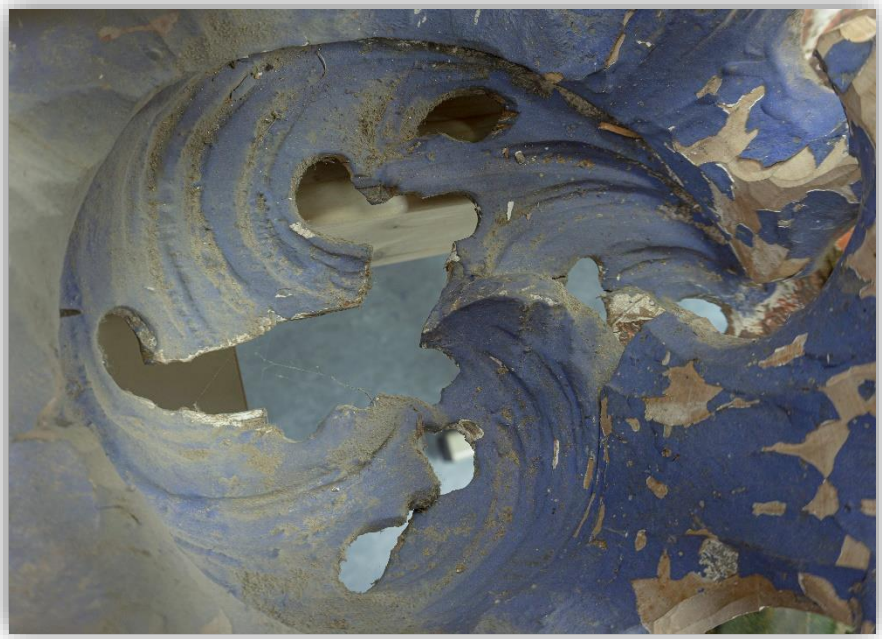
UNIVERSITY OF GOTHENBURG

DEPARTAMENT OF CONSERVATION

Cleaning Research for 18th century Unvarnished Water-sensitive Matte Tempera Paint



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ABSTRACT

This master thesis studies various cleaning techniques used to conserve the unvarnished matte tempera painted surfaces of the Per Stålhammar funeral coat of arms for the Kalmar Läns museum (KLM 014946). The polychrome sculpture is dated from 1701 and has never been conserved before. This led to a critical condition, and the object required careful and immediate preservation. During the conservation process, the areas painted with blue pigment smalt were noticed to be more fragile and sensitive to cleaning strategies applied to other areas of the polychrome sculpture.

Subsequently, the research identified the paint, ground layer, and surface material composition of this problematic area. After identifying the materials components, the artificial mockups were created to use as a surface to test cleaning methods. The selection of cleaning materials was derived from the previous research, proposing dry-cleaning methods and hydrogels, which proved suitable for water-sensitive paints.

The examination of cleaning methods was tested with Microscopes, Scanning Electron Microscopy (SEM), and an Artificial aging chamber. The overall goal was two-fold. First, contribute to the knowledge gap in the cleaning research performed on unvarnished matte tempera polychrome sculptures. And second, to find a method that will not affect the original surface and perform a safe and efficient cleaning without creating watermarks, have a pigment pick–up issue, or leave residues on the substrate.

The investigation showed that the dry-cleaning method and use of hydrogels could work together and target different tasks. Among the dry-cleaning materials, the best result was performed by Yellow fibecloth and Evolon-CR©. The novel hydrogels by Nanorestore Gel ®, the type HWR, and MWR were selected as safe materials when examining the wet cleaning methods. Those hydrogels suggest a controlled removal with a low – risk for the painting surface. This research will alleviate the future conservation decision–making process on art objects with similar matte tempera paint surface conditions.

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1. Background

In the 16th -18th centuries, it was a tradition among the wealthy, noble, and military officers to commission funeral coats of arms for burial ceremonies. These coats of arms were polychrome sculptures and were made with significant wood carving techniques by a craftsman. The funeral coats of arms were richly painted with matte tempera colors and often with silver details or gilding elements to enhance the glory of that time. Chronologically, this tradition coincides with the period in Sweden called "Stormakstiden." Nowadays, the majority of the coat of arms is stored in churches and museums. However, many of them have not been conserved or have been restored by overpainting original paint layers (Säwström, 2012).

Figure 1 The Funeral Coat of Arms for Per Stålhammar Photo credit Rosberg, Pierre/Kalmar läns museum

The funeral coat of arms for this study was made for Per Stålhammar (1613-1701). He was a heroic military officer who participated in many wars against Poland, Denmark, and Prussia during his life. In 1650 Per Stålhammar was ennobled by Queen Kristina in Stockholm Castle. His life journey was ceased in 1701 in Hultsvik, and then he was buried in Eksjö (Lars-Olof, 2007). The coat of arms for his procession was placed in Korsberga church and later moved to Salshult church (Museum, 2020). The former owners of the object were Carl Adam Stålhammar and Emi Stålhammer. The Kalmar Läns museum received the object in 1935 from Carl Adam Stålhammar. (Museum, 2020).

Nowadays, the object is hanging in the Kalmar Castle, among other similar banners. During its exhibition, the dazzling appearance was covered with accumulated dust and dirt concealing its grandeur. Therefore, it was deemed crucial to explore safe cleaning and conservation treatments. For safe implementation because matte tempera colors in their composition are hydrophilic.

The principal purpose of this research is that those studies will contribute to future conservation work on the funeral coats of arms exhibited in Kalmar Castle.

1.2 Objectives and Aim

The aim for this thesis is to determinate the cleaning material which can be safe to apply on the hydrophilic matte tempera paint. It was specified upon examination that the unvarnished matte tempera paint layers on funeral coat of arms (KLM 014946) required special attention, particularly theareas with blue paint color. The impediment in the blue areas was that the pigment was easily water- soluble. During the conservation treatments, cleaning the hydrophilic smalt matte tempera paint brought forth unprecedented challenges that required new research to successfully conserve the funeralcoat of arms without affecting its original properties. This situation encouraged me to investigate methods that might be appropriate for this case. Thus, in conservation, the cleaning treatment of the matte tempera paints on polychrome sculptures lacks research data (Eastaugh et al., 2013)(Bianchin et al., 2009)(Olstad & Ørnhøi, 2017) (Solberg, 2001). Research narrowed its focus on reviewing andanalyzing cleaning methods and materials. After searching through many types of scientific research dedicated to finding the most appropriate safe treatments for water-sensitive surfaces, it was possible to make a selection between various methods and test them on our replicated mockup substrates.

1.3 Research Question

- What is an applicable method to use for conservation cleaning treatment on polychrome sculpture, and why?
- Do dry cleaning methods alone produce an adequate result?
- Can hydrogels perform a safe cleaning on matte tempera paint?

1.4 Case

The funeral coat of arms was made for the funeral ceremony Per Stålhammar in 1701 and arrived at the University of Gothenburg Conservation Department in critical condition. As a first step, the data analysis was carried out to specify materials and the mediums of the Huvudbaner, a conservation plan

for the treatment of the banner was devised.

Distemper paint was a common medium in 17th-century Scandinavian funeral banners (i.e., Huvudbaner). The ground layer binder for the banners was usually a proteinaceous amalgamation of glues and chalk. The wooden substrate developed a fungal activity that migrated to the proteins in the ground and led to the paint film's flaking. This dry rot significantly impacts the banner's achievability. Despite the banner's fragility, an extensive collection of funeral banners from the Swedish imperial time are preserved by the Kalmar Läns museum and exhibited in the Kalmar Castle (Museum, 2020).

The unvarnished distemper painted surface is soft and opaque. Through the centuries, the painted surface has accumulated dust. The first stage of the conservation plan was the dry cleaning of the painted surface to remove dust, spiderwebs, and dirt. The second step involved aqueous cleaning of the painted surface with saliva and deionized water. During the second step, the aqueous cleaning was ineffective on the blue painted areas. At that time, it was unknown what pigment was used for the blue areas.

As a first step, the original object state and components were described after investigative analysis techniques to eliminate the possible problem during the cleaning. Among them were visual examinations, microscopy, photo-analytical techniques with ultraviolet light (UV) and infrared (IR). For more advanced analysis, the other techniques used, such as X-Ray fluorescence (XRF), Fourier – transform infrared spectroscopy (FTIR), and cross-sections, were used to determine the material composition and degradation phenomena. The result indicated that the blue pigment was blue smalt with glair as a binding component. In comparison, the binding media of the ground layer had the rabbit skin component.

After the material components were identified, the next stage was focused on cleaning method evaluations. The treatment strategy for these problematic areas was contrived through empirical research into dry and wet cleaning techniques. The dry-cleaning methods applied for the light surface cleaning were the Evolon-CR©, Akapad sponge, Make-up triangle sponge, and yellow microfiber cloth.

Special attention was paid to the hydrogel cleaning systems. This material was considered as a successful strategy for performing highly effective and non-destructive for the water-sensitive paint layer during cleaning action. The hydrogels were selected from various research studies reviews and prepared by following the Dr. Stefani Kavda recipes formulas. Her studies into the aqueous gels

contributed to creating a cleaning strategy for the transparent and highly polished poly(methyl methacrylate) (PMMA) surfaces on art objects (Kavda, 2020).

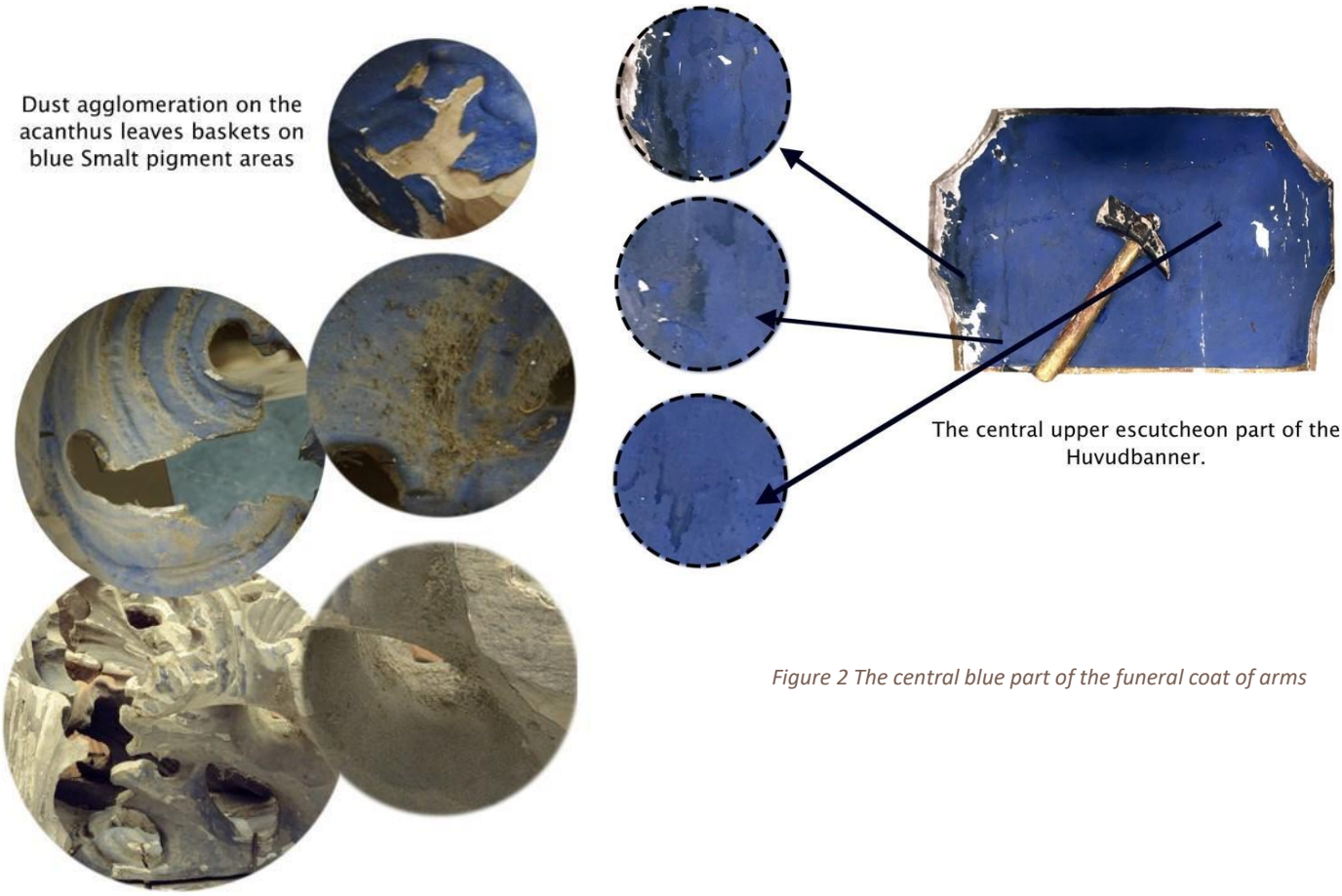


Figure 2 The central blue part of the funeral coat of arms

Figure 3 The fragment of acanthus leaves with dust layer

1.5 Methodology

The investigation on this single-based research is only build up from one particular funeral coat of arms. However, it can help other similar objects when conducting conservation treatments and support the conservation decision-making process (Reedy T. J., 1992).

