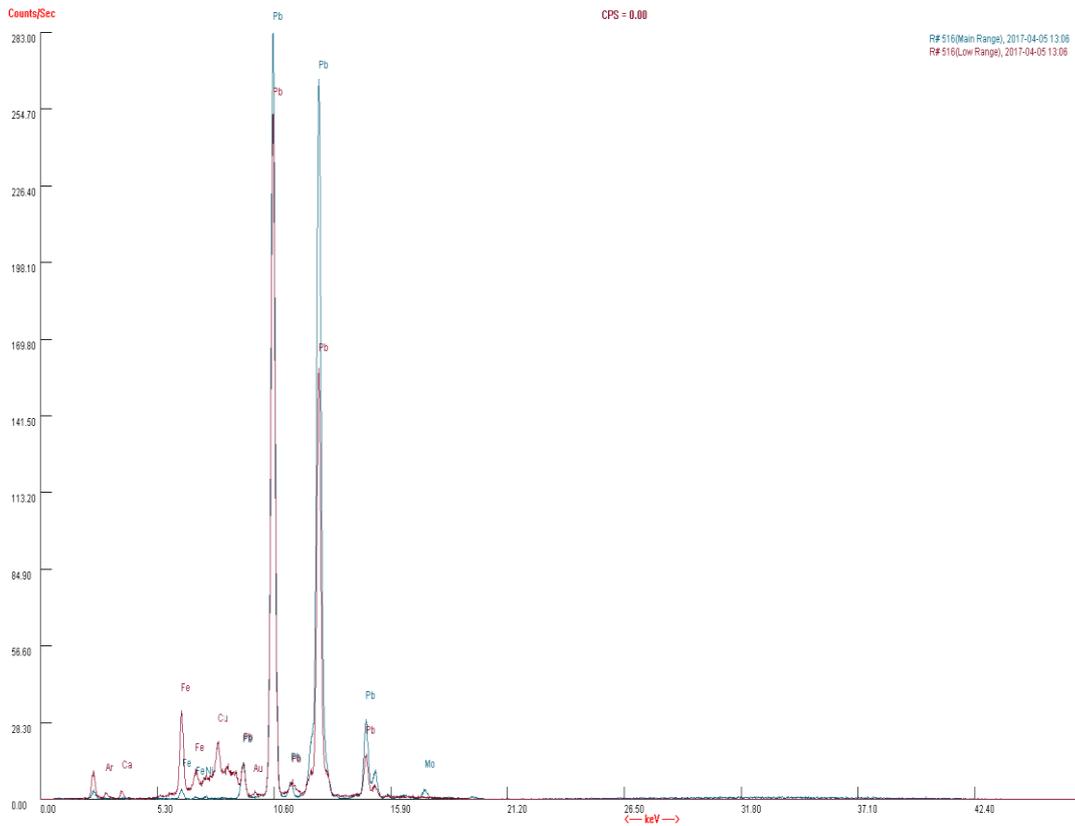
²³⁵ The description of lining method used for painting “ Cleopatra” is described in section **4.1 Support**

Appendix III: XRF analysis of painting “Saint John the Baptist”

