DEPARTMENT OF CONSERVATION

Research on the viability of the use of rigid gels for the cleaning of water-gilded surfaces

The case of Agar-agar and xPVABorax

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Degree project for Master of Science with a major in Conservation
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ABSTRACT: As the Getty Institute of conservation and other researchers said, studies are absent regarding cleaning gilded surfaces. These surfaces are extraordinarily complex to clean due to their water-sensitive nature. This research aims add some light into this field by studying two different hydrogels that control the diffusion of the water into the surface, creating a perfect condition for cleaning water-gilded surfaces. The gels tested are Agar-agar and xPVAcBorax, which are sustainable and non-toxic; this means that they are not only suitable for cleaning water-gilded surfaces but also environmentally friendly and kind to the conservator's health. For this purpose, a soiled water-gilded surface is used to test the gels and their variations. Afterward, the surface is studied to see the effectiveness by means of scientific studies such as SEM or gloss meter

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1. Background and problem

In 2018 the Getty Conservation Institute organized an expert meeting to discuss the lack of information and technical preparation towards gilded surfaces. Among other things, they pointed out the lack of understanding regarding advanced treatments for gilded surfaces (1). Malgoratza Sawiki also highlights in one of her articles from 2019 the absence of studies about cleaning gilded surfaces; she also states that most techniques used are taken from other areas inside the conservation field (2). Most treatments employed nowadays damage the gilded surface by scratching the gold or by removing the gilded layer, due to the interaction of the solvent with the underlayers.

Among all types of gilded surfaces, the water-gilding type is the most complex to treat. First of all, sometimes they are coated with a proteinaceous media[1]; according to some treaties, this can be either gelatin or shellac (3) (4) (5). The coating attracts soiling, dust, and dirt, which adheres to the surface. With time the layer of soot creates a disturbing black effect. This layer would be easily removed using water mixed with modifiers such as, chelating agents or buffers; the problem is that the surface is highly sensitive to water. Gold itself is a stable material and not susceptible to water; rather, this problem arises because of the underlayers, which are clay (bole) and chalk, two hydrophilic materials. As a result, when using water with a cotton swab, it diffuses into the underlayers. It causes swelling and attraction between the bole and the cotton swab humected in water. Since the gold is an intermediate layer when the water forces interact with the hydrophilic material, it results in removing the gold leaf as a side effect.

It is unfortunate that water cannot be used to clean water-gilded surfaces because of its diffusion into the underlayers. Especially because water is sustainable, non-toxic, and cheaper than any other solvents or material. One solution to this problem would be to control the diffusion of the water into the

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[1] Especially if the gold has lo karats; this prevents the material alloyed with the gold from oxidizing, and it also gives a warmer hue to the surface.

underlayers, which could be achieved using hydrogels. Hydrogels retain water inside their structure, only allowing a minimum amount of water into the surface, depending on the percentage of gelling agent. Therefore, if the water diffusion is controlled to only interact with the soot surface without getting into the bole or chalk layer, the gold would not be removed.

1.2 Aim and objective

This project aims to find a sustainable and non-toxic way to clean water-gilded surfaces by using water, which is a material that presents these characteristics. The objective is to find a method to control the diffusion of the water into the surface and not affect or remove the gold layer, which can be done with hydrogels.

After the literature review, the hydrogels chosen are xPVAc Borax and Agar-Agar. They will be tested by themselves and, changing different parameters, such as the concentration, the recipe, or adding chelating agents and buffers to see how the soot surface reacts and which one is more suitable.

1.3 Research questions

This research is focused on answering the following questions:

- How does the diffusion of the water in the gels affect the layers of the water-gilded surfaces?
- When and why is the gilding removed after the cleaning process with gels?
- How does the pH of the gel affect the cleaning process?
- How does the percentage of the chelating agent affect the cleaning process?
- How does the time of application of the gel affect the cleaning process?

1.4 Material and case.

For this research, it was fundamental to have dirt and soot over a gilded surface. The question is whether to have mock-ups or a tangible object to perform the tests.

When creating mock-ups, there is a need to generate superficial dirt that requires organic and inorganic materials such as carbon and iron oxide (5). This dirt can either be bought or recreated in the lab. Unfortunately, this solution created long waiting times, such as the study of generic dirt[2], creating mock-ups that required gilding which increased the price—finally, aging the material to have a surface like an already aged water-gilded object.

The second option and the chosen one was to perform the tests in an old frame with sufficient superficial dirt. This frame was found in a second-hand store; samples were taken to prove that the gilding was gold and not brass.

Once it was proven that the frame was gilded with gold, it was subjected to an investigation to find out which materials it is made of; the data and results of the investigation can be seen in Appendix 1. The samples were taken in the places marked in Figure 1.

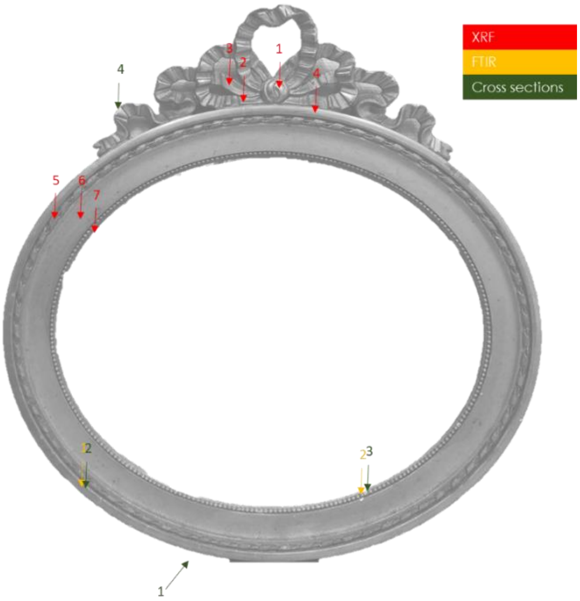

Figure 1 Samples taken for research

The characteristics of this frame are the following:

Ground layer – It appears to be two types of ground layer, one for the burnished gilding and the other for the unburnished. The composition is the same for both, which is calcium carbonate; this can be seen when comparing the XRF and the FTIR. In the burnished gilding, it seems that there are two types of ground layer, one with bigger particles and the other one with smaller ones of a reddish color,

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[2] The dirt and soot changes according to the place where the object is, for example if the object is in a marine environment the dirt would contain more salts while if the object were in an industrial environment the dirt would have pollutants its composition.

maybe from the iron of the bole. It is essential to highlight that burnished gilding can only be made over water and not oil. Therefore, since the burnished parts of the gilding show the same peaks in the FTIR as the unburnished, this corroborates that the binding media is proteinaceous and not oily. It has not been determined which type, but most probably, it can either be gelatin or animal glue.

Bole – The XRF shows iron only in those samples taken in the burnished part; this information together with the cross-section of the burnished gilding that shows a red layer, verifies that there is a layer of bole in the burnished sections of the frame. It is not possible to have a burnished surface if there is no bole layer.

Gilded layer – There are two types of gilded layers, the burnished and the unburnished. In the burnished parts, the gilding is made with gold, although the karats (purity) have not been determined, while in the unburnished parts, brass is used.

Figure 2 Sketch of the materials composing the frame

1.5 Methodology

The study is a single-object experimental and observational study. The samples are taken in one object that presents the average characteristics from objects of the same type. It is experimental because the researcher controls one or more variables. In this case, the gels are controlled, and they create different conditions over the object. The processes for this study involve as well conducting technical analyses on the object and observing and interpreting the results.

The thesis presents primary and secondary data, being the first one the researcher experiences and the second one taken from different sources such as articles, courses, or conferences.

The thesis is divided into five main chapters. Chapter one introduces the problem, explains the aim and objective, and contains the research questions. Chapter 2 contains all the theory needed to understand the problem and the solution—Chapter 3 explains the experimental approach. Chapter 4 shows the results, Chapter 5 has the discussion, and chapter 6 the conclusion. It is believed that this structure is optimal for the understanding of the master thesis. Everything is separated and categorized into their corresponding chapter, and the information can easily be found.

For this research, two are the main focuses:

- To analyze gels for the cleaning of gilded surfaces
- To add variables to the gels and study the changes happening when cleaning the soil.

Given that the number of gels that exist for conservation purposes is immense, after thorough research in the literature (see 2.1.4 Historical cleaning of gilded surfaces), two are the gels studied in this investigation: Agar and xPVAc Borax. They are tested in a water gilded frame to prove whether they are suitable or not for the cleaning of a soiling layer.

To prove the effectiveness of the gels, they are tested by:

- **Ocular study:** serves to see the more remarkable change after the use of the gel.
- **SEM**: used to know if the gels have left residue.
- **Gloss-meter**: used to measure the changes of the gloss after the gel has been applied.

1.6 Theory

The first documents that have ever collected any conservation criteria are focused on monuments and immovable heritage such as buildings (6). Nonetheless, the same criteria can be extracted for the conservation of objects. Three are the main charters on which this project is based: The Athens Charter from 1931, The Venice Charter from 1964, and the Theory of Restoration written by Cesare Brandi in 1963 (7) (8) (9).

According to them, in this project, the ethical aim is to:

- Have a broad knowledge of the type of material tested, the study of the material and techniques, diagnosis, exhaustive graphic and written documentation.
- Preserve the object's integrity by studying new methodologies that will help to do so in the future.
- Study the interaction between the material and the object to prove its effectiveness and know whether this treatment would be reversible for the objects.
- Perform the research by a qualified person who can perform the tests and read the results to guarantee optimal performance.