The study in the first stages was focused on object-based conservation research where the composition of the funeral coat of arms had a fundamental base for the analytical approach. A deductive method

was used to map original materials and the object's technical structure. By following this method, it was performed several technical analyses, because each method has its limitations. Therefore, several examinations are suggested to gain a sufficient and clear understanding of the appearance (Taylor, 1989).

The overall condition of the funeral coat of arms was suffering from a major flaking issue. For the safe performance during technical analyses, the samples were taken from the separated parts, which fell during the transportation. Thus, it eased the problem with collecting material samples for conducting analyses. Because usually, this can meet up with ethical implications since not all types of analyses can be noninvasive in their performance ability (Caple, 2012). During the investigation of the original material components also a comparative approach was obtained.

The thesis presents both secondary and primary data, but it was mainly directly observed and measured by the author when analyzing cleaning materials and treatments. The secondary data was collected through publications, case studies, and scientific reports written about water-sensitive paint surfaces and the cleaning options. This material is presened in Chapter 2 *Literature Review*. However, the secondary sources are less reliable because the research studies were not dealing with fragile material like unvarnished matte tempera (Walliman, 2010).

The last part of the examination was following empirical research methods to identify cleaning agent properties and their interaction with the paint surface. First was Microscopy imaging for the evaluation of visual changes. Artificial aging was used to see if the color properties will be affected by hydrogel applications in the future. The SEM analyses were made for studying the residue components which might be left from the cleaning materials. The Colorimeter and Spectrophotometer by Konica Minolta were used for calculating color measurements to detect specific hue change if possible. The methods and results are further explained in the Chapter 4 *Experimental* and *Results.*

1.6 Theory

This chapter presents background knowledge about theory in ethics and cleaning system selection, with principles on how to proceed with cleaning ethics when the object in this research has cultural and historical value. Furthermore, ideas were followed to create a cleaning material selection to examine unvarnished matte tempera paint.

1.6.1 Ethical Theory

When it comes to pursuing suitable cleaning material in art conservation, the conservators face many difficulties. Cleaning has always brought many challenging moments because it can potentially damage the art objects or the conservator's health. The ethical concerns have always been a pendulum to determine the intensity level of the cleaning procedure. Nowadays, the principal aim of the ethical idea is to do less intervention to the original object. Therefore, the well-known patina effect is valued, and the cleaning agents are often transformed into gel form(van Saaze, 2021) (Lora V. Angelova, 2017).

Cleaning controversies have been an extensive discussion for several decades. There were always two options on hand to decide from a complete cleaning or partial and selective cleaning. This stage is the most seen and observed by the public. People value conservators' work, which brought many disagreements and discussions with conceptual and philosophical thoughts(García, 2015).

Conservation aims to rely more on preventive conservation and intervene with remedial actions as little as possible. The cleaning procedure in conservation, together with the re-lining concept, goes under big ethical debates. Whether the conservator should consult intervein into the object with his practical skills or not, and where appropriate conservation treatment borders are. In the 1970s art conservation world witnessed many new materials that were intended to be less harmful than those used before(Stoner & Forbes, 2020). The application of various emerging conservation treatments brought new possibilities into the ethical norms. It has been analyzed that even the senior conservators noticed that their treatments became less interventive compared to the past due to those novel changes(Ashley-Smith, 2018).

Our funeral coat of arms was not conserved previously. The poor conditions in the church where it hung during its lifetime caused damaging effects to its appearance. To introduce a minimal intervention in this particular case would show indifference to the object by leaving it in a damaged and unstable state(Ashley-Smith, 2018). The lack of care towards the object is also considered unethical. It causes the present and future generations a distorted understanding of the glorious moments in history.

The cleaning treatment had to be done before consolidating. The reason for this was a tremendous amount of dust and grime all over the surface, which prohibited and challenged the following

consolidation procedure (Fig. 2-3). The term "patina" in this object plays an important role. The majority of the other funeral coat of arms have been overpainted during the past conservation treatments (Säwström, 2012). Usually with oil paint or distemper. This action was probably caused by the fragile paint technique, which had a challenging time surviving throughout centuries. Our task was to keep this painting technique and maintain the old look called "patina of age" with its paint losses, oxidized silver, and impurities (Brandi, 2005). Therefore, a selective cleaning method was used to bring out the colors chromatic intensity with the light dry cleaning methods (Press, 2002). As a result, we managed safely to remove the veil of dust from the object. Further cleaning action, particularly on blue pigment with ingrained dirt, was decided against.

Almost all cleaning methods with their intervention possibilities can include the risk of damaging the original paint layer. This can cause some unwanted changes to the painting's aesthetic appearance for a long time and not reversible actions. Having knowledge and understanding of the cleaning material actions on the blue pigment can be essential. Therefore, following the European Confederation of Conservator-Restorers' Organization's (E.C.C.O.) ideas was imperative to make research safe and emphasize it as non-invasive. The E.C.C.O. states that *"following moral and ethical obligations, the conservator should strive to use only products, materials, and procedures, which will not harm the cultural heritage according to the current level of knowledge"*-(E.C.C.O. Organisation, 2003). This ethical norm built this research mainly with mockups and without intervention with the original object.

1.6.2 Cleaning System Selection

The Figure below represents the cleaning options that were selected for this thesis research. The process of selection was designed by studying the articles which dealt with water-sensitive paint materials. Each of the materials has its disadvantages and advantages, out from which it will be easier to determine the possible applicable cleaning strategy system.

Because, the dry-cleaning methods are known for havingissues when removing ingrained dirt. While wet cleaning in the form of hydrogels has better capabilitiesto remove the dust, it causes obliteration of tiny pigment particles, creates watermarks, or leaves residues.

The requirements to select the suitable method out from the presented range of materials:

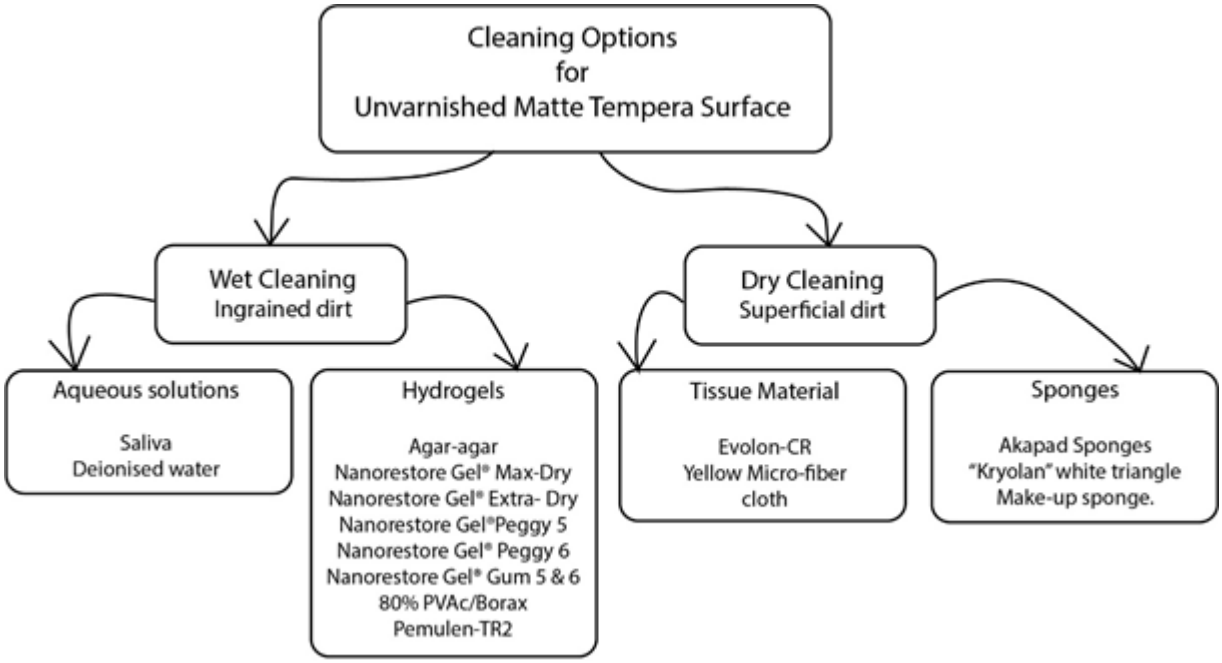


Figure 4 The Cleaning material selection table

- To avoid any kind of undue risks on the painting film surface. Those can be in the form of swelling, pigment pick-up, watermarks, gloss change, or residues.
- The ability to minimize the mechanical actions.
- The ease of use for achieving an efficient cleaning action.

The first conservation step was focused on dealing with the superficial dirt layer. It was decided to use the Vacuum cleaner with a HEPA filter and a soft brush. However, after the consolidation treatment was done, the unvarnished painting surface still required proper cleaning. It was decided to test the dry-cleaning materials and choose either sponges or tissues for this stage.

The Akapad sponge was chosen as comparative material for dry-cleaning methods evaluation. It considers being more suitable for less sensitive and more stable paint layers. In our case, this method might have some issues because the sponge has a texture that might pick- up the small amount of pigment or leave a residue.

The gels were selected to explore whether the removal of ingrained dirt can be safely achieved or not. The gel formulation was convenient to examine because it can reduce pigment pick-up, watermarks, and swelling, resulting in aqueous methods.

Nanorestore® gels are a novel material, and the Extra Dry (HWR) and Max dry (MWR) version is a chemical hydrogel specially designed for water-sensitive materials. However, the Peggy 5 and 6 version are physical hydrogels and have less liquid retention than Nanorestore® chemical hydrogels, and it was important to experiment with both types. The polysaccharide gel agar-agar is chosen because it is widely used in paper conservation and various water-sensitive materials. The 80%PVa/Borax gel has an easy ”peel off” action, which is considered appropriate on our surface. Pemulen TR- 2 was used for the comparative material because it requires mechanical action and additional clearance steps of the residues.

1.9 Results expected.

To perform a cleaning treatment with no or minimal damage for the blue pigment. The various types of analysis will indicate the pigment characteristics and the adequate cleaning treatment through various mockup samples. The hypothesis is that Nanorestore gel® HWR with its dry characteristics and 80% PVAc Borax as a vinylic gel might potentially perform an adequate result. As the desired outcome, we will achieve a vibrant and clean surface of the blue-colored area on the funeral coat of arms.

1.10 Words and Definitions

Tempera is a painting technique, and the term *tempera* derives from the Late Latin *distemperare* or verb *temper*, which means “*to mix thoroughly to desired consistency”* (Britannica, 2015).

The word tempera is usually used in modern literature to refer to painting techniques that use emulsions, either artificial or natural. The most common binding agent and most stable in tempera is egg yolk or casein base, which can withstand substantial oil additions without showing signs of degradation. This medium technique is easily diluted with water during usage, but after drying, becomes insoluble (Mayer, 1991). For this reason, the technique is different from oil and requires proficient knowledge with a thorough application process.

The binding media component in tempera is a natural egg emulsion consisting of water, albumin, lectin, and vitelline acting as an emulsifier so effectively that a considerable quantity of oil can be added to the yolk without breaking down the emulsion properties when diluted with water (B. Slansky, 1953). The oils in egg and animal make the medium dries slowly and work as a buffer, reducing protein hardening tension. This action becomes conducive against cracking in the future (Lindberg, 1991). Because of this great strength, egg yolk emulsions belong to the most widely applied tempera methods. It has a very luminous and smooth appearance with stable properties and can include gelatinous and even colloidal materials aside from the albuminous. When the binding medium of tempera is changing, it requires other terms, "glue tempera," "egg tempera," or "gum tempera" (Gettens R. J., 1966). Also, appearance might defer, from satin gloss to matte finish. It all depends on the part of the egg component used. For the more satin and glossier surface, it is recommended to use the egg yolk. For a more matte finish, the egg yolk mixture with egg white (Townsend, 2008).