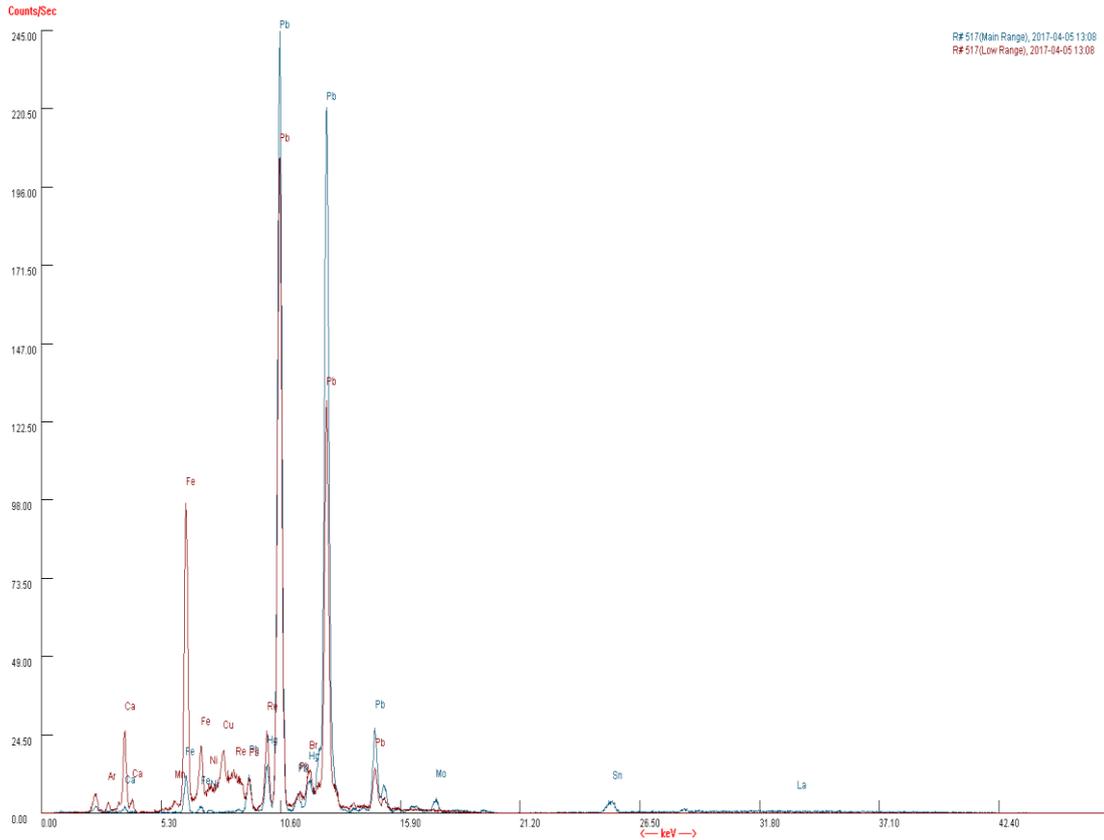




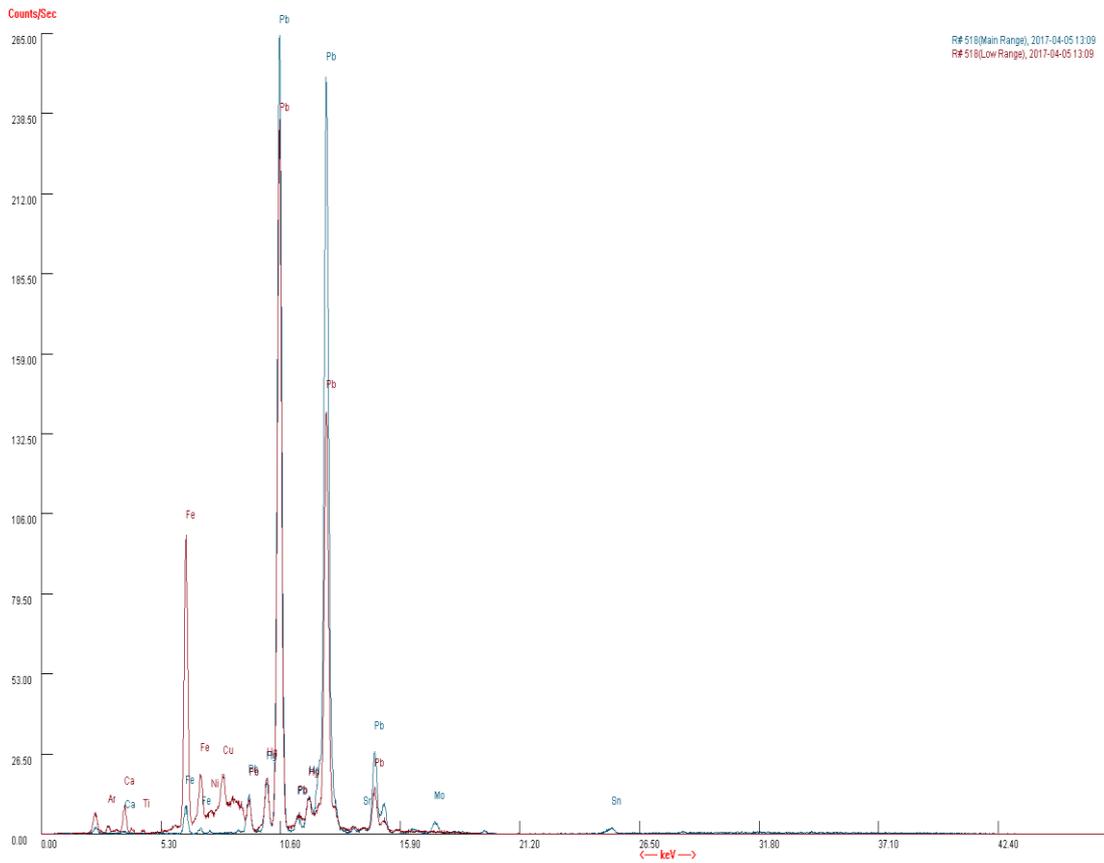
Sample N 515 ,White , John`s incarnate



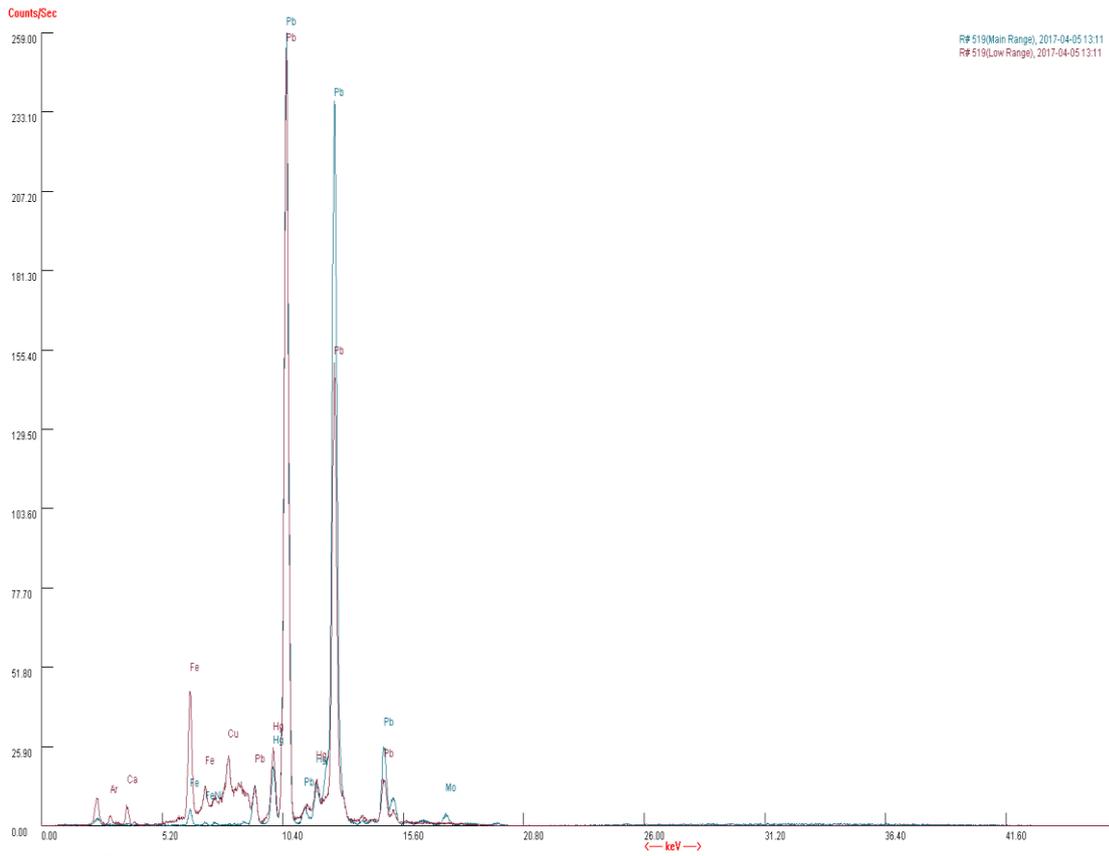
Sample N 516, White, lamb incarnate