1.7 Positioning

This research is based on two primary papers that tackle the problem of the conservation of gilded materials: The experts meeting organized by the Getty Conservation Institute in 2018 (1) and the research performed by Margorazta Sawicki in the cleaning of gilded surfaces using gels (2). The main problem highlighted in both papers is the lack of information and training in cleaning gilded surfaces. So far, the cleaning process in gilded surfaces has been performed the same way as in other conservation areas, without considering the difference between materials. That is why this research aims to find specific materials to perform the treatment in gilded objects that will not damage the surface.

1.8 Expected results

Water can be a physical solvent for hydrophilic materials, is a suitable medium for chemical reactions, such as ionization and dissociation of materials, and under specific conditions, it can trigger hydrolysis. All these properties make water the perfect solution for the removal of soil. The downside is that water-gilded objects are very susceptible to water since this one interacts with the underlayers, causing the removal of gold. The solution for this problem is the use of hydrogels as gels retain the water in their structure, making the diffusion of water to the underlayers minimal. Therefore, the removal of gold is non-existent.

2. Theoretical approach

In this chapter, the theoretical part of this research is explained. On the one hand, it focuses on gilded surfaces, the different types, and how they are made, which is helpful to understand its chemistry and how the cleaning affects the layers depending on the type of gilding. The alterations of gilded surfaces are also explained, focusing on the soiling problem since it is the topic that concerns this research. On the other hand, there is a brief introduction to gels, directed explicitly to Agar and xPVAc Borax, and why they were chosen to perform this research.

2.1 Gilded Surfaces

Gilding has been used since the XIII century (10). There are numerous types of gilding techniques; they vary from one country to another, and from century to century, (11) (12) although for the purpose of this research it will just focus on the water gilding techniques that appear in some European art treaties, such as *Il Libro del Arte* by *Cennino Cennini* or *El Arte de la Pintura, su antiüedad y grandezas* by *Francisco Pacheco*.

The most common gilded techniques in Europe are water gilding and oil gilding. The main difference between them is the biding media used to adhere the gold leaf to the surface. Traditionally oil gilding used linseed oil as an adhesive between the preparation layer and the metal leaves, while nowadays, the mixtion[3] is the most common one. The oil gilding technique is much easier than water gilding since it only requires a preparation layer, the oil, and the gold. The main advantage is that any type of surface can be gilded with this method, but the main problem is that it does not allow the surface to be burnished, so it only allows having a matt finishing and not a shiny one. Therefore, this technique has been discarded since cleaning this type of surface with water does not present a problem.

On the other hand, the water gilding technique is much complex to perform and is explained rigorously in the following section 2.1.1

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[3] This name was given to it since it is a mix of different drying oils

2.1.1 The water gilding

The water gilding technique is a complex procedure since it requires fine materials and a long production time. If any step of the process is not correctly done, this will affect the quality of the final material.

There are different ways on how to proceed according to different renascence, and baroque treaties (14) (15), this method presented here is according to the collected information from Laura de la Colina Tejeda (13) and Eva López Zamora (16), the process shown focuses explicitly on a wooden support.

1. Preparation of the wooden support

   The wooden support must be prepared before gilding. It is essential to remove any types of wood knot because any type of disturbance in this layer will show in the final result. It is unnecessary to sand it since the preparation layer will adhere better if it has some irregularities.
2. Isolation of the wood.

   Since the surface of the wood is a porous surface affected by humidity and temperature, that expands and contracts, it must be isolated to minimize these changes. Therefore, a layer of rabbit skin glue at 5% is applied while it is warm to penetrate the porous. This layer also works to achieve a better grip surface for the subsequent layers.
3. Preparation layers

   The preparation layers differ from the north of Europe and the South. In northern Europe, the most common ground layer is chalk (Calcium Carbonate). Around 5-10 layers of chalk in a mixture of 5% gelatin or rabbit skin glue are applied, sometimes even more. This is because the chalk is very thin; therefore, more layers are required to accomplish an excellent finish.

   In the southern part of Europe, gesso (Calcium Sulfate) is used in 5% rabbit skin glue, and gelatin is less common. The gesso allows two types of application, one with bigger particles to isolate the wood, 2-3 layers of this gesso are applied, and then another 2-3 layers of thin gesso are applied. This technique allows the gradual change from one surface to another, creating a soft final layer.

   When preparing either the gesso or the chalk, it is essential not to move it or stir it too much; otherwise, bubbles will appear in the application. Once the layers of chalk or gesso are done, they are sanded with the thinnest grammage, and a cotton swab with alcohol is used to remove any loose impurities from the sanding.

4. Bole layers

   The bole or polliment is a fine grain clay, and it works as the soft support for the gilded leaves. Although the most common one is the Armenia clay, which has a red tone, it exists in different colors.

   The clay must be ground and hydrated; this may take several days. Then, the exact quantity of clay is mixed with 1% rabbit skin glue and applied to the surface. Around ten layers of bole are applied because the clay particles are very thin, therefore, the hiding power is low, and it requires adding multiple layers.

   Once the layers are applied, the bole should be burnished. This can be done in different ways: using a thin cloth, a soft brush, or an Agatha stone.

5. Gilding

   This is the final step of the process. First, a mix of 1% rabbit skin glue or gelatin is applied, while it is still wet, the gold is applied. Before the surface is completely dry, the gold should be burnished with the help of the Agatha stone.

The water-gilding technique is more complex than oil gilding, but the result is finest. The bole and the diluted glue in water give the gilding the shiny finish, this can only be achieved when the object is gilded this way.

2.1.2 Alterations of the gilded surfaces

Gold is a heavy metal, malleable and stainless in water and air (17), these characteristics make gold the perfect material for gilding an object since it can be thinned out to 1 micrometer, and it handles changes of temperature and humidity without losing its shine or oxidizing (18), these are the main reasons why it is called a noble metal (19).

The main chemical problem of gold is corrosion, it only occurs when the gold is alloyed. Silver and copper are the most common metals to alloy with gold, this can be done for several reasons:

- To make it more economical (5)
- To change the final finish of the gold to a warmer or colder hue (20).

- To make it stronger, since gold by itself is a soft material which makes it vulnerable to abrasion and friction (22).

These alloys would only be a problem in gold leaves of less than 22kt. Gold would be susceptible to corrosion with lower kt, and below 18kt tarnish will eventually happen (19). To prevent tarnish from happening, varnishes are applied with a double function: to give a tonality and prevent corrosion (2)Figure 3.

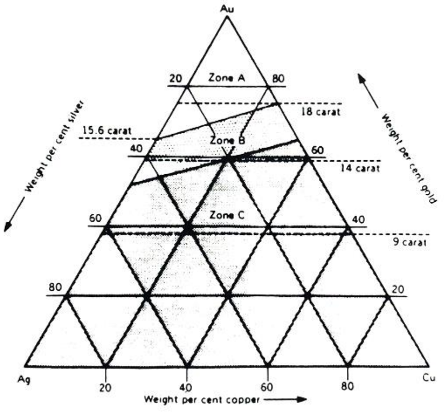

Figure 3 Corrosion regions. Zone A: Low susceptibility; zone B: Medium susceptibility; Zone C: high susceptibility (61)

A way to spot the corrosion is to see when the surface has turned black which happens to the silver in contact with Hydrogen Sulfide creating Silver Oxide (21). Another option is when the copper is in contact with carbon dioxide and forms copper oxide. In this case, the surface turns green (22).

Apart from the corrosion and abrasion, wooden gilded surfaces also suffer from other deterioration. Most of them are targeted to the support or the under layers. For the purpose of this research, the focus will be on the alterations caused by the dirt. However, many of the other alterations are perfectly explained in the Canadian Conservation Institute standards and the Coreman's Project (23) (24).

2.1.3 Superficial dirt

DPM or deposited particulate matter is one of the main problems that gilded objects suffer from, this is not only a disturbance for the eye, but it also has many consequences for the objects; they are abrasive and typically harsh for the object causing its degradation.

Pollutants, specifically DPM, differ from one place to another, as shown in Figure 4 Composition of DPM in different places. The main component of the dirt is of terrigenous origin, which is a mixture of clays and calcite. There are also anthropogenic deposits, which are composed of soot and gypsum. Different types of particles are also found due to the pollutants, both outdoor and indoor. There will be more diesel particles in an outdoor urban environment (25), while in a marine environment, more salts would be found (26). Other particles coming from indoor contamination are candles and incense, which lead to the deposits of phosphates or alkali nitrates and elemental carbon (27). These components that create a dirt layer can be either organic or inorganic, acidic or basic, and most of them are polar (5).