Tempera had been developed through centuries. This fact made tempera one of the ancient painting techniques, and it traces back to early Egyptian time, where it was used on sarcophagus made for the pharaohs (Schadler, 2017). The technical peak of egg tempera in easel paintings was reached in Italy's Renaissance time (Schadler, 2017). The use of this technique is well described by Cennino d'Andrea Cennini, who lived and studied in Florence under Agnolo Gaddi. He wrote a book called the *Libro dell'Arte*, known as "The Craftsman's Handbook," and is still appreciated by many artists in our days (Daniel V. Thompson, 1936).

The egg tempera has gained much improvement in the recipe through the centuries. The main ingredient is egg yolk combined with a small amount of water and a pinch of acetic acid as a preservation agent against mold (Daniel V. Thompson, 1936). The detailed technology of preparing tempera is described in the book *The Practice of Tempera painting*, written by Thompson.

Glair, after conducting FTIR- examination on the samples from the funeral coat of arms object on the blue smalt pigment. It showed that the tempera's media component was egg white, which also has another name, "glair." The painting technique with the egg white is called matte paint or distemper. The traditional use of glair was mainly applied in early times as a medium for book illuminations, gilding, or bole layer. It is a water emulsion, and it is known to be a stable substance that does not darken or yellow on paintings over time (B. Slansky, 1953).

Nevertheless, it has some disadvantages, and it can be experienced during the application due to a lack of flexibility while brushing (Mayer, 1991). The other drawback is that albumen's pure solution is well-

known to have a weak film with low binding qualities (Mayer, 1991). This characteristic can lead to cracks on the painting layer as it ages.

Distemper term**,** according to the book of Painting Materials, written by J. Gettens and L. Scout, is derived from England, and it specifies a painting medium with a glue-sized or casein binder (Gettens R. J., 1966). The disadvantage of this method is that it limits the artist from achieving a thin or loose application(Ghezzi et al., 2015). Usually, this term is applied to wall painting, scenography, showcard, or poster colors (Mayer, 1991).

In the 17th and 18th century distemper was used in Scandinavian countries as decorative painting material in churches. In most of the articles where the term distemper is mentioned, they note that the binder is glue-based, and it commonly has a water-soluble surface with brilliant colors (Olstad & Ørnhøi, 2017). But, it never was a popular method because it quite demanding, and just a few examples have survived(Ghezzi et al., 2015).

Matte Tempera's term was used to describe painting techniques in this master thesis. Because the proteinaceous composition of egg white as a binder makes the paint water-soluble and gives a matte finish to our Coat of Arms, both distemper and tempera terms can refer to our painting material technique and its composition. To conclude, a precise formulation of the painting layer used on the funeral coat of arms was decided to unite to Matte Tempera term.

Huvudbaners/Begravingsvapen translated to English from Swedish as a *Funeral Coats of Arms* (Engström, 1989). The funeral coat of arms was widely used in the past as part of the Honorable authorities' funeral procession. The Huvudbanners, as a content form, had the original shield of deceased ancestors (Wallin, 1948). After the funeral procession, the Huvudbaners were displayed in the churches connected to the deceased.

2. Literature Review

The literature review focuses on cleaning materials examined in various research to be suitable for hydrophilic paint surfaces. When involving case studies on polychrome sculpture cleaning treatments, there were no adjustable strategies for our work. The cleaning treatments on polychrome sculptures were focused on oil-painted surfaces, where solvents and microemulsions removed varnish layers or a thick layer of grime. Those methods are considered to be aggressive for our painting layer.

Our paint layer consisted of easily water-soluble pigment and binding material, which required investigation on a more narrowed field among cleaning options in conservation. The methods were adjusted from cleaning case studies developed for paper, acrylic paints, and wall paintings. Research written by (Owen et al., 2004) wrote an article based on *"The effect of water exposure on surface characteristics of acrylic emulsions paints."* Water sensitivity was discovered in modern artist oil paintings from the 1950s and 1960s. To identify what kind of damage the water might cause for the hydrophilic surface was described by (Tempest et al., 2010) in the article *"Sensitivity of Oil paint surfaces to Aqueous and Other Solvents"* and in the article by (Mills & Burnstock, 2008) named *"Water sensitive of modern artist oil paint."* The inference of those works excluded in our direct research contact with water on painted smalt blue areas. Thus, the deionized water and saliva were used as comparative material.

In 2017 the International Academic Projects (IAP) and the Tate research group organized the conservation conference where the theme was *Gels in the Conservation of Art.* Shortly after, the book was edited by Lora V. Angelova, Bronwyn Ormsby, Joyce H. Townsend, and Richard Wolbers. It contained many submissions presented by various conservation scientists, students, and conservators, with a primary purpose to present novel disciplines and ideas into the cleaning treatment of art objects.

The most common cleaning mixtures in conservation are solvents, but these turn out to be an environmental hazard. They evaporate quickly, making them inefficient when comparing their work abilities with gel applications (Lora V. Angelova, 2017). To maintain an environmental cleaning by using solvents for removing varnishes and grime are described in the book *"Solvent Gels for the Cleaning of Works of Art, The Residue Question*" written by Stulik, D., Miller, D., Khanjian, H., Carlson, J., Khandekar, N., Wolbers, R., & Petersen, W. C. The content of this book provides gel and solvent recipes with their structure and cleaning efficiency information. When gels are loaded with solvents,

they ensure the conservator with more efficient interaction, less pollution, an ergonomic way of work, and better control of the cleaning procedure's application (Lora V. Agelova, 2017).

In the book "*Gels in the Conservation of Art,"* the researchers studied the gel's thermo- reversibility, residues, and water retention. This knowledge played a significant role in our selection among various materials used on water-sensitive materials and mediums. The first section in the book about *"Polysaccharide gels: Agar-agar, Gellan- gum, xanthan, and methyl celluloses."* Together with the fourth about "*Novel methods,"* facilitated with the recipes and methods relevant to our case.

This aqueous approach was developed 30 years ago and is suitable for polychromeartifacts(Cremonesi, 2012). To avoid using water in its liquid-free form, it becomes viscous by addinga gelling agent and providing a more controlled application. Water is a physical solvent and tends in itspure form to create damages and undesirable effects on painting films (Cremonesi, 2012). The article *"Rigid Gels and Enzyme Cleaning*" refers to the gel types like Klucel, Xanthan Gum, Carbopol, andPemulen TR-2. Those gels prevent water release, but the most significant disadvantage is that theyrequire a rinse from the gelling residues(Cremonesi, 2012). Moreover, they tested the most commonly used gel agar-gar, and their analytical examination proved that this one does not transfer residues onto the porous paint surface(Cremonesi, 2012).

2.1 Researches on Agar-agar hydrogel

One of the most heard and used rigid gels is agar-agar. The Italian Conservator scientist Chelazzi described a lot in his studies the agar-agar gel, its advantages, and properties in articles "*Rigid Gels and Enzyme Cleaning" and in "Surface Cleaning? Yes, freshly grated agar gel, please."* Two other researchers A. Cassoli and P. Cremonesi proved that agar-agar could be suitable and safe when working on high sensitive surfaces when removing dust. The research was called *"Thermo- reversible rigid agar hydrogels: their properties and action in cleaning"* and published in 2017.

A more recent study about agar-agar gel was written by a conservation researchers team (Kanth et al., 2018) and by (Sansonetti et al., 2020). The article *"Optimizing the Rigidity of Gellan and Agar gels for Cleaning Sensitive Acrylic Emulsion Painted Surfaces"* proved that gels like agar-agar and Gellan gum are heaving a low chance of leaving any residues after gel application. Together with other examinations, it was noted that agar-agar could release water to the substrate. Therefore, it is recommended to have

control on time and avoid contact to a minimum on water-sensitive surfaces. The gellan-gum gel had better retention properties and was superior to agar-agar.

For obtaining a better cleaning performance, another research recommended adding functional chemicals such as Ethylenediaminetetraacetic acid (EDTA) and triammonium citrate (TAC) or other specific amino acids (Sansonetti et al., 2020). Also, it is possible to add to the agar-agar gel composition solvents. The author Cindy Lee Scott in 2012, wrote an article *"The use of agar as a solvent gel in objects conservations."*

However, the gels are considered safe if the conservator is aware and decreases the time on the object surface while cleaning a hydrophilic paint layer. Because it is not that just swallowing or light moisture on the surface might appear, the risk can be flattening and smoothing out the porous surface of the paint. This fact was noted in the research by a group of science conservators (Diamond et al., 2019) in the article *" The role of agar gel in treating water stains on acrylic paintings: A case study of Composition, 1963 by Justin Knowles."* By making AFM 3D images of surface roughness of the substrate, the research documented that after using 5% (w/v) agar-agar gel, the surface got more swelled and flattened more under the weight of gel, compared to the lower percentage of agar-agar gel 2.5%(w/v)(Diamond et al., 2019). When comparing agar-agar gel with other cleaning agents, we stumbled across the article by (Warda et al., 2007) written in 2007. The agarose gels were on paper conservation cleaning together with Laponite and Carbopol. It was noted that Agar is more prone to leave some moisture to the surface, and blotting the excess of moisture before applying the gel onto the surface is recommended even when the percentage of gel is higher than <1%(w/w). Nevertheless, it considers as a more safe treatment to apply because the disadvantage of Carbopol and Laponite is that they created discoloration of the color after aging(Warda et al., 2007).

2.2 Research about PVAc/Borax hydrogel

Innovative methods started to be developed with the Italian collaborative team of science conservators with a chemistry team to create gels suitable for sensitive surfaces. The important research was performed by (Carretti et al., 2010), where novel methods like rheoreversible gels, magnetic, and "peelable" gels were presented. The advantage of those gels that they are easily getting removed from painting layers. Their first article, *"New Frontier in Materials Science for Art Conservation: Responsive Gels and*

Beyond," had a detailed description of gel performances. However, the residue question had to be researched. The consequences of using those types of gel in the long term were unknown. Also, the examination was performed on objects which required a more advanced cleaning focused on varnish removal. In this article, a composition of hydrogel with poly(vinyl alcohol) together with borax formulation (PVA-B) was presented like a good "peelable " gel that was suitable for the hydrophilic surface. The science Dr. L. Angelova was dedicating her researches to this particular gel. Various publications came out about the Poly(vinyl alcohol) gel crosslinked with Borax. In 2013 a dissertation was written by her about *"Gels from Borate-crosslinked Partially hydrolyzed Poly(vinyl- Acetate): Characterization of Physical and Chemical Properties and Application in Art Conservation."* Her research work concluded that xPVAc-Borax gel is easy to prepare and create formulations precisely suitable for the specific surface.

Furthermore, Dr. L. Angelova proved a lack of polymeric residues left from the gel during application. This dissertation paper also advised being careful when working on a porous surface. A protective tissue might be used as a protective barrier.

An easily " peeling off" formula of xPVA- Borax gel was described in a research paper by (Natali et al., 2011). The hydrogel composition, which was easily removed with tweezers, was 3wt% 80 PVAc/0.75 wt% borax in water. This particular hydrogel can also be combined with solvents if the case is based on dealing with hydrophobic surfaces where oxidized varnishes of oil paintings have to be removed; adding 1-propanol into the gel will provide great cleaning controlled action and result (Carretti et al., 2009).

In 2015 L.Angelova presented the article *"Partially hydrolyzed poly(vinyl-acetate)-borax – based gel-like materials for conservation of art: Characterization and application*." This article presented deep research on working with gels and various recipes to create physical and chemical correct properties when adding additives to treat specific surfaces. Also, the use of aqueous emulsion was mentioned, which derives from the acrylic-based polymer Pemulen TR-2. This material is considered new and was introduced in 2007 at the Winterthur, University of Delaware. The cleaning strategy was described so that areas first were treated with Pemulen TR-2 and then xPVAc-borate viscous gel(Angelova et al., 2015). This combination created an efficient cleaning on textured and intensively soiled oil paintings.

As mentioned, the xPVAc-Borax gel is good for treating more hydrophobic surfaces as oil paints. However, there is a gap when it comes to an understanding of its cleaning action on more fragile materials. The article *" Polyvinyl alcohol-based hydrogels as new tunable materials for application in the cultural*

heritage field," written by (Mazzuca et al., 2020), studied the gel in the paper conservation field, where they excluded the Borax component. The research presented a chemical gel based on PVA and *tel*-PVA. The add *tel*- stands for "telechelic," and for PVA, it becomes a cross-linked agent (Mazzuca et al., 2020). This gel's composition is firm and ensures even contact with artwork without breaking issues during handling. The retentive properties are high, which are prohibiting the possibility of paper fiber swelling or ink distortion.