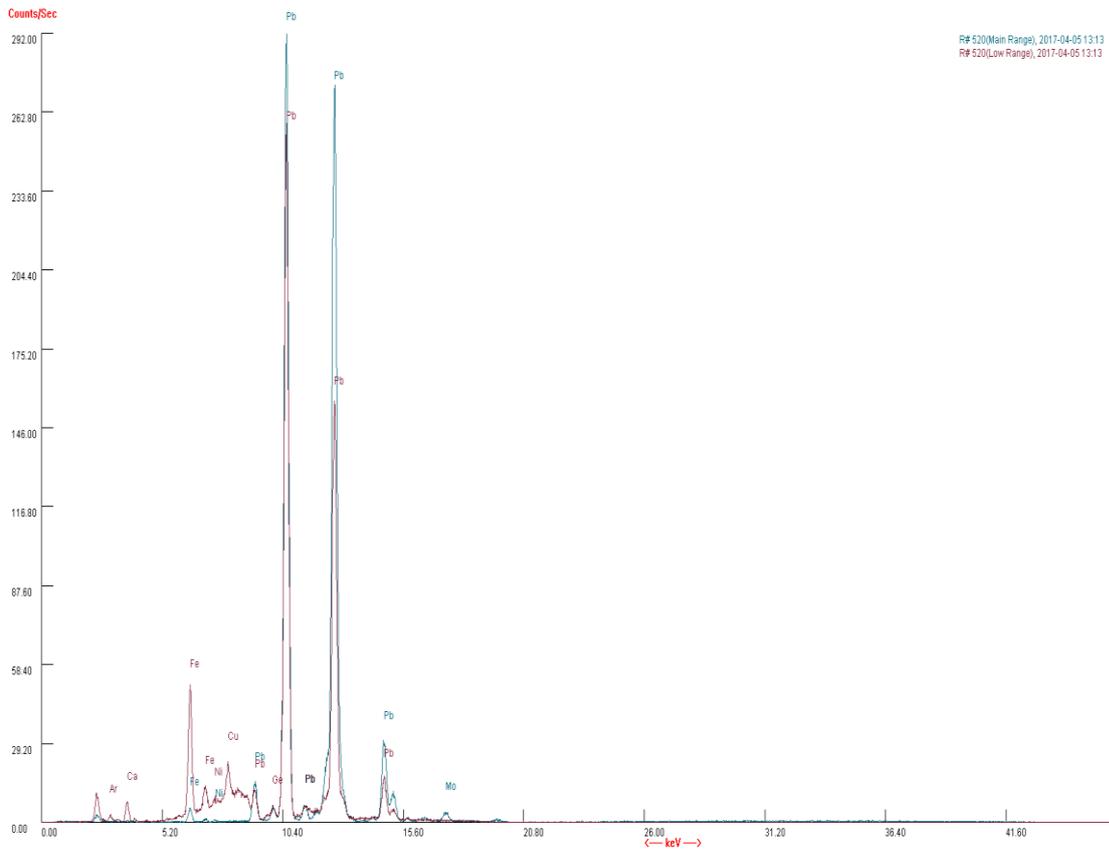
N 517. Red, Angel incarnate



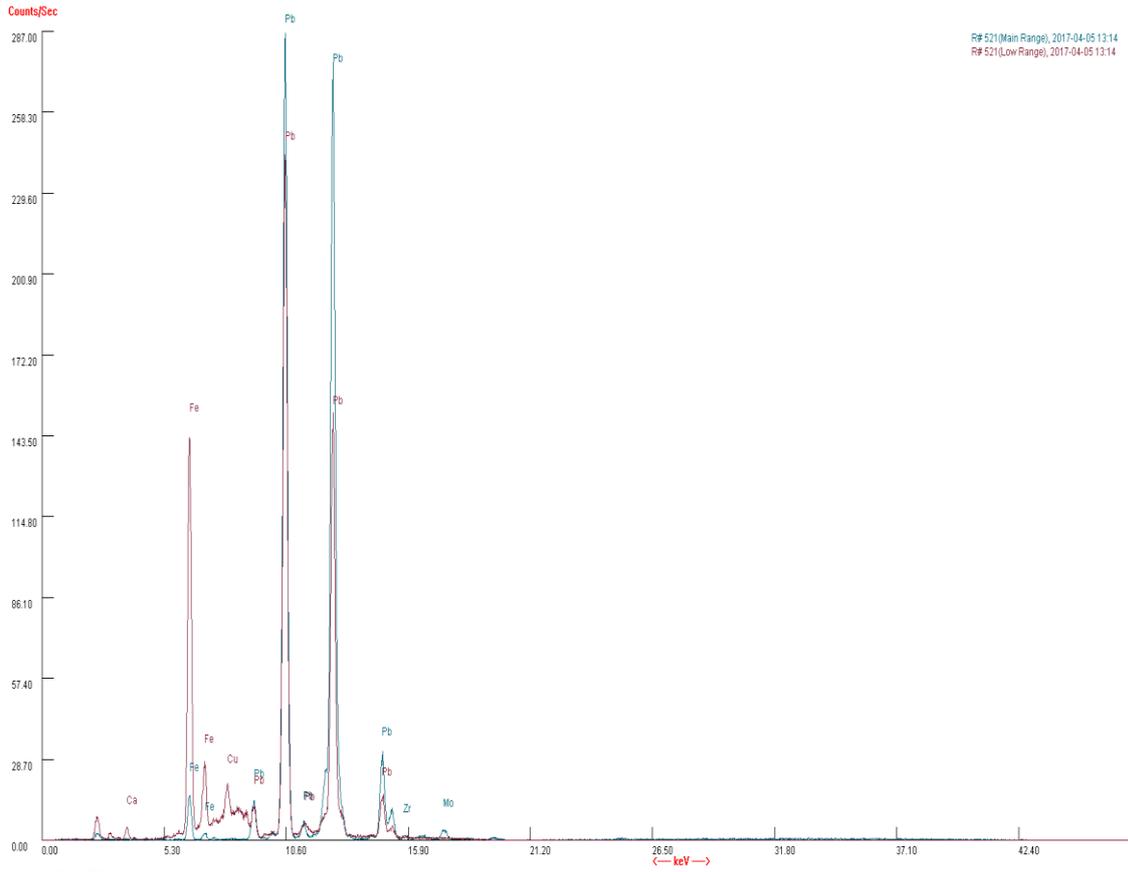
N 518. Brown - White, sky area



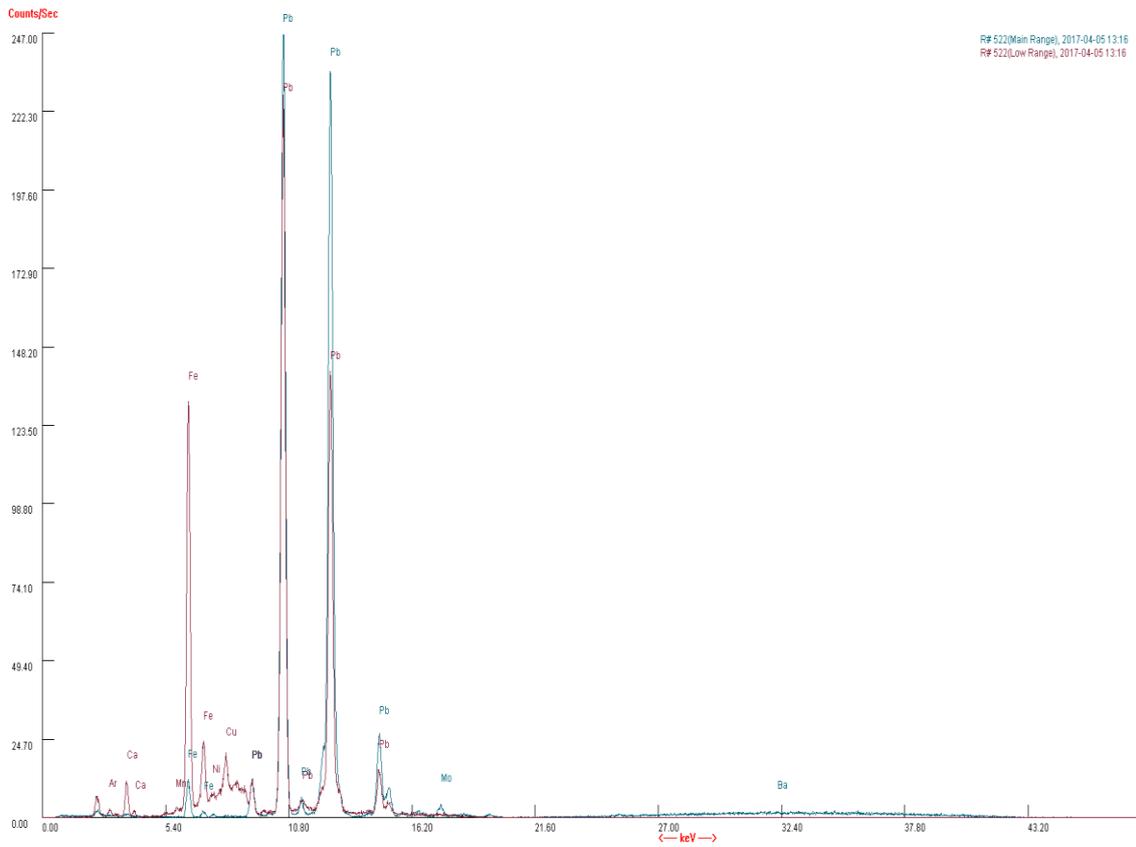
N 519. White, John's incarnate