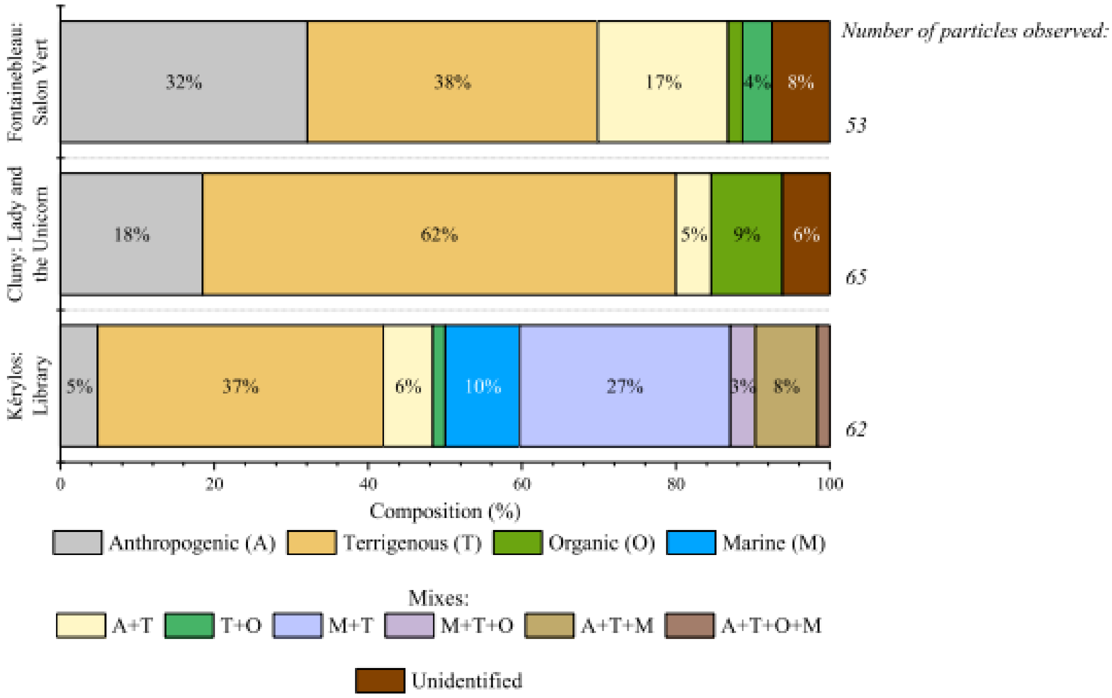

Figure 4 Composition of DPM in different places (25)

When these particles are naturally deposited in the object, they may cause the following chemical forces between the object and the soiling:

- Molecular forces, where the atoms of different materials, in this case, the surface layer and the soiling, interact with each other (28), causing chemical transformations such as the tarnish of silver or the oxidation of copper.
- Electrical forces, where there is a flow of charges due to the potential difference (positive or negative charge) between the molecules (29)
- Capillarity forces, the particles may also attach to the surface due to the irregularities of this one, whether it has cracks or pores. These types of forces are more common in small particles in a high relative humidity environment.

Depending on the particle size, the smaller the particle, the molecular and electrical forces may decrease, and the Coulombic and capillary forces will increase.

Another issue is that the dirt is highly hygroscopic, while this could be beneficial since by interacting with water, the dirt can be easily removed. When it is found in a humid environment, it presents a risk for gilded surfaces. Among the significant damages that water can cause to this type of surface are the following:

- Salty blooming on varnishes may occur since the salts found in the DPM absorb water. Therefore, the deposition of the water that condensed would interact with the varnish creating a velvet effect on the surface (30)
- The water acts as catalysis creating hydrolysis. Wood is explicitly susceptible to water and, the acid hydrolysis may eventually reduce the mechanical strength of the wood (31)
- Sulfur-rich particles can be oxidized into sulphuric acid, responsible for pigment discoloration and metal corrosion; if the gilded object is formed with golden alloys such as copper or silver, the particles will affect this as well.

2.1.4 Historical cleaning of gilded surfaces

Malgoratza Sawicki summarized the methods more commonly used for cleaning water-gilded surfaces, although, as already said before, this practice has not been deeply studied. According, to her (2), the most common methods are:

- Basic dry cleaning or dusting with a brush
- Mechanical removal, i.e., with a scalpel.
- Laser cleaning systems.
- Aqueous solutions, i.e., artificial saliva or water-based solutions with chelating agents (mainly tri-ammonium citrate (TAC) or ethylenediamine tetra-acetic acid (EDTA)), with buffers and varied pH values, applied with swabs.
- Hydrogel systems and emulsions, with TAC or EDTA

In Table 1, there is an overview of all the methods used to clean gilded surfaces, not exclusively targeted to water gilding but also for oil gilding, since there is scarce literature on the first one.

Cleaning methods for gilded surfaces				
DRY CLEANING				
Method	Type of gilding	Type of cleaning	Advantages	Disadvantages
Sponges and rubbers	Oil and water	There are no articles about dry cleaning	The soot and dirt will be removed when using these methods gently	The gilding is very sensible to friction
Laser (32)	Oil and water	It works with any type of layer that has to be removed, varnishes, soot, dust, over paint…	Removes everything that is wanted. It is very efficient. The intensity is controllable.	The laser may heat up the surrounded area, and the metals may be affected by it as well. (Normally, it does not happen if the beam is tested and controlled beforehand)
FREE SOLVENTS				
Water-based systems (infusions, extracts, decoctions) (33)	Egg gilding	Cleaning an icon covered in dirt deposits	These types of ecological systems can be an optimal nonaggressive cleaning alternative for gilded old wooden artifacts and safe for the restorer.	The gold is sensible to the friction. It is moved, losing its natural form. The bole and other hydro-sensitive layers may be affected by the water in the long term.
Ethanol, Ketone, Shellsol D40, White spirit	Water	Cleaning superficial dirt and soil	It cleaned the dirt	No sensitivity is related to solvent, but the gilding is sensitive to friction.

GELS				
Klucel G (34)	Lacquer (Japanese technique)	To smooth an arabic gum repaint and making it easier to be removed	A good option, since it is a gel, the water does not penetrate in the under layers.	It is not a rigid gel, and the process of removing it may not be suitable for the gilding.
Agar (34)	Water	Removal of superficial dirt-encrusted to the surface	It removes the dirt, does not rub the surface, and is ecological. Many applications are needed to have a homogenous surface	It has to be applied at the right temperature. More than one application is needed to get a homogeneous surface.
Xanthan gel with solvents	Oil	Removal of overpainting	Overpaint could be removed after three applications	The higher concentrations resulted in a quicker reaction. However, the gilding underneath was affected and removed when cleared using a swab
PVOH/ borax gel (2)	Oil	Removal of overpainting	It was easy to remove in one piece; it did not stick to the surface. There was no need for clearing.	Nothing.
Pemulen with solvents	Oil	Removal of overpainting	Not very effective, it removed the overpaint	It does not remove it homogenously,

Table 1 Cleaning methods for gilded surfaces

As said, there is little investigation for the cleaning of water gilded surfaces, and as Table 1 shows that laser is the best solution known to clean gilded objects, it is a new technology, and although it is already being used, many studies are still focusing on it. Apart from that, the main disadvantage is that it is costly, and most conservation studios cannot afford one. Therefore, there is the need to find a more affordable way to clean gilded objects as gels.

Gels are a feasible solution. They are more affordable than laser, the solvent diffusion is controlled, and at the same time, they trap the soil of the surface without damaging the under layer.

2.2 Gels

Gels were introduced in the conservation community in the '80s with numerous advantages, such as having maximum control in the diffusion of the solvents into the paint surface, favoring the mixture between substances that are not miscible, and their ability to be improved by adding cleaning agents. Another advantage is that if the material to be removed is studied, the gels can be targeted to clean that specific material. In addition, the toxicity of the solvents is reduced because the evaporation time of the chemicals is delayed (35). For these reasons, gels are being used for the cleaning of surfaces.

A gel is a colloidal solution with two phases, the dispersed phase, which is formed of tiny droplets surrounded by a liquid that is called the continuous phase. Hence, to form a gel, there are two essential elements: the liquid and the thickener. The liquid used would determine the type of gel. If it is water, then the solution would be a hydrogel, while if it is an organic solvent, it is called an organogel. The solvent chosen is also important to determine if the mixture will be polar or non-polar, and therefore be able to target a specific material to be removed (5). The other essential element is the thickener which gives consistency to the liquid creating a colloidal solution. It can be either inorganic, such as clays, or organic, like xPVAc and Agar-agar (36).

The thickener has a macromolecular structure (large polymers). This relates to the thickening capacity, which is also related to the molecular weight of the polymer. Their structure is normally linear or slightly branched, which allows the formation of intramolecular forces between their own molecules and the molecules from the liquid, creating hydrogen bonds or dispersion forces.

In this research, the focus is on hydrogels since water can be a physical solvent for hydrophilic materials. At the same time, it is a suitable medium for chemical reactions, such as ionization and dissociation of materials, it also triggers hydrolysis. Nevertheless, by its nature, if it is wrongly used, it can be a hazard for water gilded surfaces due to high diffusion and capillarity, which can interact with the underlayer of the gilded surface (37). That is why using hydrogels will allow the removal of the soiling layer since the water in the gel will not be absorbed by the substrate, and the solubilized dirt particles will be partially reabsorbed by the gel (38)

Hydrogels are a network of hydrophilic polymer chains[4]. In the colloidal solution, water is the continuous phase, and the polymer the disperse phase. The crosslinking of the molecules can either be physical or chemical. For physical crosslinking, the molecules create hydrogen bonds or chain entanglement. Among others, pH or temperature play a crucial role in the formation of the gels. Chemical crosslinking creates covalent or ionic bonds between the molecules, forming irreversible gels (39).