2.3 Research on Novel hydrogel methods

In meanwhile, the other type of gels was discovered through the *"Nanoscience"* innovative technology. Together with Professor Piero Baglioni and David Chelazzi, in 2013, the book *"Nanoscience for the Conservation of Work of Art"* was published. Their study on gels recommended using highly retentive hydrogels for water-sensitive surfaces. At the same time, organogels might be more suitable for working with the surface, which can be damaged upon interaction with water (e.g., parchment, leather, and collagen-based objects) (Baglioni P. &., 2013). The book underlies that a chemical type of hydrogels is having advantages when working with water-sensitive materials. They prevent swelling and possible mechanical damage. One of the compositions that performed with good water retention was the copolymerization reaction of 2-hydroxyethyl-methacrylate (HEMA) and *N* -vinyl-1-pyrrolidone (VP). A more advanced formula was reached by (semi – interpenetrated networks of p(HEMA) with (PVP), this chemical composition can allow more versatile options when it comes to hydrophobic ratio, compactness, and water retention capabilities.

The formula p(HEMA)/PVP was first prepared and described for biological use by Wilhterile and Lim. Nevertheless, the J.A.L. Domingues developed it for chemistry purposes. It was proved to be suitable for water-sensitive surfaces after two types of research published by (J. A. L. Domingues et al., 2013) (J. Domingues et al., 2013). After testing them in ATR-FTIR, it was confirmed that polymers residues were not observed and detected (Chelazzi et al., 2018).

The chemical gel p(HEMA)/PVP is now manufacturing by Nanorestore Gel® company and is found in types Max-Dry (HWR) and Extra Dry (MWR). Nanorestore Gel® produces other types, and there is also a formula called Peggy 5 made of (PVA) and (PVP), while Peggy 6 is just out from (PVP). The last ones were evaluated by the TATE conservator Sciences on the artwork *"WHAAM!"* by Roy

Lichtenstein. The painting was water-sensitive. Moreover, after comparing all the types of gels, the best cleaning efficiency was performed with Peggy 6 (Bartoletti et al., 2020).

The previous studies on creating gel formulas build on poly(vinyl alcohol) and polyvinylpyrrolidone. Achieved the best formulation, with 25%PVP (PVA/PVP(3:1)_FT) using freeze-thawing (FT) method, where water release was just at about 20mg/cm²(Bonelli et al., 2019). While the mixture is done in cast-drying (CD), had water release on the much lower number at 4.1mg/cm². The CD gives a very rigid gel formula that is unsuitable for the rough or textured painted surface. Proportions in the gel-making process become very important. If the proportion of (PVP) is too high, the gel gets unstable during mechanical actions, while (PVA) in a high amount makes the gel rigid, which leads to poor contact with the cleaning surface (Bonelli et al., 2019). When mentioned previously about water release, the research made a significant calculation with different rigid gels. The gels are known in the conservation field, like agar-agar, Gellan gum, and Klucel has water release at about 30-40mg/cm²(Bonelli et al., 2019). These values are a bit too high for achieving a safe treatment on water sensitive-surfaces, where the suitable amount is recommended to be between 12 and 24 mg/cm²(Bonelli et al., 2019).

Another research was performed on water-sensitive lime-based wall paintings using Nanorestore Gels "*Removing Ingrained Soiling from Medieval Lime-based Wall Paintings Using Nanorestore Gel® Peggy 6 Combination with Aqueous Cleaning Liquids".* The Peggy 6 gel was tested together in combination with (TAC) and Apolar Coating (ApC). The paper mentioned that cleaning efficiency could also achieve a high level of cleaning by working with the Peggy 6 gel alone without adding any additional liquids (Segel et al., 2020).

2.4 Research in dry-cleaning methods

After analytically studying articles and research, hydrogels have been tested on sensitive oil paintings, unvarnished surfaces, wall paintings, and paper. However, the research on gels lacks the investigation performed on the other type of paint materials such as tempera or gouache. The other cleaning methods were examined on water and mechanically sensitive surfaces by the team of researchers (Cordova, 2017)(Daudin-Schotte et al., 2013). Those cleaning materials were various sponges, gums, erasers, and cleaning cloth applied on the unvarnished matte paint surface. Those methods were dry-

cleaning materials which are a good treatment when dealing with superficial dirt. However, they can cause problematic situations for the surface during usage in the form of gloss, abrasion, erosion, polish, or residues left after material when applied to acrylic, oil, alkyd oils, and gouache. The article "*Conservation of Contemporary painting: A Comparative Study of the Effect of Dry-Cleaning Techniques"* tested samples with Reflectance Transformation Imaging (RTI). Also, the article notes that materials such as Akapad sponge and Milan gum eraser® were the ones who left the most of residues. The other materials which failed where compact erasers, which created an abrasion situation and gloss to the surface.

The other range of material tested on unvarnished gouache surface was made by a group of conservators (Daudin-Schotte et al., 2013). Where the Groom Stick performed the opposite result from the previous research. Both studies prove that erasers based on (PVC) and Akapad sponges are unsafe and not applicable for matte paint. The conclusion in the article *"Dry Cleaning Approaches for Unvarnished Paint Surfaces"* recommended the Yellow- microfiber clot with a Make-up sponge. The research marks that the only disadvantage with a make-up sponge that the manufacturer is constantly changing composition (Daudin-Schotte et al., 2013). So, the makeup sponge used in this article is no longer on the market.

As a final point of the information which was found to be suitable for water-sensitive surfaces or was developed for this purpose had a lack of information based on how those methods can be applicable for matte tempera. Our specification is around blue pigments smalt. Comparing it to other colors on the polychromes sculpture, it was more hydrophilic. The advantage will be to test some of the mentioned methods on this fragile surface to identify if any of those materials will be efficient.

2.5 Conclusion

After concluding a review of the conservation literature related to the development of aqueous gel cleaning for the paint layer on the art objects, the importance of this study was determined. All the presented hydrogel and dry-cleaning methods were not tested on the porous, highly hydrophilic tempera paint. The absence of this information will be researched and studied in this particular work. Because the water in its pure form is not suitable for the safe approach and a scientific study showed that water affects hydrophilic acrylic emulsion paints. It can potentially change the color parameters

or cause erasure when using a cotton swab (Owen et al., 2004). Therefore, a gel method with high water retention properties can solve the case with dry-cleaning methods.

Most of the articles confirmed that the residues left after the hydrogels would not affect or infiltrate the surface. The researchers used ATR- FTIR, FTIR, and X-Ray spectroscopies (XPS and NEXAFS). It was proved to be a suitable and non-invasive method to study the residue issues (Willneff et al., 2014). Our research is based on mockups which allow us to experiment with other methods. The strategical approach created during the evaluation of hydrogels on the painting "Whaam" by Roy Lichtenstein was adopted in our research. To evaluate the cleaning methods properties. It was used SEM analyses to study residues, colorimeter to see the changing colors, and microscopy to study cleaning trials.

3. Analytical Methods

The polychrome sculpture is a historical object, and therefore it is a document that contains information about which sort of materials it was made of and its life history (Caple, 2012).

The first section presents stages with different analysis methods used to extract painting and ground layer material composition. The analyses to detect component information were ATR-FTIR, XRF, Optical Microscopy, and cross-section. To be able to reconstruct the mockup replicating the original surface from the funeral coat of arms. For the creation of mockup samples, it was used contemporary equivalent materials, with the rely on historical recipes. The mockups were then used as a substrate for further steps.

The second step was structured with data examinations to identify the application properties of the cleaning methods and their effects. To complete a relevant and reliable cleaning evaluation result, it was used Colorimeter, Spectrophotometer, Optical Microscope Examination, SEM-analyses, and Accelerating aging.

3.1 Data analyses methods

To collect the data of material composition, the data analysis methods were used. Here is the aim to extract useful information about components in the painting layer and ground layer. To understand the structure and technology of the past.

3.1.1. Fourier – transform infrared spectroscopy (ATR- FTIR) analyses

The ATR- FTIR (Fourier-transform infrared spectroscopy) was used to analyze the blue pigment, ground layer composition, and binding material. This technique analysis exploits the atoms' vibrations in a molecule under the irradiation of infrared rays **(Stuart, 2007)**. When the bonds in molecules absorbing the rays at a specific wavelength, the frequencies in a spectrum indicate the bands. This technique allows us to examine the binders' material information, pigments, minerals, adhesives, corrosion products **(Galeotti, 2009)**.

To analyze blue pigment and binding media were used samples that were previously detached from the original sculpture. For comparison, we used samples that were scraped out from mockup models

for identifying the binding media. The physical samples were then placed on a Platinum ATR single reflection diamond stage with a crystal element. Afterward, the sample was closed with the pressure applicator. The reflectance spectrum was performed with Alpha-R attachment, where IR radiation passed through the crystal stage element and interacted with the sample multiple times to collect data for the detector. The sampling measures were adjusted on range 4000-400 cm with 100 scans on spectral resolution of 4 cm-1. The graphs of the FTIR- analyses are shown in (Fig.21-23)

3.1.2. X-Ray Fluorescence Spectroscopy (XRF) analyses

X-Ray Fluorescence examination was made by using "Elio Device SN1253, Bruker". This technique measures the elemental composition of pigments **(Stuart, 2007).** Mapping measurements on the funeral coat of arms were performed with the tube voltage of 40 kV, a tube node current of 20 μA, and an acquisition time of 60,0s for each area. The method involves the emission of characteristic X-rays while irradiating the sample region with high-energy photons **(Dran, 2009)**. Measurements were performed on the blue pigment area taken from the Coat of Arms' upper area on the helmet turban detail (Fig.24).

3.1.3. Optical Microscopy

Optical microscopy was made to determine the pigment particles under the microscope. It shows us the dimension and characteristics of the grain (Eastaugh, 2013). For this examination technique, it was used Nikon Alphaphot YS Binocular Microscope with Four Objectives. The sample was scratched to the pigment particle size and placed onto the glass slide with a drop of glycerin coated with cover slides. The pigment particles were then compared with the illustration and description material from the book "Pigment compendium: a dictionary of historical pigments" (Eastaugh, 2013). The results are in Appendix (Fig.25-28)

3.1.4. Cross-section

The cross-section technique is considered the primary and most readily available technique to study various paint samples' structure and technological approach (Sandu et al., 2012). For studying organic materials in polychrome layers, it was used dyes.
To perform a microscopic examination, the painted fragment was covered with Technovit 2000LC liquid. This liquid is a highly transparent embedding resin based on methacrylate. Further treatment was made in the Technotray CU light-curing device, which has a blue light inside. The temperature for drying was approximately 60- 90°C. When the sample cubes were very dried and ready, we used sandpaper to polish the samples. The smoothly polished cube gave us a plane surface for focusing and studying cross-sections under the optical microscope.

The staining technique focuses on using different dyes that can form colored compoundswith organic materials, such as proteins, polysaccharides, resins, and oils. It was used Ponceau S stain to find out if the ground layer has proteins (Fig.32). Ponceau S is a negative stain that binds to the protein's positively charged amino groups (Sandu et al., 2012). We added a 1. Drop of Ponceau S diluted with acetic acid on top of our sample for locating protein bonds. It was staying and setting in for 20 min until it was removed with water.

The second stain sample was made with Sudan Black (Fig. 33). We used it because it identifies compounds like neutral triglycerides and lipids (Johnson, 1971). Therefore, it helps us determine if it was used oils as a binding in the ground layer. The dye consistency is in dark brown-black powder and yields a blue-black stan solution. The mixture of Sudan black was mixed in the proportion given /60 ml of ethyl alcohol and 40ml distilled water/. We gave it 40 min to set in on the sample.

3.2. Experimental Analyses Methods

Experimental data analyses are a core stage of the master thesis. With those technical tools, evaluation of the cleaning method will be approached in several stages. All the analyses will be performed on the mockup samples.

3.2.1. Color measurements

Measurements were performed on the funeral coat of arms blue pigment surface before all the conservation treatments. The colorimeter tool was the Konica Minolta CR-300 Chroma Meter type, which measured the surface's reflective colors. This tool could provide measurements of the color changes which could appear after cleaning gels application. The color measurement Konica Minolta was used before and after application examination with gels, and the final step was focused on examining selected aged samples after accelerated aging. To spot any possible degradation processes. The Measurement area on the substrate surface was at Ø 8 mm, using diffusion illumination and a 0° viewing angle (Minolta, 1991). After that, it was sampled in a triplicate mode from the sample surface spot. The data values were calculated for each sample and averaged E* with the deviation calculation in Microsoft Excel software (Bartoletti et al., 2020). In the end, CIE (1976) L*a*b* color difference was calculated for data analyses (Owen, 2004).