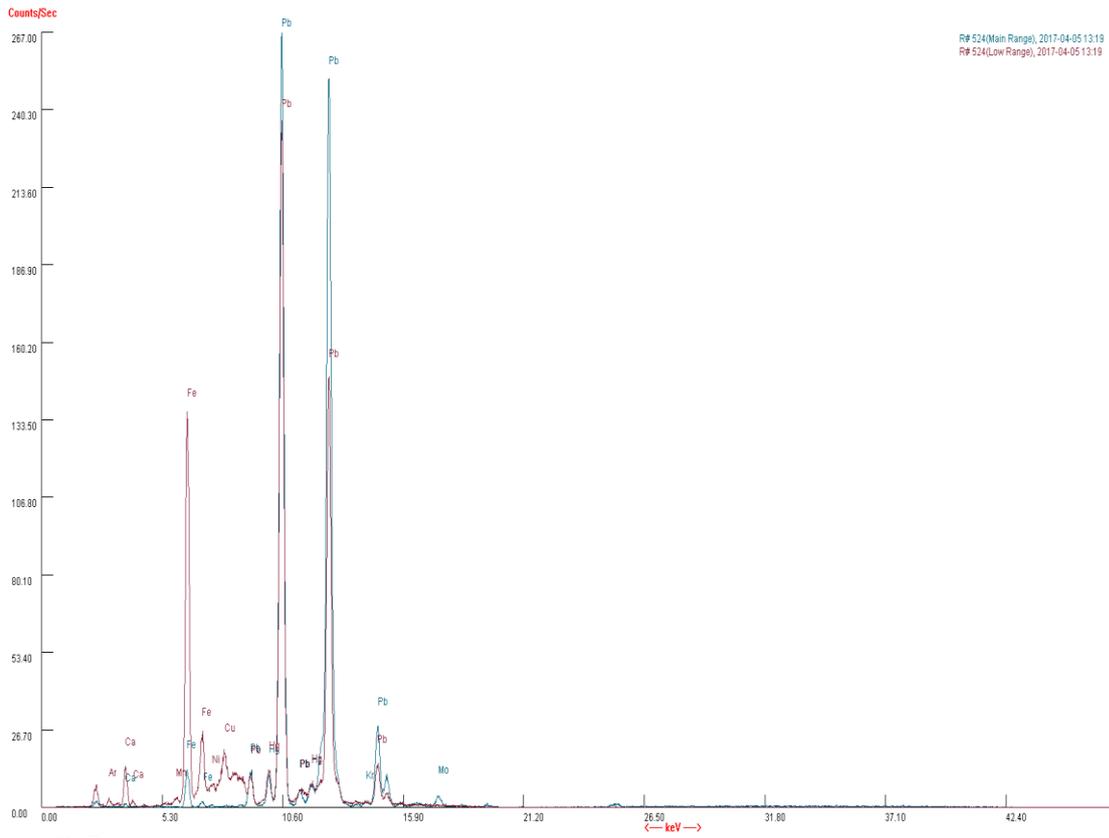
N 520. Red, John's incarnate



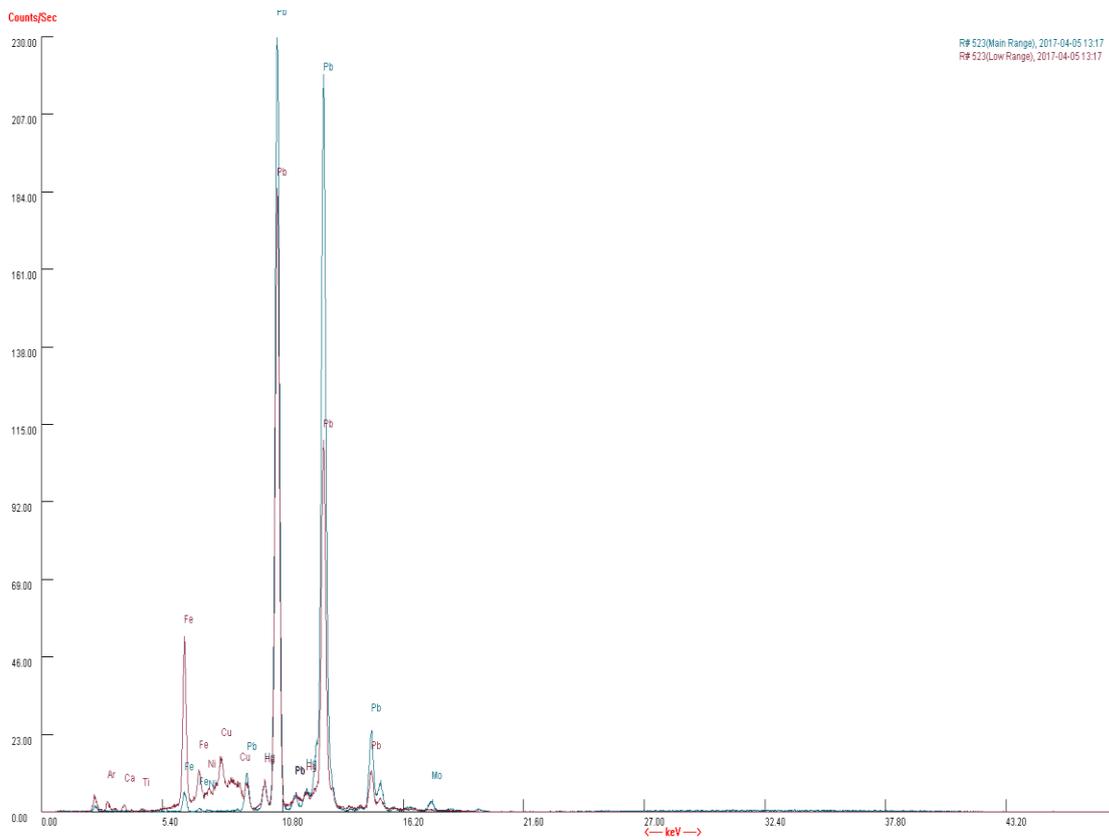
N 521 Red, lamb incarnate



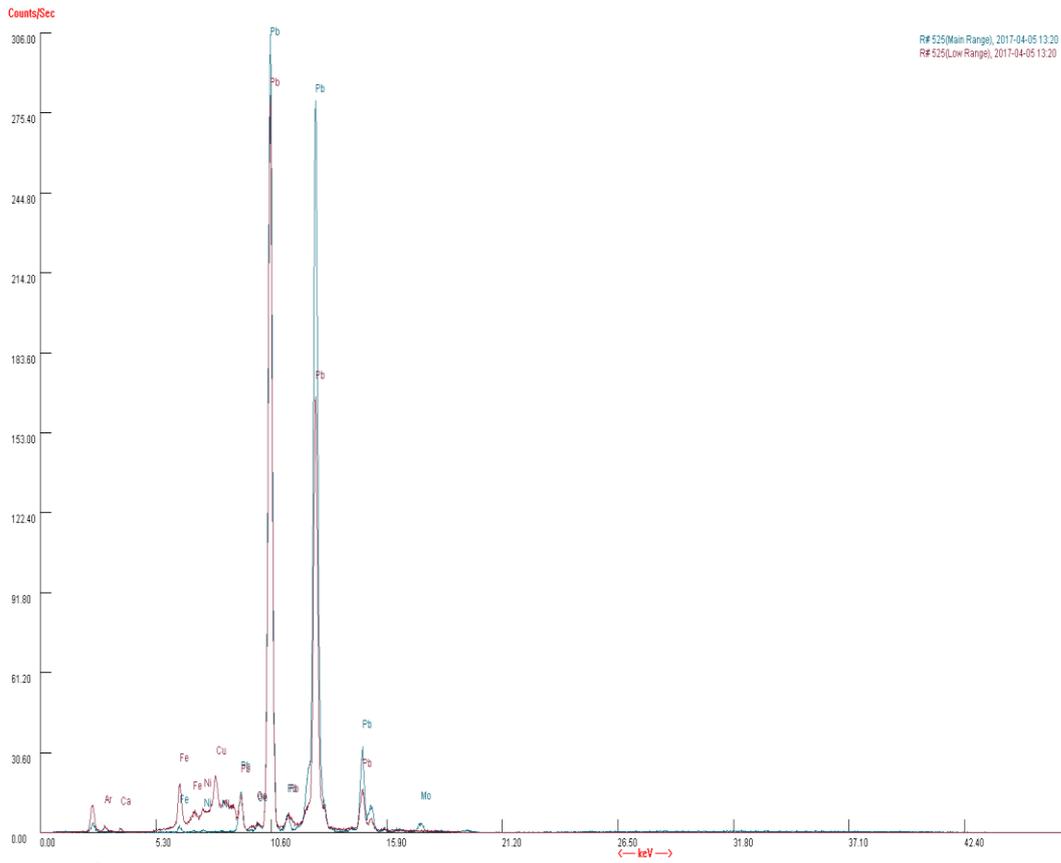
N522 Red-brown , John`s incarnate