The characteristics of the gel sought in this research should be as follows:

- It is a hydrogel since the use of solvents brings with it a series of disadvantages already discussed.
- That it works both by dissolving the substances to be cleaned and by trapping them into the gel structure.
- That it does not need to be rinsed afterward, as this would damage the gold, in case it does not have a protective layer

Given the characteristics above, the gels that have been chosen for cleaning are Agar-Agar and xPVAc Borax. The first one has been deeply studied in the conservation field and it has proven to be very effective, while xPVAc Borax it is a new addition to the field and not many studies have been done. Since agar-

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[4] Is a type of molecule attracted to water molecules and tends to be dissolved by it, this is due to their charge and polarity, creating hydrogen bonds. Since they are polar, these molecules can also be dissolved in other polar solutions apart from water (62).

agar has been shown to be effective in cleaning gold-plated surfaces, it will serve as a comparison between a gel that is known to work and one that is less well known. They have also been chosen for how sustainable they are, since they do not require any organic solvent for their preparation, which makes these two gels a better option for the environment and for the conservator´s health. At the same time, other elements can be included to improve their properties. In addition, depending on the application, they are rigid gels and therefore do not require clearing after the application (37)

2.2.1 Agar-agar

Agar-agar, better known as Agar, was first used in Japan for the food industry (40) it is a phycocolloid. This name is given to a group of natural polysaccharides extracted from seaweed (41). The Agar is formed of two main polysaccharides: agarose $[C_{12}H_{14}O_5(OH)_4]_n$ (42) ; which composes the 50- 66%, it is a linear polymer with repetitions of agarobise units, and agaropectin, that has the same basic structure as agarose, but containing impurities, like sulfates, and it composes the 5-10% (5)Figure 5 Linear structure of Agar-agar. Due to its high molecular weight (100.000 -150.000) is a suitable polymer for the formation of gels (43). Pure agarose is the element that forms the gels and is sold by itself for restoration. The drawback is its high cost. However, Agar, which is not as pure because it contains sulfates that reduce the gel-forming property (44), is still a good option and does not present any disadvantages for the material to be cleaned.

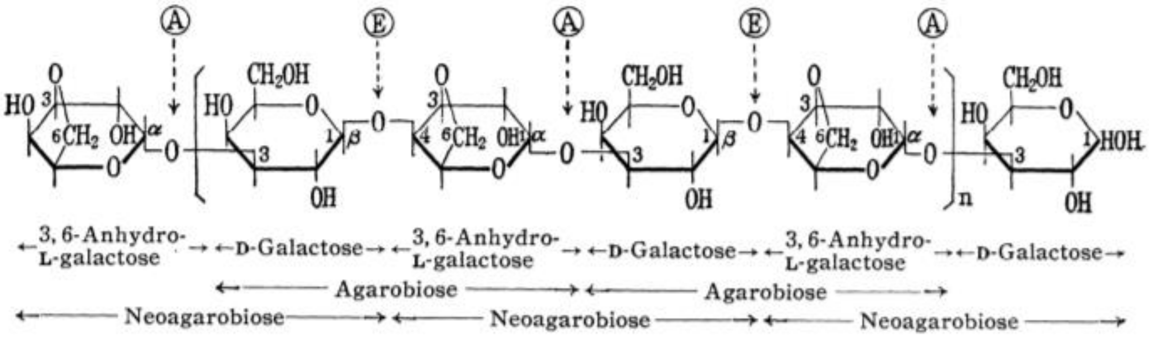


Figure 5 Linear structure of Agar-agar (42)

The Agar is formed by hydrophilic and hydrophobic bonds, which means that it is amphipolar. The amphipolar property allows the gel to form. The hydrophobic parts of the molecule face inwards while the hydrophilic face outwards when heated, forming a tight double helix formation that retains a large amount of water in its structure (45). It is also a physical gel, which means it is form by hydrogen bonds. Each molecule is independent of the others but tied together by conductivity forces. When the temperature rises, the chains with helicoidal form tangles, trapping the water between the curls. During cooling, the tails of the chains that has not been tangle with another, starts tangling and forming the rigid gel (43). Agar is a reversible gel since it can be transformed again to liquid when the temperature rises, and when cooling down, it goes back to the gel form.

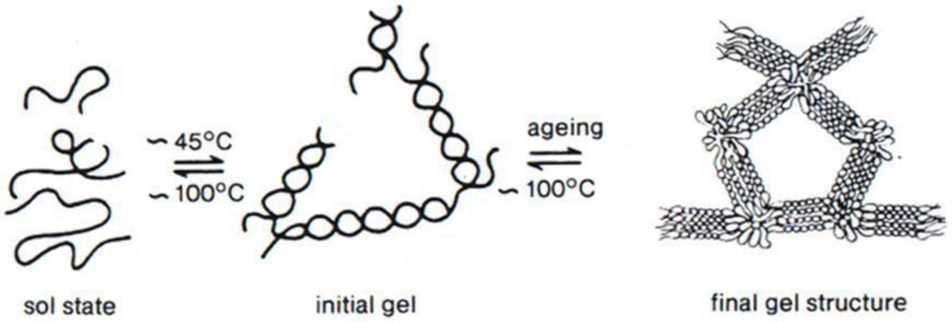


Figure 6 formation of the Agar gel (46)

From the family of *Agarophytes*, different types of Agar weeds are extracted; this causes the gelling temperature to vary from one commercial type to another. Nevertheless, it is always around 30-45° (40)

Agar family	1.5% solution, gel temperature
Gelidiella	42-45° C
Gracilaria	40-42°C
Gracilariopsis	38-39°C
Gelidium	36-38°C
Pterocladia	33-35°C

Table 2 Typical gel temperature of Agars extracted from several agarophyte (40)

An advantage of Agar is that it is environmentally friendly since, for its cultivation, only solar energy is needed. Hence, they show a low energy cost, and it does not need fertilizers for its growth. Additionally, it has a significant intake of CO_2 throughout photosynthesis, contributing to the decreasing of CO_2 in the atmosphere (47). Agar is also non-toxic when not combined with other chemicals and is safe for the conservator to use without protection (5).

Preparation of an Agar gel

There are different recipes for the preparation of Agar gel. All of them are simple to conduct and do not require expensive materials. First of all, the quantities of Agar and water will change depending on the gelling level of the gel desired. If the percentage is low, the gel is more fluid, allowing more water dispersion into the object. In contrast, if the percentage is higher, the gel is thicker, and therefore the water dispersion into the object would be minimized. Then, the gel has to be boiled its solubilization temterature (between 80° and 90°C), the mixture should be stirred to favor a homogeneous solution. The mixture then has to be cooled down. Around 30°-40°C is the gelling point, and it can be applied at this temperature to have a semirigid gel, or it can be applied when the Agar is completely cold and gelled. If this process is repeated, this favors the retention of water into the gel (48).

The Agar can also be prepared in a microwave at 500 W, repeatedly stopping after some seconds to mix the solution. When the solution comes to a boiling point, it should continue for 30-60 seconds and then stopped. Same as in the other case, the solution can be let to cool down until the Agar is gelled, or it can be used as a semirigid gel at a temperature around 30°- 40°C (45).

2.2.2 xPVAc Borax

xPVAc Borax or PVOHBorax is commonly known as a gel, although the literature has described it as a weak gel (49), high viscosity polymeric dispersions (HVPDs) (50), or the most appropriate slime (51). This plurality of names is due to the rheological characteristic of the gel, which is a strain stiffening response to shear and a storage and loss moduli response in relaxation times that are not characteristic of gels (52). this characteristic is also known as non-Newtonian fluid. In simple words, it is a fluid that behaves like a solid when temperature or pressure is applied to it.

The pseudo gel is formed of three main components, water, xPVAc, and Borax. The polyvinyl alcohol (PVA or PVOH) used in conservation has some degree of hydrolysis, which means that acetate and hydroxyl groups are attached to the backbone of the PVA Figure 7. The hydrolysis percentage allows the gel to be in a water-solvent mixture. PVOH by itself has a high polarity and, therefore, cannot be mixed with an organic solvent. However, by lowering the percentage of hydrolysis, the gel will accept more percentage of organic solvents. A similar thing happens when chelating agents are applied to the gel. Since the pH level has to be around 7.5-8, adding a chelating agent will lower the pH. Thus, a buffer can also be applied. This will as well depend on the hydrolysis level of the PVA Table 4.