3.2.2. Spectrophotometer Measurements

For this measurement, it was used Konica Minolta CM-26d. This tool offers a precise accuracy for measuring color parameters. The spectrophotometer was horizontally aligned with the measurement area on Ø3mm. The color parameters were then calculated with L*a*b value system on a CM-CT1 Configuration Tool software following the (ISO 7724/1) norm.

3.2.3. Optical Microscope examination

For the evaluation of the cleaning method, it was used the Optical Microscope Leica S9D model. With the 122 mm allowance of working distance, it was easy to manipulate the sample to see the gel surface condition after application on the substrate. The high magnification for up to 55x and 9:1 zoom helped overview details to achieve an efficient process. This stage focused on evaluating the gelling agent's surface or the dry cleaning methods to study the pigment pick-up or the residues left on the mockup surface. The description of 32 samples taken is in Appendix (Fig, 37-47)

3.2.4. Scanning Electron Microscopy (SEM) analyses

The SEM scan process was carried out on mockup sample surfaces to evaluate the cleaning gel residue on specific samples after cleaning. The instrument which was used is HITACHI S – 3400N with the settings at about 10kV, Probe current 40 with emission on 100µA (Jourbert, 2017). The magnification varied from 40x and up to 900x. The samples for the examination were covered with carbon.

3.2.5. Accelerating aging

As the last stage for evaluating the gel residue affection, the selected samples are supposed to be placed into the Atlas Xenotest 440, a highly versatile weathering instrument. The International Organization for Standards (ISO 16474-2) norm is suited for examining the paints and varnishes in indoor conditions(Standard 11266, 2014). The samples were placed in the machine for 120h, with radiant exposure on 12332 kJ/m², irradiance 50W/m², temperature 38 C°, black standard temperature 65C° and relative humidity 70%. Irradiance control was set at 300-400nm. With the help of xenon-arc light, this condition is reproducing the weathering condition indoors with daylight filtered through the window glass(Sierra, 2007)

3.2.6. Evaluation

Evaluation of the cleaning methods characteristics and their disadvantages and advantages will be presented in various ways, like imaging and diagrams. The most convenient evaluation will be to use the Star diagrams graphical method to give the information in a precise format. Where cleaning systems presentations will be rated with a scale from 1 (Inadequate/week) to 5(most appropriate), as the higher number its riches, the more promising result is accomplished (Bartoletti et al., 2020).

4. Experimental Approach

The fourth chapter describes the preparation, material recipes, and their description. Those materials will be then evaluated and examined in Chapter 5 *Results*. Here it will be first described how the mockups were prepared for sampling. The next part will be describing the cleaning methods selected with their qualities and how they will be applied and prepared. Most of the hydrogels were prepared by following the Dr. Stefani Kavda formulations.

4.1 Preparations of Mockups

The mockups' preparation was created as a surface to carry out the test for comparing the application characteristic of the cleaning methods. The mockups were prepared on the wooden panel sample boards, with the recipe close to the original funeral coat of arms, by following the description from (Lindberg, 1991) (Townsend, 2008) (Mayer, 1991). The size of a mockup testing area is 50x45mm.

1. Stage

   The impregnation stage was performed with 5% (w/v) rabbit skin glue concentration to prepare the wooden sample surface. The wooden substrate was from pine and birch wood.

2. Stage

   The ground layer's application was performed with 5% (w/v) rabbit skin glue and Champagne chalk from "Kremer," with four application layers covering the wooden surface. All the layers were applied after the previous application was utterly dried, with the time gap at around 12 hours. The last ground layer was polished with fine-grained sandpaper to achieve a smooth area.

3. Stage

   This third stage was based on preparing the binding media for the painting, where the main component was from the egg white. The first step of preparation was focused on breaking down proteins. It was accomplished by whispering glair to a white rigid porous substance. After, that the content was left in the fridge for 35pprox..12 hours. After the separations, we remove the white foam, and the glair was ready to use.

   Fine pigment Smalt from "Kremer" was used to find the right proportion of painting

composition. The best application result was achieved by diluting 1 gr of fine-grained smalt with 1ml of glair with one drop of Ethanol as a surface tension ingredient.

4. Stage

To achieve an even applied opaque surface, the ground layer was covered with three layers of painting color. Each layer was applied after the previous was completely dry. The time between each application was approximately not less than 6 hours.

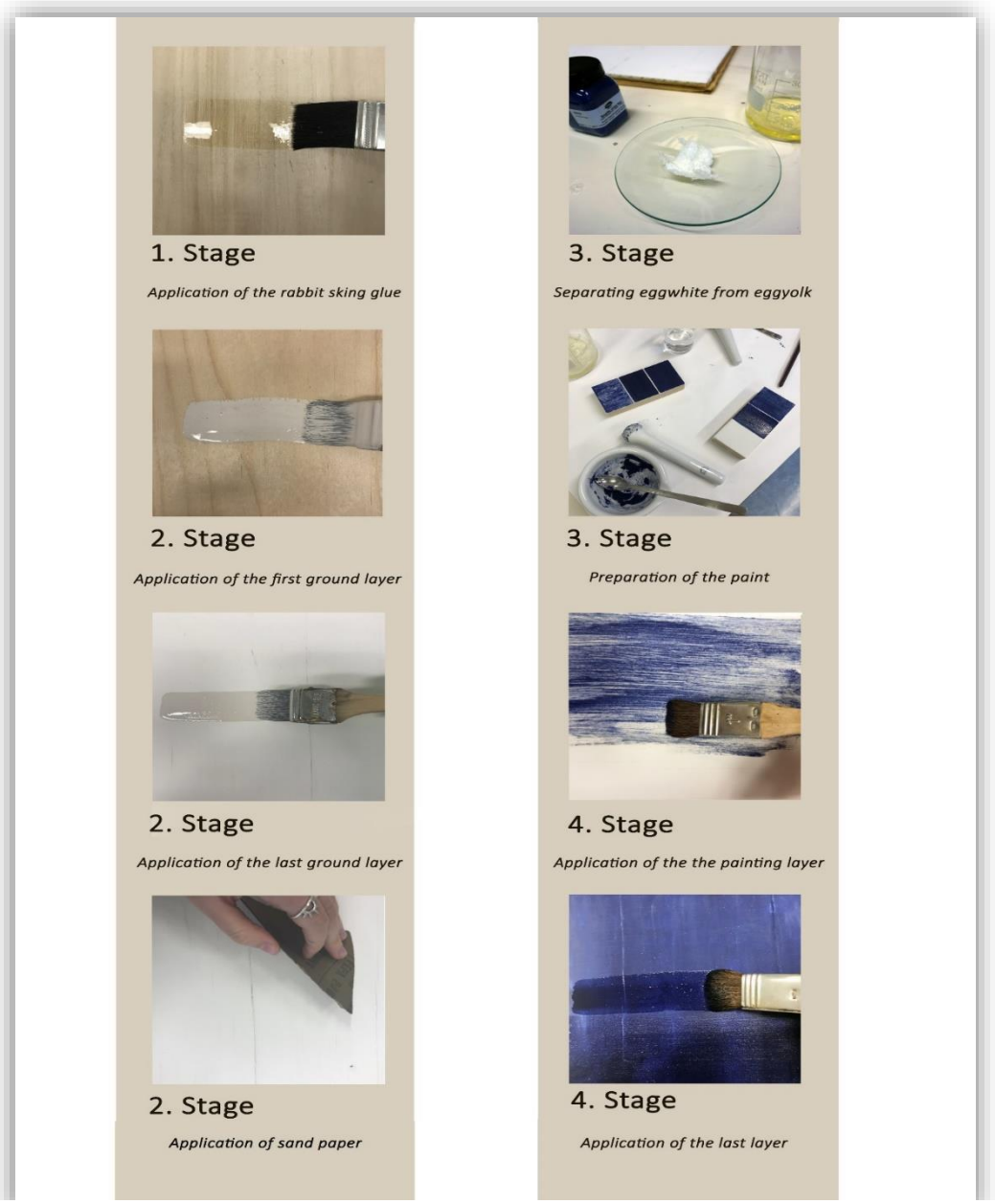


Figure 5 Preparation stages for the mockups

4.2 Cleaning Examination on Mockups

Evaluation stages on Mockups

The testing was performed on an imitative substrate after following the original surface technique. Cleaning sample methods were applied on the 50x45 mm wooden surface area on the distemper smalt paint layer. In the lab, conditions where the environment temperature and humidity were at (+22°C, 50% RH). Application of the cleaning materials was performed with close contact with the paint surface. To research if any of the materials will cause abrasion or polishing particles away, which might be quite particularly feasible.

The observation was achieved with the attention to 4 stages of evaluation:

-Microscopy analyses to study the stability of the painting pigment particles left on the cleaning material.

-Colorimeter and Spectrophotometer to measure color parameters.

-SEM to check the residues of the removal media.

-Accelerating aging to detect any changes of residues left on the surface.

4.3 The dry-cleaning methods

The dry-cleaning methods can be suitable to remove superficial dirt on unvarnished surfaces sensitive to any aqueous solutions. These methods are prevalent in textile and paper conservation (Zervos & Alexopoulou, 2015) (Estabrook, 1989). However, there is an issue that occurs by working with this type of cleaning method because it is suitable for non-ingrained dirt. To analyze and select a method congruous with the surface painting properties, research was conducted with the following materials: Evolon-CR, yellow micro-fiber cloth, Akapad white, and white triangle make-up sponge. Those materials are commonly used for working with sensitive surfaces. However, apprehension might appear in the form of potential residue from the cleaning material left as sticky parts of residue(Daudin-Schotte et al., 2013).

4.3.1. Akapad sponge

The Akapad sponge, also known as WishAb, is a ubiquitous dry-cleaning tool for cleaning textile, paper, oil painting, wood, frescoes. The component in the dry-cleaning sponge is synthetic latex and practice (AKA Art, n.d.). Sponges are divided into two parts where the blue part has a ruff texture and is used as a grip, while the white/yellow part is an active cleaning layer. The research used the white-colored one because it has a softer texture and surface and is more suitable for our material. Besides, the Akapad sponge material's quality is known to have some disadvantages and cannot be used indiscriminately over all the objects. Indeed, the sponges may leave residues in the form of crumbles (Cordova, 2017) (Eipper, 2018).

4.3.2. The Yellow micro-fiber cloth

The Yellow microfiber cloth is a non-woven textile. It is made from Polyethylene terephthalate (PET), polyester, and Nylon 6(polyamide). It was used in the Cultural Heritage Agency of the Netherlands (RCE) project from 2006 to 2009 to evaluate dry-cleaning material application properties (van den Berg, 2016). The research results showed a pretty solid characteristic for this material. They proved to be a fine cloth to use on materials, like on the oil paint layer, which was sensitive to water, and on the unvarnished gouache paint layer (van den Berg, 2016).

4.3.3. Evolon-CR®

Evolon- CR® is an innovation presented in the art conservation world for the first time in 2013 at the Institute for Conservation Science in Cologne after Staatliche Akademie der Bildenden Künsten completed deep research in 2006 (Michelle Vergeer, 2020). The producers of Evolon-CR® created a textile mixture which is consisted of polyamide and polyester fibers that are spun into filaments (Evolon Technology, 2018). To achieve a hydrophobic and hydrophilic property in the material.

Primarily the filaments under the production are uniformly spread out on a surface. Then under the high water pressure and water jets, the filaments are getting split and fixed into microfilaments (Evolon Technology, 2018). The outcome of this process is to make non-woven microfilament textile that has solid absorbent characteristics and can be used in various conservation tasks such as cleaning, removing varnish, and overpaint with the use of solvents.

Our research used Evolon-CR® 77,4 grams/m² from conservation material supplier Deffner&Johann to observe disadvantages and advantages by applying the Evolon-CR® to an unvarnished layer of distemper smalt paint. (Deffner & Johann, 2016) That material was chosen because Evolon- CR® microfiber paper eliminates mechanical surface treatment and softly absorbs the dirt.

4.3.4. "Kryolan" white triangle Make-up sponge

The make-up sponge is a tool in art conservation as a dry-cleaning material. For the research, it was also decided to test the "Kryolan" N.1449 professional make-up sponge, which derives from a vegetable origin (Kryolan, 2021). The "Kryolan" is a natural rubber latex material. It consists of pure poly-cis-1,4 isoprene from a chemical view, at which the end of the macromolecules can be bounded non- isoprene structural units, known as proteins, phospholipids, and amino acids. While, on the backbone of macromolecules, there are epoxide, ester, aldehyde, and lactone groups (Dinsmore, 1951). The pH of the product is varying from 6.5-7.0. However, there are many alternatives and variations in marked when it comes to make-up sponges. The rubbers can also be synthetical. The closest similarity to our latex sponge can be found in Styrene-butadiene rubber (SBR) and Isoprene rubber, butylated hydroxytoluene (BHT), because of their random copolymer (Omnexus, n.d.).