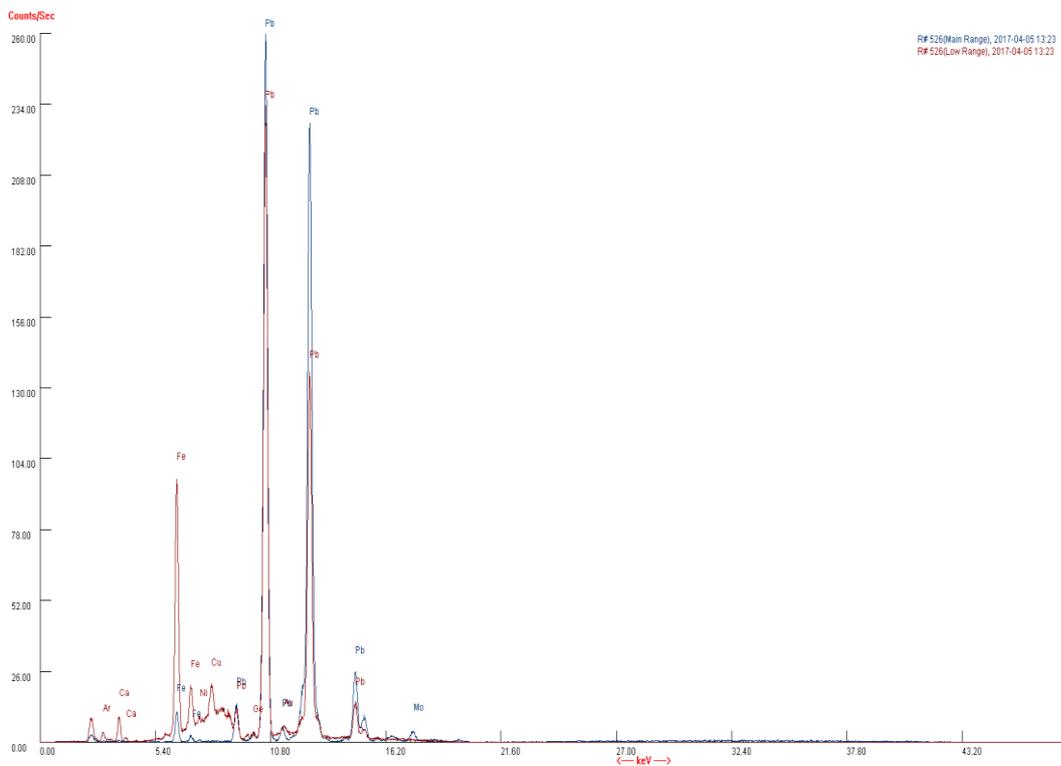
N 523 Blue, sky area



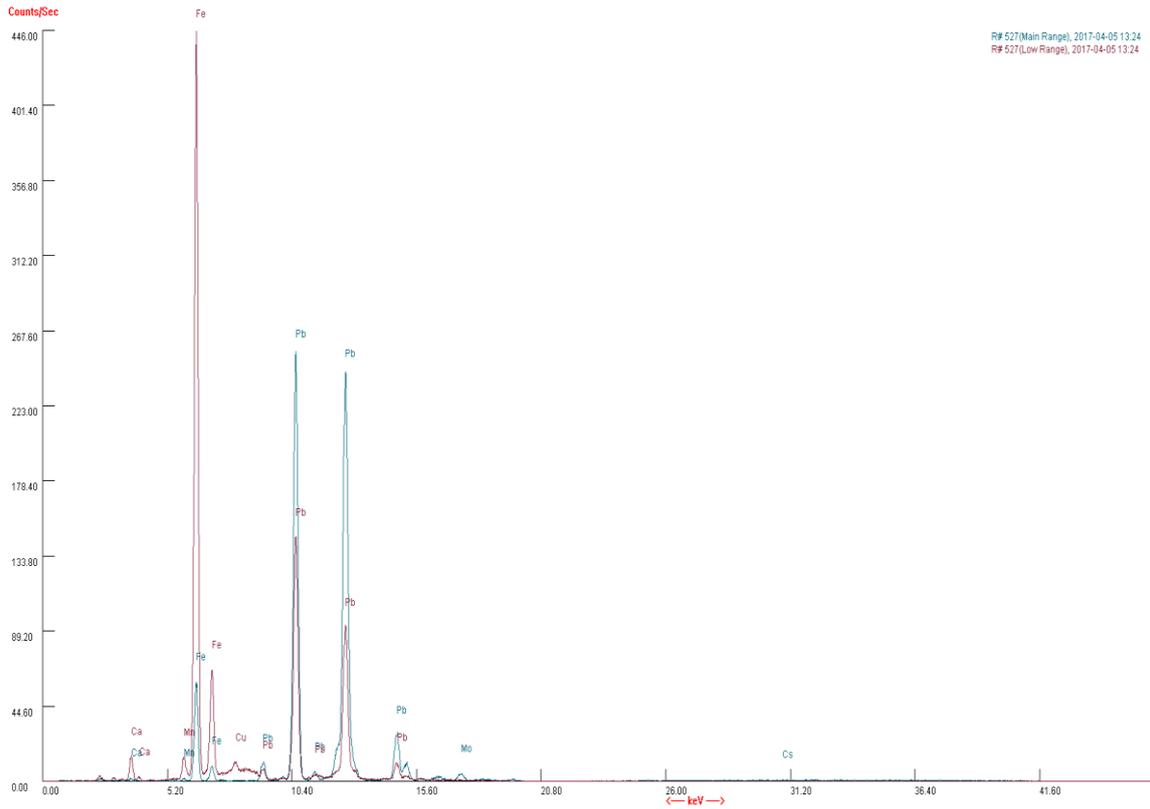
N 524 Blue, sky area



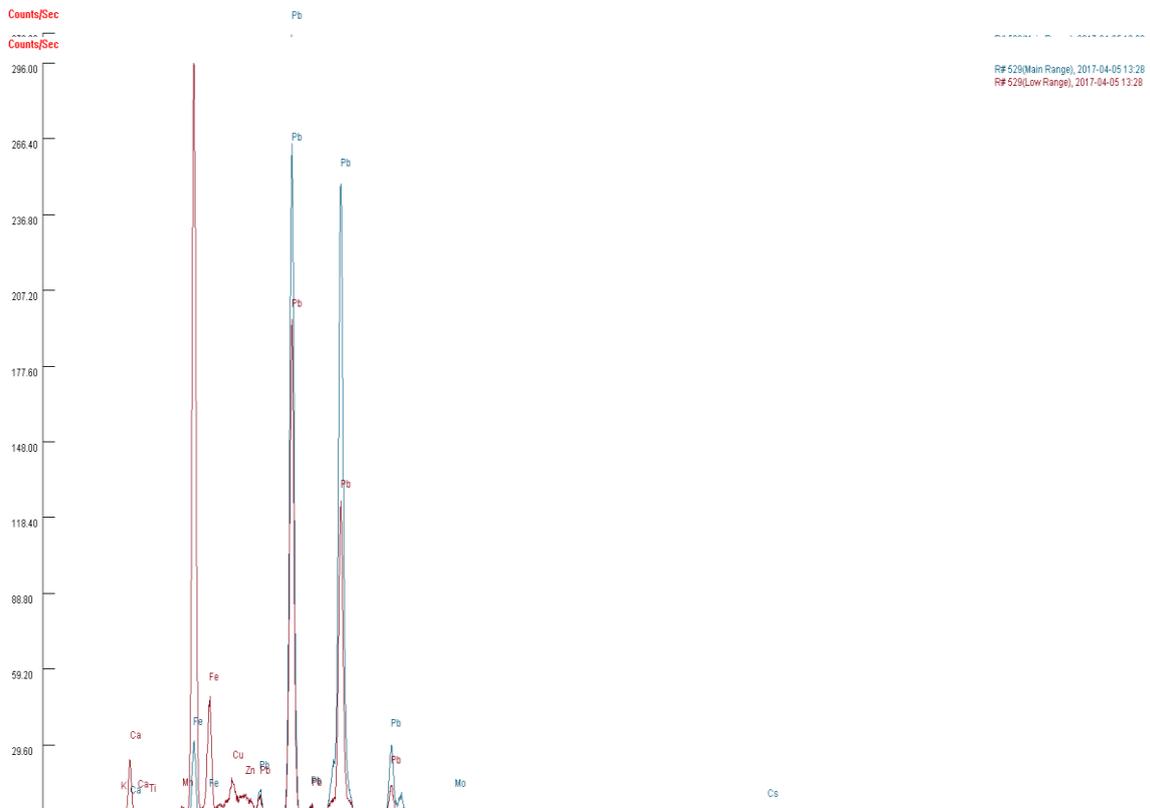
N 525 Green, leaves