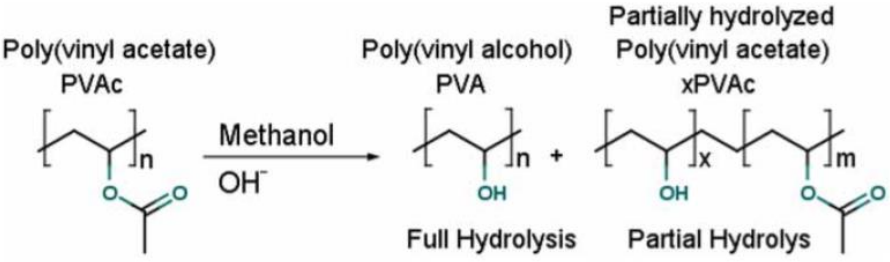
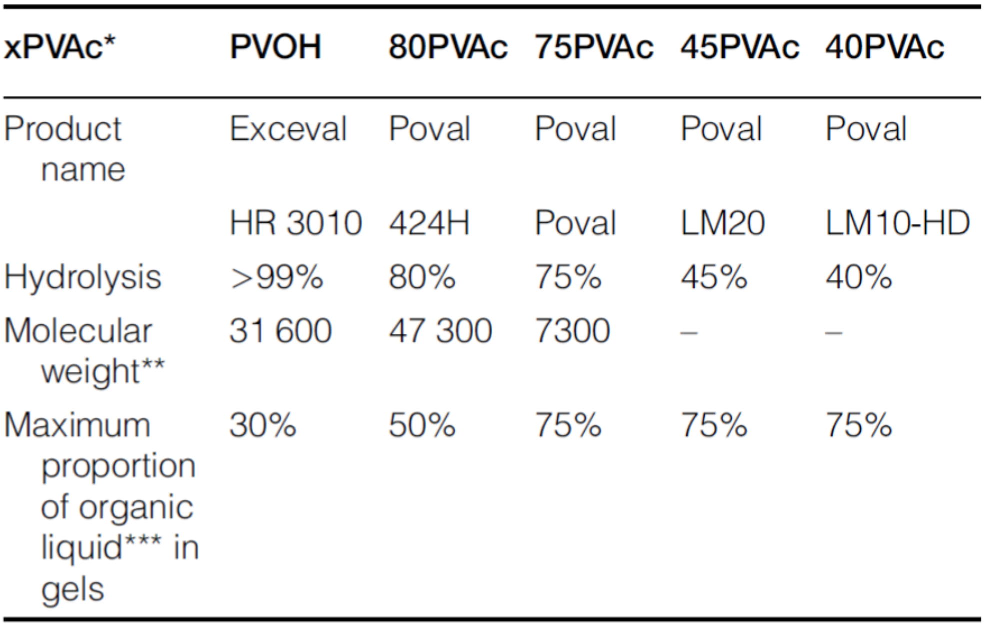
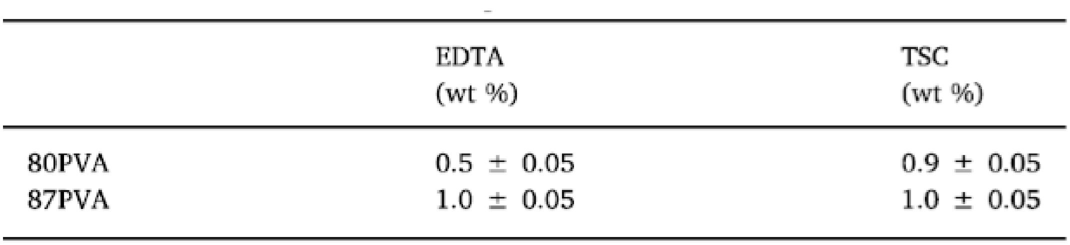


Figure 7 Preparation of partially hydrolyzed poly (vinyl acetate) during the production of poly(vinyl alcohol) from poly(vinyl acetate) (53).



xPVAc*	PVOH	80PVAc	75PVAc	45PVAc	40PVAc
Product name	Exceval HR 3010	Poval 424H	Poval Poval	Poval LM20	Poval LM10-HD
Hydrolysis	>99%	80%	75%	45%	40%
Molecular weight**	31 600	47 300	7300	–	–
Maximum proportion of organic liquid*** in gels	30%	50%	75%	75%	75%

Table 3 Summary of polymers obtained from the Kuraray and their properties (50)



	EDTA (wt %)	TSC (wt %)
80PVA	0.5 ± 0.05	0.9 ± 0.05
87PVA	1.0 ± 0.05	1.0 ± 0.05

Table 4 Maximum amount of chelator loadable into the 4.0 wt% xPVAc 1.0 wT% in water based HVPDs at room temperature

When the PVA solution is mixed with the borax solution [5], it results in a significant increase in the viscosity of the solution. The viscosity increase has been attributed to crosslinks between vicinal diols[6] on the polymer chains (52). These are the interactions that occur on the PVA with Borax, according to one of Lora Angelova's articles about xPVAc Borax (53):

> "When the xPVAc concentration is above the gelation threshold, the borate ion undergoes an esterification reaction with two adjacent hydroxyl groups on one polymer chain; the second esterification occurs to another set of adjacent hydroxyl groups either on the same polymer chain or on a different polymer chain. The enthalpy of formation of these crosslinks as well as the activation enthalpy for their cleavage, are low, allowing the crosslinks to form and break with ease" Figure 8

---

[5] When the salt borax [$Na_2B_4O_7 \cdot 10H_2O$] is dissolved in water forms two compounds: boric acid [$B(OH)_3$] and borate ions [$B(OH)_4^-$]

[6] Any diol is when two hydroxy functional groups are attached to adjacent carbon atoms.

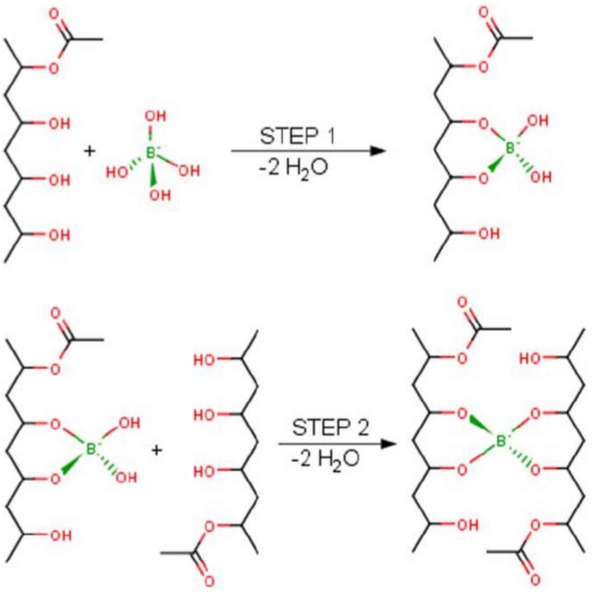


Figure 8 The mechanism of crosslink formation between xPVAc and the borate ion

xPVAc Borax gels can only be formed at a pH of 7.5-8. When the pH is lower, the crosslinking will not happen, and when it is higher, it will increase the gel's stiffness (53). The same thing happens with the proportion of PVA and Borax. When adding less amount, the gel will not form, while adding more results in stiffer gels. In addition, an excess of Borax can disrupt the balance between electrostatic repulsions and screening, causing a two-phase system (53)

Preparation of a xPVAc Borax gel

To prepare the xPVAc Borax, the first thing to do is to choose the quantities. More PVA will result in thicker gels.

The mixture has to be prepared in two phases. In one recipient, water and PVA has to be boiled at 50° until it dissolves, the percentage may change depending on the desired thickness, in the other container 1% of Borax in water has to be boiled at 50° until it is dissolved again, when both of them are dissolved they have to be mixed in a proportion of 9:1 PVA: Borax, and stir vigorously (52)

To add solvents, the mixture should replace the water used for the PVA and boil it at 50° until the PVA is dissolved. Same procedure if chelating agents have to be added. (52)

2.2.3 Variables in the gel recipe and application

Water by itself acts as a solvent for many materials, in some cases can act as an electrolyte[7], as it is polar and has a dielectric constant, the electrolytes are strongly attracted to it, breaking the bonds between them, and creating new ones with the water (28). However, by controlling different variables and adding new chemicals to the gel matrix, the cleaning properties will change, which will allow targeting a specific type of dirt and soil. This chapter shows these characteristics specifically for the gels Agar and xPVAc Borax.

Type of thickener

Of all the variety of thickeners that can be found on the market, choosing the right one has significant advantages for cleaning. In this case, the thickeners chosen are Agar and xPVAc Borax, but there is also a great range within these, so it is necessary to choose between them.

In the case of Agar, the chosen one should be the one with the lowest gelling temperature, this allows to apply it in liquid form so that it adjusts to the shape of the object without causing blooming due to the heating of the underlayer (5). It is also advisable to choose the purest Agar possible, bearing in mind that the purer the Agar, the more expensive it is. In this case, the one from Kremer was chosen since the gelling temperature is 35 °C (54)

In xPVAc Borax, the hydrolysis level as seen before is a key for adding chelating agents and solvents. Partially hydrolyzed PVA is used since it is the one available at the laboratories of the University of Gothenburg. This PVA allows between 0.5 and 1% of the chelating agent to be added in the composition and 75% of solvents.

The concentration

The concentration of the gels can also be controlled. In both cases, lowering the polymer's concentration would result in a more porous gel, therefore more aqueous and less rigid. While augmenting the concentration, the gel captures

---

[7] Electrolytes are substances that have free ions in their composition, that is why they are drawn to interact with water due to its dielectric constant (62), e.g., if NaCl is in contact with water the molecules will separate creating Na^+ and Cl^-, hence dissolving into the water.

more water between their chains, forming a more rigid gel (55). It is necessary to achieve an equilibrium. Thus, different concentrations have to be tested.

Method of application

There are multiple possibilities for applying gels, especially Agar gel. Cremonesi has published several articles explaining the benefits of using Agar in different ways. The latest studies show how it can be applied through a paint spray, which makes the application of the Agar completely homogeneous. Also, it can be applied through a hot syringe, which is beneficial for applying the Agar in defined spots (56).

It is essential to control the temperature of the application. It is sometimes helpful to have higher temperatures. When the temperature increases, this will create more dissociation between the salts, the electrolytes, and the water. Therefore, they will be easily removed (28). At the same time, this temperature must be controlled since high temperatures will also affect the gel formation and the underlayers, causing blooming.

In the case of xPVAc Borax, it can only be applied cold. When applied through Japanese paper, the diffusion is diminished. This can be controlled with the concentration of the gel.

Hydrogen potential

An acidic material is a compound that gives up hydrogen ions (H$^{+)}$ in a solution (water), while a basic material gives up hydroxide ions (OH^{-}). When a material behaves like an acid, gives up H^{+} to the other material that acts as a base by capturing the ion, the same happens in the other direction (57). Being able to control the pH allows controlling the solubility of the materials.