The make-up sponges are suitable for cleaning due to their specifically very soft texture and great flexibility. Before usage onto the artwork surface, it is recommended to rinse the triangle in demineralized water and dry it out (Daudin-Schotte et al., 2013). The application obtains with slight pressure in one direction.

4.4 The wet–cleaning methods

The investigation on aqueous rigid cleaning methods is made to establish a gel formulation best suited for the smalt pigment. The properties of hydrogels have good advantages because they hold large amounts of water in their 3D networks. Some of the restrain liquid form can be adjusted with buffers and chelators to clean the result of ingrained dirt better. Each gel formula will be measured in the first stage by observing the amount of pigment particles in the microscope attached to the gel surface.

4.4.1. Deionized Water

The usage of aqueous conservation methods was introduced at the beginning of the XXI century as an alternative to traditional organic solvents (Prati S. V., 2018). However, deionized water cannot dissolve oily or fatty substances (Eipper, 2018). That is why deionized water is mainly applied to oil paintings as a light cleaning media for the dust on non-water sensitive surfaces. While our surface is highly hydrophilic, it can cause some problematic outcomes. Because, for unvarnished hydrophilic surfaces, it can work as a physical solvent. The water characteristics proved to be aggressive with protein-based painting techniques (A. Casoli, 2010). Unfortunately, our paint layer on the substrate is made out of hydrophilic materials, where the egg is a medium binder. Moreover, water use might also affect the ground layer because of the proteinaceous glue binder. Knowing the disadvantages that might occur, the deionized water was chosen for this examination to compare the material to evaluate the hydrogel's effectiveness.

4.4.2. Saliva

The most widely used cleaning agent is saliva. The enzymes contained in saliva can efficiently deal with the dirt. This fact became a scientific statement after the chromatography research on dirt revealed that fatty acids and phospholipids are the main lipid components of dirt, combining the

inorganic and organic residues (Romio et al., 2020). Therefore, the saliva produces cleaning action when saliva's first class of enzyme-lipases manages to catalyze the degradation of fatty substances and the second class hydrolases, catalyzing hydrolytic substances' degradation process (Den Tandt, 1984) . In the art conservation world, saliva usually shows promising results in many kinds of research when used to clean paintings (Eipper, 2018). It can be relevant to add to the research, mainly as a comparative cleaning agent material for evaluating hydrogels.

4.5. Rigid Hydrogels

There is a wide variety of gels known to the conservation world, and the improvement is a constant development. As a form, the gel is a colloidal composition created by liquid and thickener. The liquid part is a base in the composition, which specifies the gel type. In our examination, we are focusing on hydrogels which are having a liquid water base, which gets thickened down to the gel form by using organic ingredients. The organic ingredients can be agar-agar gel, gellan gum, PVAc. However, there are also other types of gels called organogels where the composition is dismissing water components.

Rigid gels such as agar-agar and gellan gum are known as physical gels and were introduced in 1980 to the conservation field (Khandekar, 2000). They are used and tested commonly on cleaning paper and painting surfaces, but several advantages were recognized during treatment application (Casoli et al., 2013). Their substance has a rigid porous structure by having electrostatic interactions around polymer chains. Agar-agar and gellan gum contains a similar constitution with polysaccharides that transform into hydrogels after adding distilled water and exposing it to heating at around 90°C (Funami et al., 2008). By altering the gel powder concentration, it possible to manipulate the variation of the viscosity, absorption, and dispersion for the given experiment or treatment (Wikipedia, 2020). As an outcome, when the gel is cooled down to around 38°C, it reaches the three-dimensional structure, which holds water in its interstices and forms solid hydrogen bonds (Casoli et al., 2013).

4.5.1. Nanorestore Gels ®

The Naorestore gels® is a novel cleaning method of aqueous-based gels series, offering unique water retention and a promise of enhanced performance for water-sensitive paintings. The Nanorestore gels® were developed in CSGI (Consorzio Interuniversirario per lo Sviluppo dei Sistemi a Grande Interfase/ Research Center for Colloids and Nanoscience) Florence, Italy (Baglioni P. a., 2013) . For the examination it was tested 6 types of Nanorestore gels®:

- Nanorestore Gel ® Max-Dry (HWR) and Extra Dry (MWR) is transparent chemical hydrogels based on poly (2-hydroxyethyl methacrylate) and polyvinylpyrrolidone in a semi-interpenetrated network which can have maximum retention of liquid (CSGI-Consorzio per lo Sviluppo dei Sistemi a Grande Interfase, 2019).

- Nanorestore Gel® Peggy 5 and 6 was made in a sheet form and as a Gum. Those gels formulation is an opalescent hydrogel based on poly (vinyl alcohol) in the polymeric network (Segel, 2020). The difference between 5 and 6, is that the Peggy 6 has lower retention of loaded liquid than the Peggy 5 formula(Solutions for Conservation of Cultural Heritage, 2015). Because Peggy 5 consists of a blend of polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP) while Peggy 6 is just made from (PVA)(Bartoletti et al., 2020). However, both of the gels are elastic and flexible and more suitable for applying on rough and irregular surfaces. (Solutions for Conservation of Cultural Heritage, 2015). The Peggy Gum has the same properties but is shaped in a parallelepiped shape and can be used in a light mechanical action as an ultra-delicate eraser.

The Nanorestore ® Gels and application method

When each of the gel types was dispatched from the package, each sheet of the cleaning material was immersed into a small volume bath full of demineralized water. The manufacturer recommended cleaning it for 24 hours before the first application. It was important to blot the gel in the filter paper on each side for 1-2 sec before the cleaning treatment. Then the gel was gently applied to the substrate with the pallet knife. The adherence after the application was achieved with the pincette by peeling it away from the surface (CSGI-Consorzio per lo Sviluppo dei Sistemi a Grande Interface, 2019).

4.5.1. Agar-Agar gels

Agar gel was chosen for this examination because it is the oldest cleaning gelling agent known in the conservation field (Cremonesi, 2016). The main component of the Agar is seaweed with the two polymers agarose, which forms about 70% of the mixture, and agaropectin(Funami et al., 2008).

For assessing this experiment several proportions were prepared of the Agar Agar gel :2%, 4%,5%,6%,8% and 10%. The fact that the sulfate groups contained in the Agar can decrease the cavities of its reticulum (Cremonesi, 2016). It can also lead to the process when protein molecules transform into an aqueous solution because cavities are still large enough if agar-agar gel has a low percentage concentration of 2%(w/w). To improve this issue with possible water penetration on the surface, the concentrations must be increased up to 4-10 % (w/w). This percentage increase will change the pores to a smaller size in the gel, improving water retention. However, when the percentage concentration increases in the gel formula, the time application process must be adjusted differently. The samples with agar-agar gel with the time applications are listed in a table Appendix (Fig. 43-46)

The 2% Agar Agar gell preparation recipe

The first stage was commenced by diluting at room temperature disperse 0.9g, Agar-Agar, with 45 ml of deionized water (2wt.%). Then it was brought to a boiling point at around 85-90°C in a bain-marie. After it reached the boiling point, it was left to cool down. Then the gel solution was re-heated in the same way to improve the gels' water retention properties. After the gel was ready, it was poured down into a petri dish to cool down. The pH of the gel was measured, and it was 7.6 points. Then squares for around 4x4cm were cut out with the scalpel and placed accurately onto the painting surface with the time control. After its cleaning action, it was lifted carefully with the pincette and painting knife.

4.5.2. xPVAc/Borax

The xPVAc/Borax is a viscous gel, which is excellent to use as a cleaning agent because of its easy "Peel-off" ability. The gel mixture is made by viscoelastic dispersion of borate- crosslinked with partially hydrolyzed poly (vinyl acetate) (xPVAc) (Angelova, 2015). This gel form can easily control its physical and chemical properties when a chemical reaction of the hydroxyl groups such as borate with its ions connected with the fully dissolved aqueous formulation of poly(vinyl acetate) transforms into a highly viscoelastic appearance (Al-Emam, 2020). Using this gel on the surfaces to remove overpaints or varnishes showed good cleaning action without any detectable xPVAc or Borax residues(Natali et al., 2011). This was a reason to choose this gel to examine and analyze its performance abilities in the smalt distemper substrate. The gel forms at pH 7.5-8; if the pH decreases, the gel crosslinking will fail.

80% PVAc/Borax gel preparation recipe

For the preparation of (4 wt.%) concentration, it was used 0.2 g PVA in 3.75 g deionized water with pH at 7. After adding PVA into the aqueous solution, it is important to leave it undisturbed for at least 30 min. However, it was observed that 30 min was not enough for polymers to swell and become transparent. To resolve this case, the mixture was left over the night or heated up in bain-marie not higher than 40°C.

The second stage comprises by adding 0.05 g of Borax with 1g in deionized water (1 wt.%) in a separate container with some heat assistance. When both the mixtures were homogeneously limpid, the solutions were added into one jar and stirred vigorously with a spatula without heat. Until the homogenous transparent gel was formed, the gel was left undisturbed for one hour before applying it to the surface. Then the semi-hardened shape was placed with the pallet knife on the sample with the time measured application. To achieve a gel form, the pH should be at 7.5-8 points. Otherwise, the crosslinking phase will fail.

The gel's stiffness might also be varied by increasing or decreasing the polymer and Borax concentration. The various concentration was tested to correlate the perfect stiffness, allowing a great peel-ability of the cleaning agent, which can be easily removed from the surface in one mechanical step with the help of tweezers(Natali et al., 2011).

4.5.3. Pemulen TR- 2

The Pemulen TR-2 is a polyacrylic acid- polyacrylate (C10-C30) as an ester block copolymer that can form a homogeneous gel in an aqueous emulsion (Sofia Hennen, 2017). It was first introduced to art conservation in 2007(Angelova et al., 2015). Its primarily used in the make-up industry as a remover. The pH of Pemulen TR-2 can be low and requires the buffer to reach the viscosity form, which occurs at the pH range from 5.0-9.0 (Agent, 2000).

The Pemulen TR-2 gel preparation recipe

This emulsion with concentration (1.wt.%) is prepared in three stages. In the first stage, the 0.2g of Pemulen TR- 2 is slowly added in 10ml deionized water with constant stirring. In the other container, as a second stage, it is essential to dissolve the buffer TEA (Triethanolamine) in 10 ml deionized water (5 wt.%). As a final stage, both mixtures get mixed to reach the homogenous mixture and hand stirred with a small whisk until a weak basic gel reaches the pH of 8.0 point. To apply the high-viscosity gel onto the substrate pallet knife was used as a tool. The mixture was removed with a cotton swab. The residues access was taken away with cotton swabs moistened with benzyl alcohol(Nevin, 2019). It is recommended to use a barrier film between the Pemulen TR-2 and the surface if it is sensitive to moisture. These barriers can be Japanese paper or Evolon-CR©.

5. Results

This chapter is presenting the results of two different approaches. The first task was focused on investigating the paint layer and ground layer from the original banner. The setting and description of analysis methods are in Chapter 3: *Analysis Methods*. The first examination was undertaken by using ATR-FTIR, XRF, and Optical Microscopy, with a Cross-section. All the tables, photos, and graphs are listed in the Appendix part.

The second task is about evaluating cleaning methods actions when they are in contact with the mockup substrate. This stage presented results with optical microscope examination, star diagrams, Colorimeter, Spectrophotometer, SEM, Tape method, and Accelerated Aging.

Results from the Object material research

5.1 ATR- FTIR analyses

The FTIR analyses were carried out on the blue pigment area to research the binding media and pigment compound.

The peaks were observed on the double bond region stretching (1500-2000^{-1}cm) with carbonyl compounds (C=C) for identifying the binding media. It was detected several times peak on – 1651 $^{-1}$cm, which denotes proteinaceous organic media from bone glue. This frequency might come from the ground layer. Throughout the deeper analyses, one peak on -1654.71 $^{-1}$cm can specify the albumin compound, probably egg white, according to the article (Centeno et al., 2004), but another article includes this peak number to identify the egg yolk composition (Ghezzi et al., 2015).

For making a more precise conclusion about binding media, the mockup samples were made, with three different binding media mixed with smalt fine pigment. Since, the albumin compound was found in the original samples from the banner object. The binding media samples were made from egg white, egg yolk, and whole egg composition.

Comparing the C-H stretching region with the original sample and mockups, it was not detected fatty acids in the original graph with smalt pigment (Fig. 21). This can happen by preparing matte tempera paint with pure egg white because the fatty acids are removed before using it as a binding media. The egg yolk and whole egg had peaked at about -2920^{-1}cm, which shows a fatty acid compound that was not detected in the previous original samples (Fig.22).