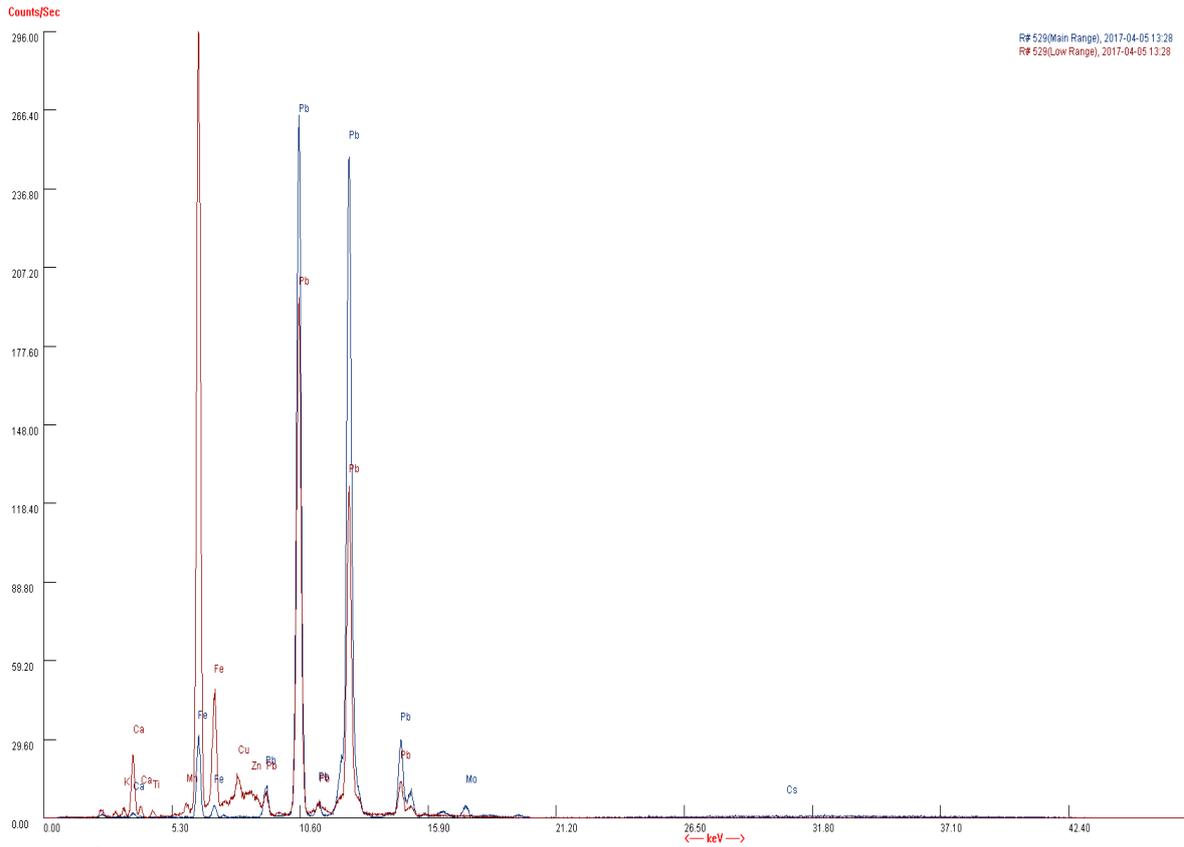
N 526 , Black , dark background



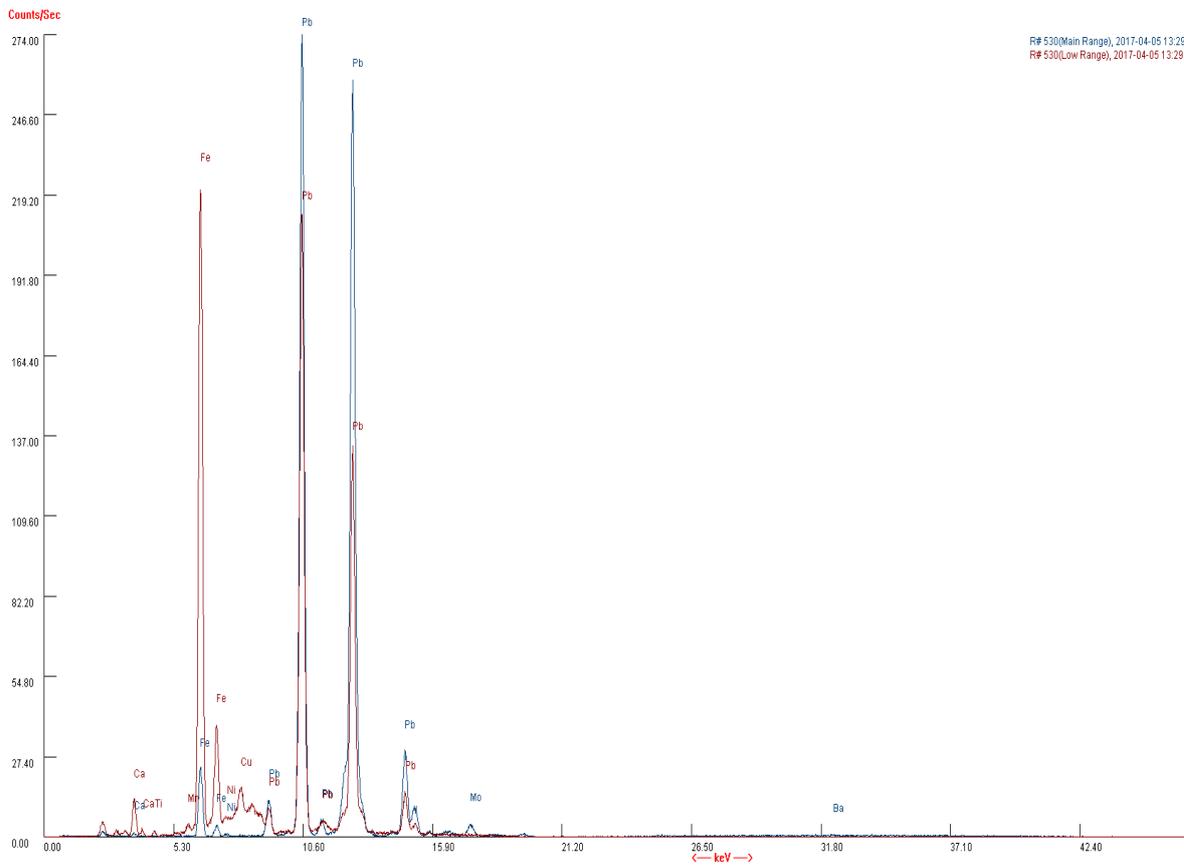
N 527 Brown-black, landscape



N 528 Green, lower section of the painting



N 529 Ochre, manuscript