To remove the soot, the pH of the Agar must be close to the pH of the substrate.

In the case of xPVAc Borax, the pH level cannot be changed since the formation of the gel only happens when the pH is around 7.5-8

Chelating agents

Chelators are a compound that contains at least two or more functional groups that act as electron donors that will interact or bond to individual metal atoms in a solution. They are introduced into aqueous systems to solubilize insoluble complexes or metals like carbon (28).

The advantage of using chelating agents with xPVAc Borax is, according to Lora V. Angelova, that the covalent attachment of a chelating agent to the polymer used to prepare such gels may make the treatment process more straightforward by eliminating the possibility of chelator deposition on the cleaned surface (52).

3. Experimental approach

In Chapter 2 is explained how the hydrogels Agar-agar and xPVAcBorax work in contact with gilded surfaces and why they are beneficial to use to clean soot in these objects. It is also explained how they can be modified to achieve a better cleaning treatment by changing the concentration, the pH or by adding chelating agents.

There are two main sections in this chapter, the description of the tested parameters and the tests. The realization of the experiment is shown by describing the methodology of gel preparation, application, and results.

3.1 Description of the parameters to test

In this chapter, the different tested parameters are explained according to the theoretical approach given in the pages above. It is essential to highlight that no material is the same, and the parameters here expose are not universal. Hence tests in other objects must be carried out before doing any treatment.

3.1.1 Concentration

As seen in the theoretical part, the choice of a concentration is essential for cleaning the frame. A gel with little concentration of the gelling agent causes a high diffusion of water into the underlayer of the gilded object. While a gel with too much gelling agent does not interact with the object, no cleaning would be carried out. Therefore, the concentration is of great importance.

In the case of Agar-agar, the concentrations chosen are 2%, 4%, 6%, 8% and 10%. The concentrations are chosen to test the porosity of the gel, knowing beforehand that 2% is not suitable for the object since it is deficient, and the water diffusion will damage the object. These concentrations follow the mathematical series 2n (where n is the last number); this is done in other to notice the difference between one concentration and the next one.

3.1.2 Application method

Although there are multiples methods of applying the gels, especially for Agar, the methods chosen were two.

- Application of cold Agar for 1 and 3 minutes
- Application of warm (45°C) Agar for 1 and 3 minutes.

The times were chosen according to the amount of dirt; probably with the application of the gel for less than one minute, the reaction with the dirt would not happen. Nevertheless, at the same time, 3 minutes allows the high concentrated gels to act with the dirt.

If the application of cold Agar for 1 minute is not successful, then the other tests are canceled. Moreover, the same rule applies to the xPVAc Borax.

3.1.3 Hydrogen potential

As previously said, xPVAc Borax needs a pH of 8-9 to be formed. Hence, this parameter cannot be changed for this gel. At the same time, Agar-agar accepts solutions that modify their pH.

In this case, the pH of the dirt is measured by scraping it from the surface using a scalpel and put it in deionized water. The solution is shaken and left for 5 minutes to allow the exchange of electrons between the dirt and the water. Then the pH is measured with a pH meter.

In this object, the pH given is 5. Consequently, the Agar gel is made with a pH 5 buffer.

3.1.4 Chelating agents

The chelating agents chosen for the recipe were EDTA and TAC (triammonium citrate). In the case of the Agar-Agar, only EDTA was chosen to minimize the samples since it is known that Agar admits any type of chelator and will form a gel. The proportions used are 0,5 and 1%

In the case of xPVAcBorax, after the studies of Angelova, EDTA was chosen since it shows the proportions that xPVAcBorax accepts in its composition. To try another type of chelating agent that was not studied before, TAC was chosen. The number of chelating agents added is according to Angelova's recipe

3.1.5 Total samples

The total samples with all the variables are 77, taking into consideration the samples with water and saliva to prove that aqueous free solutions are not suitable.

N.º	Gel	Concentration	Application method	Chelating agent	pH	Time
1	Water		Cotton swap			
2	Saliva		Cotton swap			
3	Agar	2%	Cold			1
4	Agar					3
5	Agar			EDTA 0,5 %		1
6	Agar					3
7	Agar				5	1
8	Agar					3
9	Agar		Warm			1
10	Agar					3
11	Agar			EDTA 0,5 %		1
12	Agar					3
13	Agar				5	1
14	Agar					3
15	Agar	4%	Cold			1
16	Agar					3
17	Agar			EDTA 0,5 %		1
18	Agar					3
19	Agar				5	1
20	Agar					3
21	Agar		Warm			1
22	Agar					3
23	Agar			EDTA 0,5 %		1
24	Agar					3
25	Agar				5	1
26	Agar					3
27	Agar	6%	Cold			1
28	Agar					3

29	Agar			EDTA 0,5 %		1
30	Agar					3
31	Agar				5	1
32	Agar					3
33	Agar		Warm			1
34	Agar					3
35	Agar			EDTA 0,5 %		1
36	Agar					3
37	Agar				5	1
38	Agar					3
39	Agar	8%	Cold			1
40	Agar					3
41	Agar			EDTA 0,5 %		1
42	Agar					3
43	Agar			TAC 0,5		1
44	Agar					3
45	Agar			TAC 1%		1
46	Agar					3
47	Agar				5	1
48	Agar					3
49	Agar		Warm			1
50	Agar					3
51	Agar			EDTA 0,5 %		1
52	Agar					3
53	Agar				5	1
54	Agar					3
55	Agar	10%	Cold			1
56	Agar					3
57	Agar			EDTA 0,5 %		1
58	Agar					3
59	Agar				5	1
60	Agar					3
61	Agar		Warm			1
62	Agar					3

63	Agar		EDTA 0,5 %		1
64	Agar				3
65	Agar				3
66	Agar			5	1
67	Agar				3
68	xPVAcBorax	Angelova´s recipe			1
69	xPVAc Borax				3
70	xPVAc Borax	4%			1
71	xPVAc Borax				3
72	xPVAc Borax		TAC 0,5%		1
73	xPVAc Borax				3
74	xPVAc Borax	6%			1
75	xPVAc Borax				3
76	xPVAc Borax		TAC 0,5		1
77	xPVAc Borax				3

Table 5 Number of tests

3.2 Description of the methods and analysis

To check the success or failure of the gels, different parameters are tested. Firstly, employing an ocular analysis that allows appreciating with the naked eye the result of the gels because those tests in which the golden color is removed are failure tests to which it is not necessary to submit to any other type of analysis.

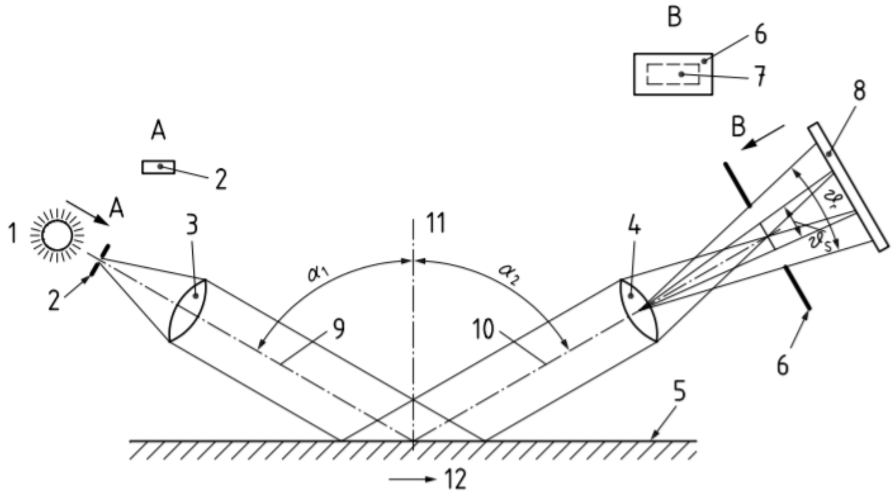
In those tests that at first glance seem to be successful, several analyses are carried out, such as testing of the color changes and glossiness using a gloss meter and SEM to prove if the gel has left any residues or not.

3.2.1 Glossmeter

According to the ISO 2813 (58) the optical property of a surface, gloss is characterized by its ability to reflect light specularly. The gloss value is indicated by gloss units (GU) (58).

According to this definition, when light hits an object and is scattered, the object is seen as matt, while when the light hits an object and is reflected in the main specular direction, the object is glossy. The intensity of the glossiness depends on the surface material and the incident angle of the light into the object.

The gloss meter works by projecting a beam of light to the object and measuring the reflection that is captured by a photodetector, as seen in Figure 9



Key

1	light source (source)	9	optical axis of the incident beam
2	source image aperture	10	optical axis of the receptor beam
3	source lens	11	surface normal of the test specimen
4	receptor lens	12	direction of measurement
5	test surface	α_1	angle between 9 and 11
6	receptor field stop	α_2	angle between 10 and 11
7	image of the source aperture in the receptor field stop	ϑ_r	receptor aperture angle
8	photo detector (receptor)	ϑ_S	source image aperture angle

Figure 9 Representation of how a gloss meter works (58)

3.2.2 Scanning electron microscope

The scanning electron microscope, also known as SEM, has an electron gun that projects a beam of high-energy electrons into a sample that generates a variety of signals absorbed by the detector (59) that reveals essential information about the object, for example, the morphology of the surface or the chemical composition (60).

By revealing the surface morphology of the object, in theory, this analysis can reveal whether there is residue in the samples or not after having applied and removed the gel.