For the clarification of the blue pigment, the ATR- FTIR analyses were used, and the result was obtained in the Si-O antisymmetric stretching band. The smalt pigment was lying in between – 1030 and 1080 $^{-1}$cm (Fig. 22). To compare results from FTIR where just pure smalt grain was researched. The similarity was conclusive with the light vibration at -1077 $^{-1}$cm and prolonged distributions at -600 because of the glass particles (Vetter & Schreiner, 2017) (Fig.22). The Ultramarine wavelength was not seen in spectra with its high peak on -1008 $^{-1}$cm.

Another measurement was undertaken to examine the ground layer component. The graph shown in (Fig. 23) contains a peak in C- H bending at -871.71 $^{-1}$cm, which stands for calcium carbonate in the ground layer. The exact peak number was detected in all FTIR- analyses taken from the banner with the ground layer.

5.2 XRF- analyses

The XRF examination pointed out several essential elements that indicated the blue pigment as smalt. One of the main element compounds in smalt will be arsenic, and in XRF, the concentration was at 2,23%. Another one is cobalt with a 1,3% concentration since smalt is based on powdered blue cobalt potassium silicate glass. The last component pointing of smalt was nickel (Ni) with a concentration of 0,38% (Rae, 2020). These three elements' combined presence is considered a good marker for smalt pigment (van Loon, 2020).

The highest concentration was observed with a silicon element peak of 61,19%, indicating ultramarine and smalt. However, the amount of sodium (Na), one of the main element components to indicate ultramarine natural with XRF- analyses, was not detected (Mosca, 2016). This leads to an assumption that it might be smalt as a blue pigment. The graph with the measurements conducted from the XRF examination is in (Fig. 24)

5.3 Optical Microscopy

The microscopical test gave an unclear result on the blue pigment. Compared to the illustration and characteristics described in the Pigment Compendium book Nicholas Eastaugh (Eastaugh, 2013). The pigment particles could be compared to ultramarine pigment characteristics. The ultramarine is an essential constituent of the mineral lapis-lazurite (Plesters J. , 1966). Lapis – lazuli unite a complex mixture of blue mineral lazurite, iron pyrites, and calcspar (Gettens R. J., 1966). Under the microscope, we can see uneven coloration (Fig. 25). This might occur because pigment comes from early times and contains imperfections in the form of dust or light discoloration(Eastaugh et al., 2013). The particles' typical shape would be narrow-shaped and curvy on the edges (Eastaugh et al., 2013). The hue is vibrant blue, with a violet stain on it (Fig.26).

The samples from microscopical photos on (Fig. 27-28) having a different appearance. The particles are transparent, have sharp edges, and round forms, known to be characteristic of pigment smalt. Since smalt consists of tiny glass particles, the blue hue appearance might vary in different sizes (Eastaugh et al., 2013).

Results from the Cleaning material evaluation

5.4 Optical Microscope examination of cleaning materials

The application of the hydrogels and dry-cleaning methods showed different results. To summarize the microscope images for the clear evaluation, it was made diagrams. All the detailed information descriptions and images are listed and presented in Appendix (Fig. 37-47)

The acceptable results were achieved by using Nanoresotore gels H.W.R. and M.W.R. In dry cleaning methods, the adequate result was obtained with latex Make- up sponge "Kryolan" and Yellow micro-fiber cloth.

5.5 Cleaning system evaluation with star diagrams

For a clear presentation of the Micro images taken by Leica Microscope S9D, Triangle and Polygons diagrams were made. This system for evaluation was created by the Cultural Agency of the Netherlands(Cordova, 2017). Where various parameters were rated from 5 (most appropriate) to 1 (inadequate)result. The star diagrams provide a clear vision of the gel parameters. When the form aligns with the polygon shape, it equalizes an adequately promising good result. The diagram's modification towards the triangle shape was created to adjust to the dry-cleaning systems. Because cleaning parameters differ from dry-cleaning and hydrogels. The method allows us to evaluate and see a clear image of the gel and dry-cleaning applications and how they interfered with the substrate.

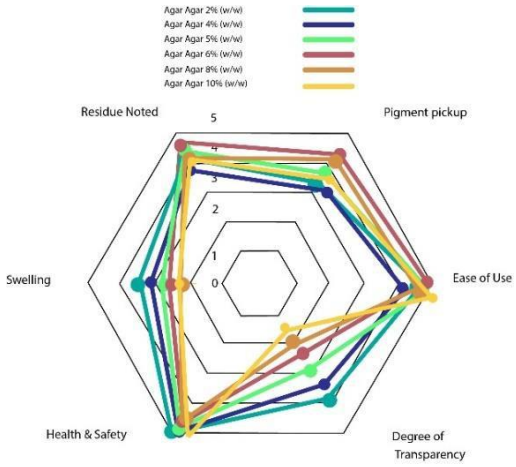


Figure 8 The Star diagram with Agar-agar gels

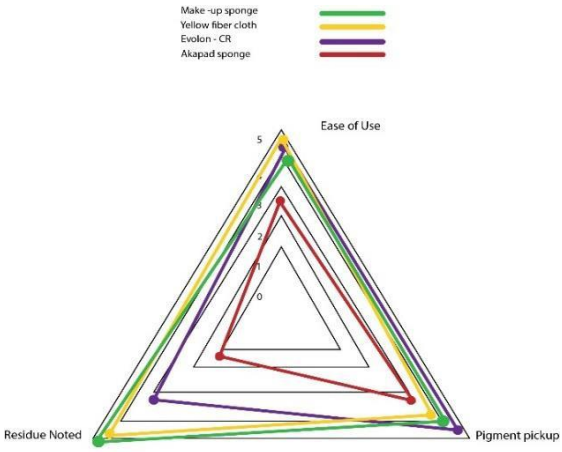


Figure 7 The Star Diagram with dry-cleaning materials

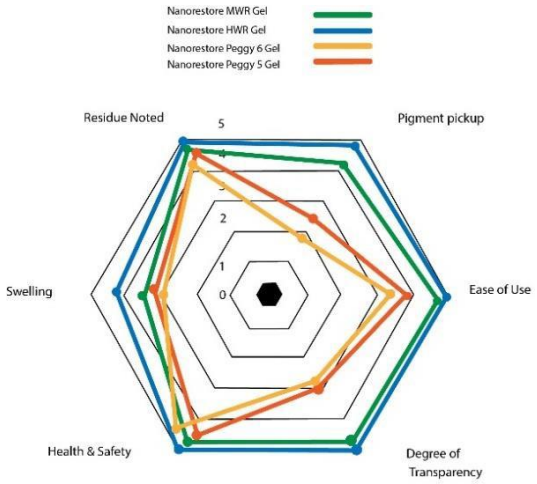


Figure 9 The Star diagrams with Nanorestore gels

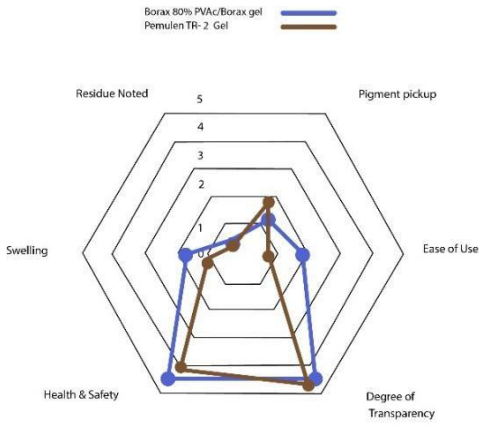
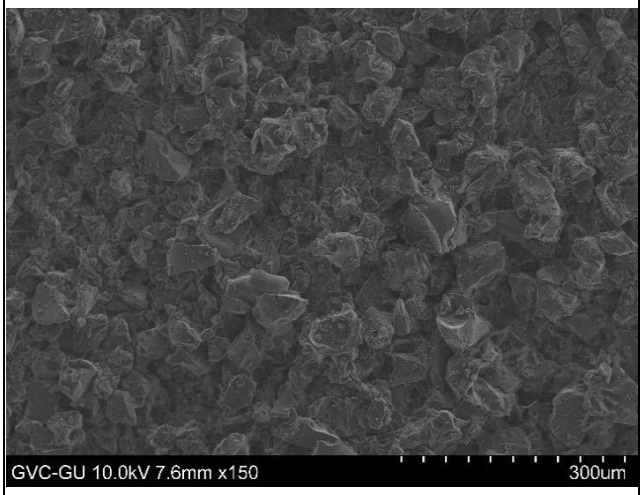
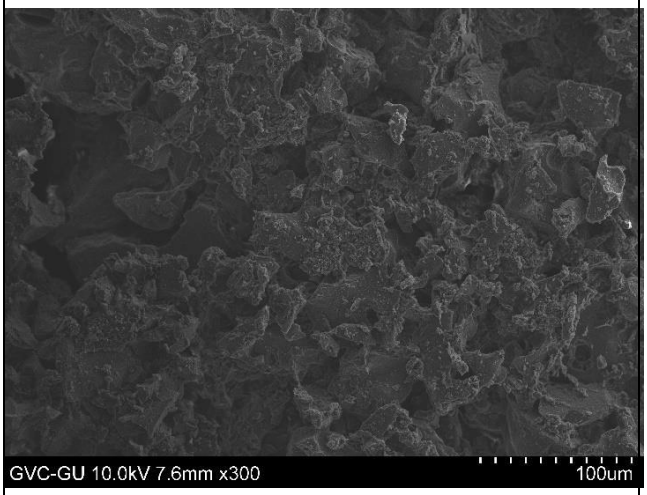
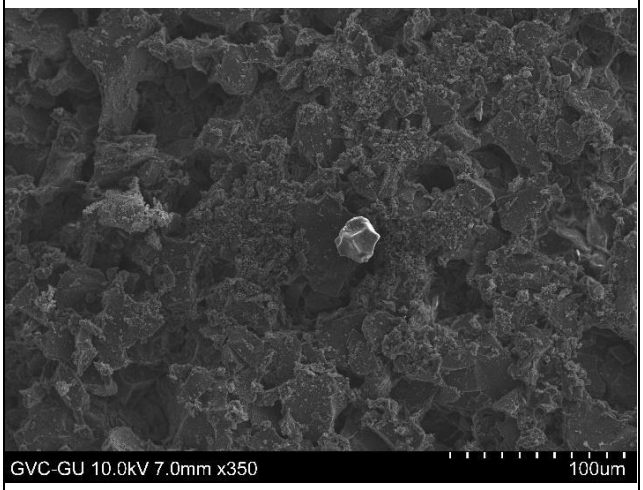
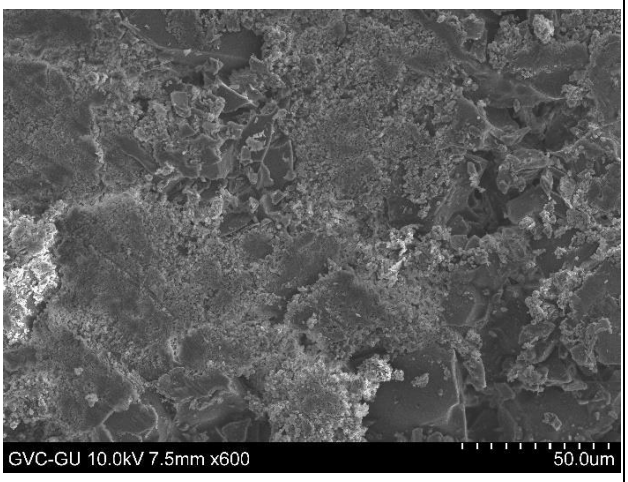
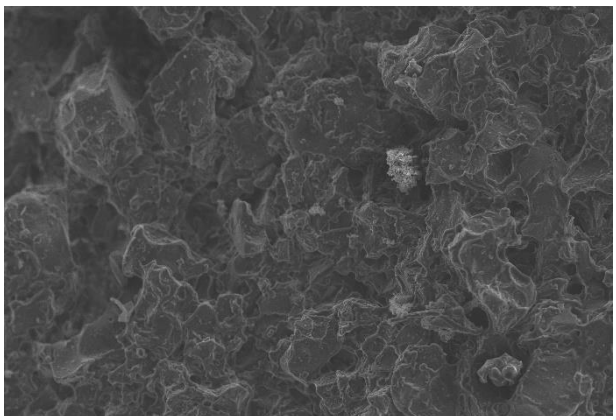


Figure 6 The Star diagram with xPVAc/Borax and Pemulen TR-2 gels

5.6 Scanning Electron Microscopy (SEM) examination

SEM analyses were carried out on 5 paint fragments taken from Mockups with smalt. The specimens were soiled and unsoiled with hydrogels. Scale bar varied from 50µm up to < 300 µm, with magnification from x 150 up to < x 600.