N 530 White, angel incarnate

Appendix IV: Photo documentation

Pictures taken by Mihail Staško



Picture before cleaning



Picture after varnish removal



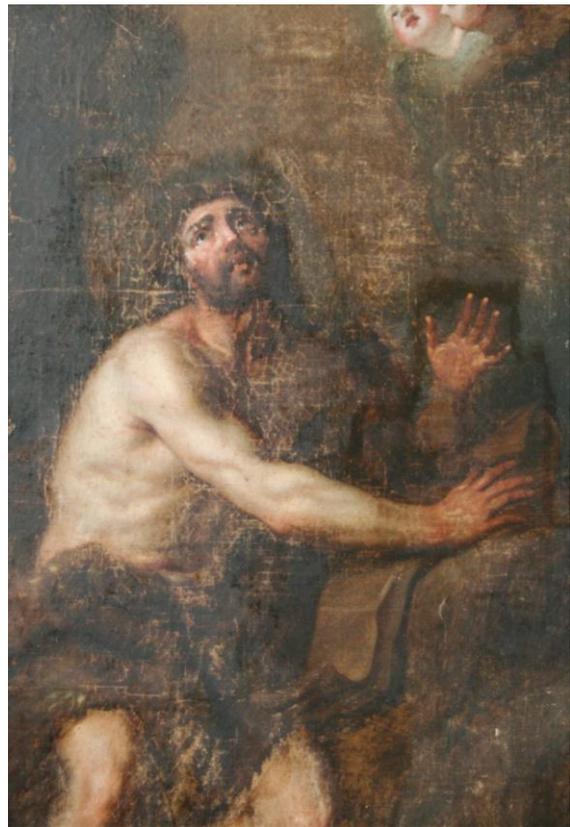
Picture after intermediate varnishing



Picture after retouching



Painting backside before and after conservation



Fragment pictures illustrating the conservation process of painting „Saint John the Baptist”