3.3 Realization of the experiment

In this chapter, the practical part of the experiment is shown, the different recipes used with variables to make the gels, the application method, and the results of the experiment.

3.3.1 Preparation of gels

As said, all along this project, two main types of gels are used: Agar-agar and Borax, and here is explained how they are made

Agar-agar

When creating an Agar gel, the most crucial part is the concentration, since depending on this, the gel acts completely different when it has a concentration of 2% or 8%, as said in previous chapters of this thesis. For the purpose of explaining the recipe, the concentration chosen is 4%, and the methodology to create an Agar gel is the following

96g of deionized water had to be added to each 4g of Agar, this mixture is heated up in a water bath until the Agar reaches a temperature of 75-80ºC, it has to stay at that temperature for about 5 to 10 minutes and then it can be cooled down.

If the Agar gel is going to be applied in the cold, the mix must be spread into a recipient and saved until solidified. If the Agar is going to be applied warm, the temperature of the application is critical. As said before, the application of high temperatures to an art object it could cause several damages. Therefore, it is recommendable to applied at a temperature of 45ºC or lower.

The recipe slightly varies when adding different variables to the gel, such as changing the pH. or adding chelating agents.

In the case of adjusting the pH, like in this object, it has to be adjusted to 5. A buffer has to be added to deionized water drop by drop until de desired pH is obtained. Once the water is adjusted, the procedure to make the gel is the same one as explained before, but the water used will be the one buffered to a pH of 5.

When adding chelating agents, the water that will be added to the Agar already has the percentage of chelating agents on it. For example, if it is 1% EDTA, 1g of EDTA is added to 99g of deionized water. In the case of a 4% Agar 1%EDTA Agar gel, 96g of deionized water with EDTA will be added to 4g of Agar.

xPVAc BORAX

To create the borax gel, two different methods were used, one is Angelova's recipe (52), and the other one was created with the advice of the senior lecturer in chemistry from the University of Gothenburg, Zaaren Abbas, this recipe allows to have different concentrations of gels, to make it more or less stiff.

Angelova's recipe for 10g batch:

Dissolve 0,6g of xPVAc in 7g of deionized water, slightly stir while heating it, at no more than 50°C, in a separate container dissolve 0,1g of Borax in 2g of deionized water, once the two preparations are fully dissolved (it takes around one hour) mix them while stirring vigorously. For adding chelating agents, this may be added into the borax mixture, and the pH has to be checked to be between 8 and 9. Otherwise, the gel will not form

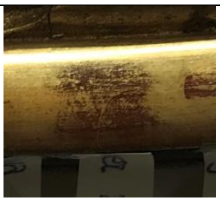
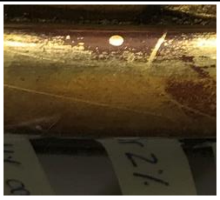
Recipe 2 for a 10g batch:

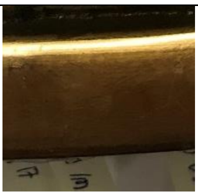
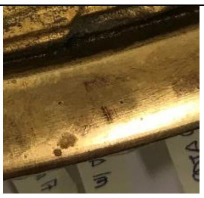
To create a 4% xPVAcBorax gel, dissolve 0,4g of Borax into 9,6g of water, and stir it at a temperature of 50°C, in a separate container dissolve 0,1g of Borax in 2g of deionized water, once the two preparations are fully dissolved (it takes around one hour) mix them while stirring vigorously. For adding chelating agents, this may be added into the borax mixture, and the pH has to be checked to be between 8 and 9. Otherwise, the gel will not form

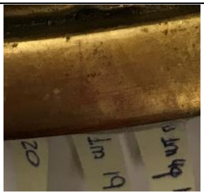
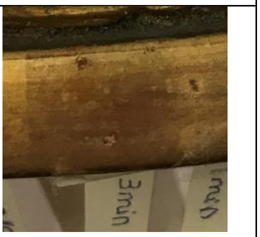
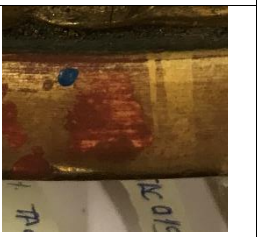
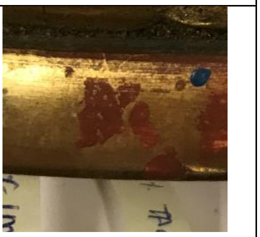
4. Results

The results are expressed according to 3 different tests: Ocular, SEM, and Glossemeter.

4.1 Ocular

OCULAR					
N°	Gel tested	Time	Application method	Observations	Photo
1	Water	-	Cotton swab	It removes the gold and bole	
2	Saliva	-	Cotton swab	It removes the gold and bolo	

3	Agar 2%	1 m	Cold	The water diffusion is too high, and the gold is removed, no trying other possibilities with this percentage	
4	Agar 4%	1m	Cold	The water diffusion is too high, and the gold is removed, no trying other possibilities with this percentage	
6	Agar 6%	1m	Cold	The water diffusion is too high, and the gold is removed, no trying other possibilities with this percentage	
7	Agar 8%	1m	Cold	It did not remove the dirt, but it did not remove the gold either.	
8	Agar 8%	3 m	Cold	It did not remove the dirt, but it did not remove the gold either.	
9	Agar 8%	1m	Warm	It only removes the dirt; gold is intact	
10	Agar 8%	3 m	Warm	It only removes the dirt; gold is intact	
11	Agar 8% EDTA 0,5%	1 m	Cold	It does not clean the dirt thoroughly, but it does not remove the gold	

12	Agar 8% EDTA 0,5%	3 m	Cold	It removes the gold	
13	Agar 8% pH 5	1 min	Cold	It removes everything, gold, and bole	
14	Agar 10%	1m	Cold	It is too thick. It does not remove anything.	
15	Agar 10%	3m	Cold	It is too thick. It does not remove anything.	
16	Agar10%	1m	Warm	It is too thick. It does not remove anything.	
17	Agar 10%	3m	Warm	It is too thick. It does not remove anything.	
18	Agar 10% EDTA 0,5	1m	Cold	Perfect, the gold is clean and untouched	
19	Agar 10% EDTA 0,5	3m	Cold	It seems that 3 mins are better than one and is gentler with the surface	
20	Agar 10% EDTA 0,1	1m	Warm	The liquid Agar removes the gold	

21	Agar 10% pH 5	1m	Cold	Removes the gold	
22	xPVAcBorax Angelova	1m		The gel is not perfectly done. Although the recipe was tried multiple times, it did not work.	
23	xPVAcBorax Angelova	3m		Although the gel was not perfectly made, it worked with 3 mins application	
24	xPVAcBorax 4%	1m		It cleans the surface without removing the gold, is better to use when just made	
25	xPVAcBorax 4%	3m		It cleans the surface without removing the gold, and the surface is spotless	
26	xPVAcBorax 4% TAC 0,5	1m		Wrong, it removes the gold	
27	xPVAcBorax 4% TAC 0,5%	3m		Wrong, it removes the gold	

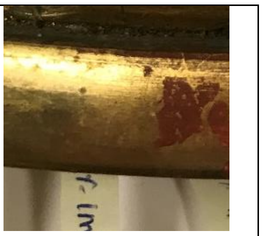
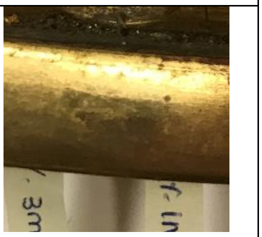
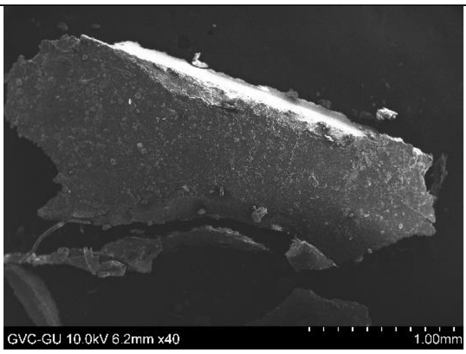
28	xPVAcBorax 6%	1m		It works, but there is still some dirt	
29	xPVAcBorax 6%	3m		With more time of application, the gel can capture all the superficial dirt and completely clean the surface	
30	xPVAcBorax 6% TAC 0,5%	1m		Wrong, it removes the gold	

Table 6 Ocular results

4.2 SEM

The following images show the SE (Scattered electrons) captured by the SEM. The samples were taken in 4 targeted places to show the effect of the gels overall. Considering the fact that the same gel in different forms will leave the same amount of residue.

BE IMAGES			
N°	Test	Comments	Image
1	Sample before cleaning	The piece is wholly soiled with dirt	

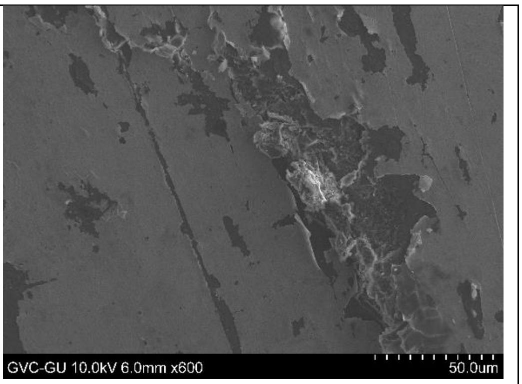
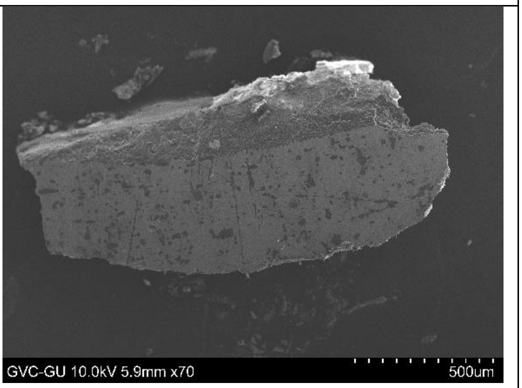
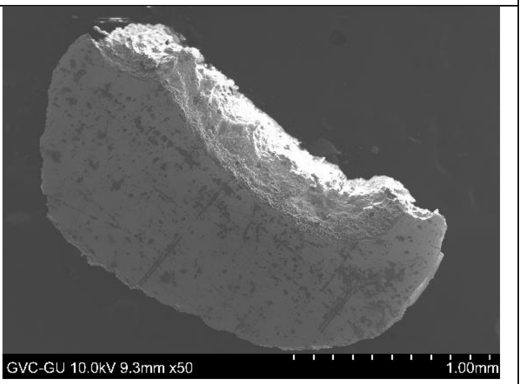
2	Agar	It seems to have some residue	
3	Borax Angelova Recipe	There is no residue	
4	xPVAcBorax	There is no residue	

Table 7 SEM results

4.3 Gloss-meter

The tests with the gloss meter gave ERROR since the curved surface was not enough area for the device to be stable and completely sealed without allowing light to enter through any hole.

Starting to perform three tests on each sample gave utterly different results without any kind of coherence. Therefore, this method was finally discarded as unreliable. However, the possibility that the samples will be made on a larger surface in a future investigation is not discarded.

5. Discussion of the results

This discussion consists of two parts, one discussing the Agar gel and the results obtained, and the other discussing the xPVAc Borax results.

5.1 The case of AGAR

In the case of the Agar, it has been seen that the most critical parameter is the concentration. When having a low concentration, the diffusion of the water into the underlayer is higher, and therefore the gold is easily removed. This parameter also depends on the time of application. For example, an application of Agar at 4% for 1 minute will give a similar result as the application of Agar 8% for 6 minutes, although this parameter will need further testing.

The other parameters tested work according to the theory explained in chapter 2. Furthermore, applying the chelating agents to the Agar gel does not affect the gel in any way, nor does it deprive it of any of its main properties.

Finally, it is important to comment that the use Agar leaves a small amount of residue on the surface, which is only seen with the scanning electron microscope. It would be recommendable to rinse after removing the gel, although the amount is so minimum that aging would be needed to find out how it can affect the object.

Depending on the surface dirt that the object presents, for example, if it is very incrusted to the surface, the use of Agar would not be sufficient for its removal, since when applying it in a rigid and cold form, the function that performs the gel is to soften the layer of dirt but not to trap it. For removing these residues, it would be necessary to use warm Agar since, in a first phase, the Agar would soften the superficial dirt, and in the second phase of cooling, this dirt would be trapped in the structure of the Agar.

The advantage of Agar is the ease with which it is formed. It does not require much preparation time and can be mixed with almost any additive, even with some organic compounds. The disadvantage of this method is that it requires many tests to obtain the perfect solution for cleaning the water gilding. In addition, as previously mentioned, the hot application is usually more efficient. However, it can cause a greater diffusion of the water to the substrate, taking the gold.

4.2 The case of xPVAc Borax

In the case of Borax, the same thing happens as with Agar; the concentration affects the diffusion of the water; therefore, the diffusion will be higher the lower the percentage of PVA and the shorter the application time. In addition, when the percentage of PVA is higher, around 8 or 10%, it becomes very rigid and loses its elasticity. Therefore, it loses one of its most essential characteristics: being able to adapt to the shape of the support.

Although the proportion of TAC added to the xPVAc Borax is minimal, its effect on the surface increases exponentially since the gold was removed with the gel in both cases. This is probably due to the ionization of the surface dirt and the gold upon contact with TAC gel. They begin to interact, causing the gold to be washed away once the gel is removed.

The main advantage of using xPVAcBorax is that it does not leave residues, so there is no need to rinse after removing the gel, even after using chelating agents, as can be seen in the images taken with SEM. In addition, due to the Borax salt in its composition makes the surface dirt adhere to the gel and eradicate it, always depending on the surface and the type of xPVAc Borax composition used. In addition, due to the nature of the gel, it could be used as an eraser, which will allow the dragging of the surface dirt and its removal.

Despite the excellent functionality of this gel, there are two significant disadvantages. The first one is the difficulty of preparation, as the measurements have to be adjusted to the second decimal place for it to work. Even then, any change in the environment, such as relative humidity or changing temperature, can cause the gel not to form. The second disadvantage is that the number of variants that it allows is relatively scarce, not being able to manipulate the application temperature and only adding a limited number of modifiers, among other things that are not studied in this research.

5 Conclusions

Regarding the aim of the research and answering the research questions, it has been seen that the diffusion of water in the gels affects the water-sensitive surface. When the diffusion is too high, the gold is removed, but with the perfect concentration, the gold is not affected. As said in the chapter above to lower the time and the concentration of the gel can have a great effect on the removal of the water gilding. The time and method of application, as well as the agents, added such as the pH variables or the chelating agents affect as well helping by speeding the process of the reaction surface-gel.

Overall, it has been proven that hydrogels containing water are an excellent alternative to organic solvents. It can be used although the surface is water sensible. They help in the cleaning process without removing the gold, they are also more sustainable than the use of organic solvents, and more beneficial for the health of the conservator.

It is essential to emphasize that the importance of this research lies in testing whether hydrogels can be used for cleaning water-gilded surfaces, and it has been proven that they can in a pure research environment. This research cannot be taken as a universal guideline for cleaning water gilded surfaces, as each object is unique and will require different percentages depending on the type of support and soiling which varies from place to place, so testing should be done before carrying out a full cleaning.

6. Further studies.

This master's thesis aims to expand the knowledge on the cleaning of gilded frames, as it is a subject that has been slightly touched upon in previous studies. For this reason, this work opens countless possibilities for future studies such as the following ones:

- The study of different alternatives for the cleaning of gilded frames.
- The use of different modifiers in the gel recipe.
- The study of cleaning on gilding on more controlled surfaces such as mock-ups.

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APPENDIX 1

The results are the following:

Nº	Place	Results	Discussion
1	Upper decoration burnished	Fe – 5,9% Ca – 5,9% Au - 3,07 % Cu – 0, 17%	The calcium shows that there is a preparation layer. The iron comes from the bole There is also gold, with a copper alloy. The percentages are low since the sample showed silicate and potassium, but the percentage of error was also high.
2	Upper decoration unburnished	Ca – 75,13 % Cu -10,83 % Fe – 2,3 %	There is no gold or bole in the unburnished gilded surfaces; it is gilded with copper.
3	Upper decoration unburnished	Ca- 86,86 % Cu – 10,35 %	There is no gold or bole in the unburnished gilded surfaces; it is gilded with copper
4	Outside oval burnished	Ca- 33,42 % Fe – 26,87 % Au – 13, 22 %	There is gold in the burnished places, although in this sample, there was no alloy, or it may be such a small quantity that it did not show in the results
5	Decoration oval in the middle unburnished	Ca- 83,02 % Cu – 7,91 %	There is no gold or bole in the unburnished gilded surfaces, and it is gilded with copper

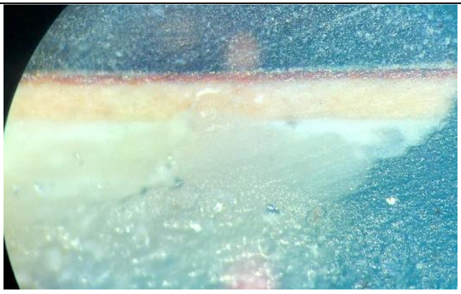
6	Big oval unburnished	Ca – 93,06% Cu -4,93 %	There is no gold or bole in the unburnished gilded surfaces, and it is gilded with copper
7	Inner oval decoration unburnished	Ca – 89,55 % Cu - $,6 %	There is no gold or bole in the unburnished gilded surfaces, and it is gilded with copper

FTIR was carried out, the samples were only taken from those parts that were already damage, not to create a new lagoon, this research helps to find the binding media, and the results are the following:

N°	Place	Characteristical peaks	Discussion
1	Burnished oval	1° -1424, 876, 712 2°- 1653,1533,1448,1333,1237	The first peaks are from calcium carbonate, while the second peaks come from a proteinaceous binder; it is challenging to know which since most of the show peaks in the same range
2	Inner unburnished oval	1° -1424, 876, 712 2°- 1653,1533,1448,1333,1237	The first peaks are from calcium carbonate, while the second peaks come from a proteinaceous binder. It is not easy to know which since most of the show peaks in the same range

Both samples showed the same results, although they were taken in different parts, meaning they have the same binding media.

CROSS SECTIONS were done to know the exact composition of layering of the frame. These are the results

N°	Place	Cross section	Discussion
1	Side of the frame		There is a thick layer of preparation layer, and the copper is "thick" when compared to a golden leaf
2	Burnished oval	N/A	-
3	Inner frame unburnished	N/A	-
4	Upper decoration burnished		There are two layers of preparation layer, the first which seems to have thicker granulated, and the second which is thinner and colored in light red. There is a layer of bole, and finally, a skinny layer of gold.