Untreated Mockup surface  *Figure 10 Untreated Mockup in SEM*	The clean surface, showing the structure of Smalt pigment appearance.
Nanorestore HWR  *Figure 11 After using Nanorestore HWR gel. SEM image*	By examining the surface under the magnification on x 300, it appeared clean. Difficult to note any difference from the original Mockup sample.

Nanorestore MWR  *Figure 12 After using Nanorestore MWR gel. SEM image*	It was spotted small crumbles, n magnification X 350 it was noted one particle. Otherwise, the surface is considered clean without any restudies from the hydrogels.
Agar-Agar 6%  *Figure 13 After using Agar-agar gel 6%. SEM image*	It was seen as relatively large crumbles on top of the surface, but they were not arriving from the hydrogel. Probably it was crumbles from the ground layer.
80PVAc/Borax 4 %  *Figure 14 After using 80PVAc/Borax gel. SEM image*	A viscosity residue layer covered the pigment particles, which most likely got attached to the substrate after gel application.

5.7 Colorimeter examination

The color parameters were measured with Konica Minolta CR-300 Chroma Meter. This method was chosen to compare the color difference on six different samples with the $\Delta E\ value\ L*a*b*$. Where L* worked as a lightness variable, a*, and b* for the chromatic coordination (Minolta, 1991). The measuring was collected and calculated in equations. The data was converted in color in Photoshop software with Lab color Mode. Afterward, the measured values of specimens were compared in Excel to get the total color difference by the equation below.

$$\Delta E = \sqrt{(\Delta L*)^2 + (\Delta + a)^2 + (\Delta - b)^2}$$

	Sample Name	**L*a*b* color parameters**
1	Sample after artificial aging (120 hours)	L 28/ +a 13 / -b 28
2	Mockup sample	L 26/ +a 15 / -b 30
3	Mockup sample after accelerating aging with 80PVAc/Borax4%	L 31/ a + 12 / b – 28
4	Mockup sample after acceleratin aging Pemulen TR-2	L 26/ +a 13/ -b 29
5	Dust surface on the funeral coat of arms	L 41/ +a 5 / -b 19
6	Clean surface on the funeral coat of arms	L 40/ +a 10/ -b 29

The Table 1. Samples taken with Colorimeter

As a result, the color parameters differ from the sample numbers 5 and 6, with a total number 11 in the color difference. This ended up being considered a big difference in hue and value and seen with an ocular examination. The -b parameter difference indicates that Sample 5 is bluer and Sample 6 has a more yellow hue. According to the article, if the difference is not higher than ΔE* < 2, it means that the difference is not seen for the human eye (Catenazzi, 2017). For example, the color parameter difference between samples 1 and 2 showed a slight variation. The aged sample got lighter just on 2 points in color comparison.

The highest measurement was reached by comparing sample 6 with 2. In total number, it reached 14.9 points as a result, which indicated that the original smalt pigment was lighter than the mockup one. Unfortunately, the color differences in samples 3 and 4 were very subtle. Sample 3 just got lighter on 3 points compared with sample 1 color parameters. The sample with Pemulen TR-2 under the

number 4 was compared with a sample before accelerated aging, which is sample 2. The difference is not even visible to the human eye sensitive it changed just for 2.2 points.

5.8 Spectrophotometer

The measuring of color light parameters was achieved by using Spectrophotometer. The intensity of the color was measured by the wavelength of light. The evaluation was done by comparing color differences with the clean sample, which was not aged. The table presented below, the two samples number 6 and 7, shows that the color difference here stays unchanged. The lines marked red are having color change which is considering to be high. The highest color change was with Sample 8: 80PVAc/Borax 4% Aged with the 4.7 total value. While sample 4, which was aged after Nanorestore gel ® Peggy 5, had no change in color comparing with the clean aged sample. This assumes that Nanorestore gels ® will not affect the color properties in the future time.

	Nr	Name	ΔL*	Δa*	Δb*	ΔH*	ΔE*	ΔE00
	0	**Clean sample**						
	1	Aged Sample	3,50598	-1,52318	0,04628	-1,44601	3,82284	2,82679
	2	Agar 6 % not aged	1,02484	-0,26394	0,1408	-0,20795	1,06761	0,75412
	3	Agar 5 % Aged Sample	1,86267	-0,80166	-0,32864	-0,86304	2,05431	1,56837
	4	Peggy 5 Aged Sample	3,65262	-1,25603	-0,10425	-1,23223	3,86395	2,86941
	5	Pemulen TR2 Sample Not Aged	3,52358	-1,40661	2,60281	-0,55762	4,60096	2,80021
	6	Peggy 6 Not Aged	0,02172	-0,10981	0,57776	0,07577	0,5885	0,3004
	7	Borax 4% Not Aged	0,33089	-0,29071	0,5821	-0,09668	0,72995	0,33917
	8	Borax 4% Aged	4,43182	-1,65943	0,66925	-1,39721	4,7794	3,42086

Table 2. Samples taken with Spectrophotometer

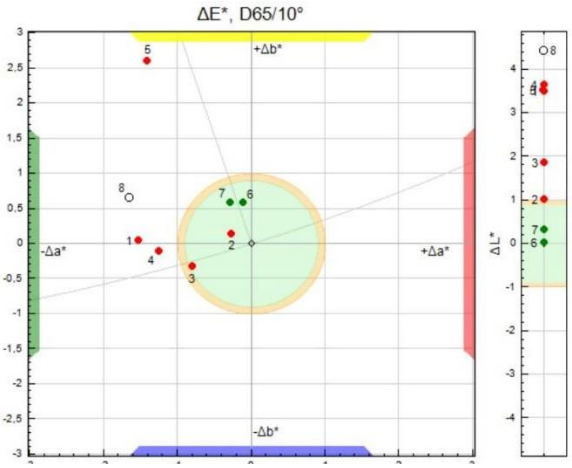


Figure 15 The Spectrophotometer graph

The diagram to the left depicts the color position points listed in the table above. The ones which are closer to the comparing sample: *Clean sample* is marked with green color.

5.9 Accelerating aging examination

This examination was focused on the investigation of any particular effects on the substrate surface using the hydrogels. The 12 samples were subjected to accelerating aging to evaluate the reaction and any effects of temperature and relative humidity with UV-light exposure. The following samples are listed in the table below.

Nº	Name of the Hydrogel	Sample application time	Changes after Accelerating Aging
1	Agar 10 %	1 min	No difference observed
2	Agar 10 %	10 min	No difference observed
3	Agar 2 %	30 sec	Appearance is slightly lighter
4	Agar 2 %	1 min	Appearance is slightly lighter
5	Agar 5 %	1 min	No difference observed
6	Agar 5 %	1 min	No difference observed
7	Nanorestore HWR	30 sec	No difference observed
8	Nanorestore HWR	1 min	The minor difference observed, small marks.
9	Nanorestore Peggy 6	30 sec	Changes in color value. Lighter appearance. The hydrogel is not causing this reason.
10	Nanorestore Peggy 5	30 sec	Changes in color value. Lighter appearance. The hydrogel is not causing this change.
11	80PVAc/Borax 4 %	30 sec	The areas where 80PVAc/Borax 4 %, was used is significantly lighter
12	80PVAc/ Borax 2 %	30 sec	The areas where 80PVAc/Borax 2 % was used is significantly lighter

Table 3. Samples taken with Accelerating Aging

After the measurements, the results of color parameters were unchanged. The most significant change was measured with Colorimeter. On the sample with 80PVAc/Borax 4 %, the average ΔE* value reached 3.16 of the color change parameters.

5.10 The tape method examination

To examine any possible changes and defects of the paint layer on the mockups after accelerating aging. The scotch tape test was applied. It is used to document the chalking amount of the coating after using adhesive tape. It was recommended to use commercially available, flexible tape and transparent (Standard 11266, 2014). The norms were used from International Standard ISO 4628-6 for the evaluation of degradation of coatings. The smalt pigment in itself is very coarse-grained in its characteristics. Therefore, the examination was performed on the mockup sample before and after accelerating aging. After the accelerating aging, a slightly more significant amount of pigment was noted on the scotch tape. It indicates that pigment chalking condition on the funeral coat of arms is more prone to pigment pick-up when hydrogels are employed.

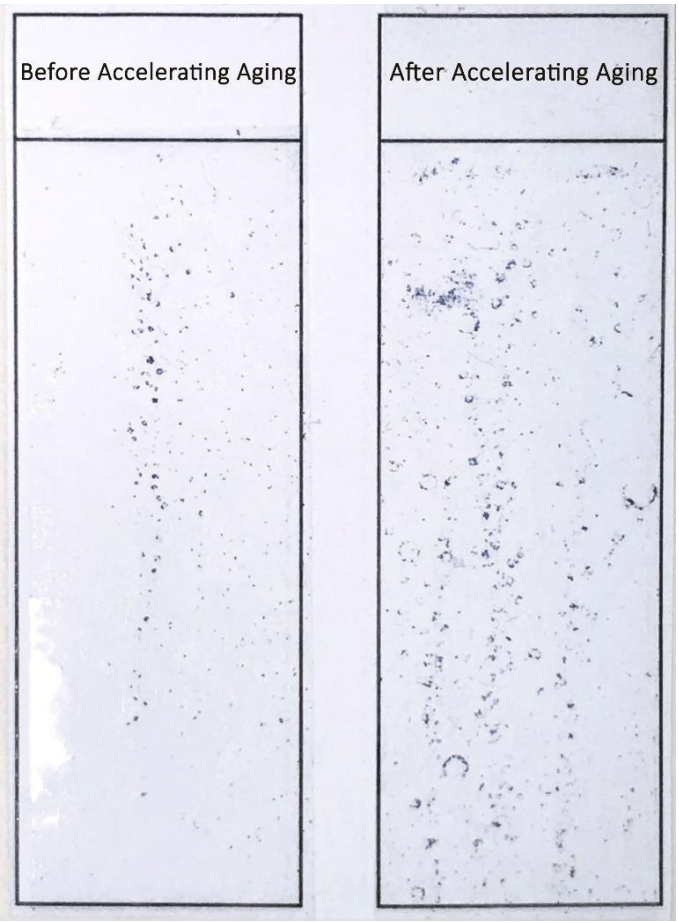


Figure 16 The tape method taken from mockup surfaces

6. Discussion

The investigation on the funeral coat of arms (KLM 014946) material composition showed that it is not that common in its ingredients. The results of ATR-FTIR showed that the binding component was from egg protein for the ground layer and mainly form the albumin part. This component is creating a very fragile and unstable hydrophilic appearance. The pigment was indicated by making XRF analyses together with the examination of cross-sections. The result was that pigment is smalt,and during the "Stormakstiden" it was one of the most used paints, including indigo blue. .

6.1 The dry-cleaning methods results

The dry-cleaning materials are easy to use and prepare. Moreover, their limited cleaning action in comparison to wet-cleaning methods, are having some advantages. In particular, when we are bringing up ethical aspects. After testing the materials, it was proved that the Akapad sponge is not suitable for this purpose. The unvarnished matte tempera required more delicate cleaning methods. During the test, the Yellow micro-fiber cloth had a good result when extracting the dirt from the surface with a minimal pigment-pick-up. The Evolon-CR© had some issues when testing it on mockup substrates. The material was leaving residues in the form of fiber threads. This happened to the sharp, potassium glass fractions in the smalt pigment, which scraped out the filament fibers out. The Yellow micro-fiber cloth remained stable at this specific point.

Nevertheless, the pigment smalt degrades over time, and on the original polychrome sculpture, the dry cleaning material Evolon-CR© might perform differently. The smalt pigment is not just changing the color during aging but also get changed in its chemical and physical properties in the paint film. The scientific literature reports that the shrinking of glass can appear when a large number of alkaline components are leached. The contraction of the glass can be at around 14wt% K_20. (Spring et al., 2005) This fact should be taken to account, and Evolon-CR© should not be expelled from the list. Because when the material was tested on the original pigment layer on the banner, it had a good result. The absorption of the dust and grime layer was high, and no damages were observed on the paint layer, or either no pigment pick-up was seen on the non-woven filament surface.

The make-up sponge showed exceptional results, with no problematic specifications observed through the microscope or the ocular examination. The cleaning action of this soft textured material cant be examined in this research on the original surface. Although, one of the researches on the dry cleaning material showed SEM analyses images of the cleaning action of the make-up sponge (QVS) on an unvarnished gouache painting layer(Daudin-Schotte et al., 2013). Where the sponge imbibes the dirt without bringing any damages to the surface of the substrate.

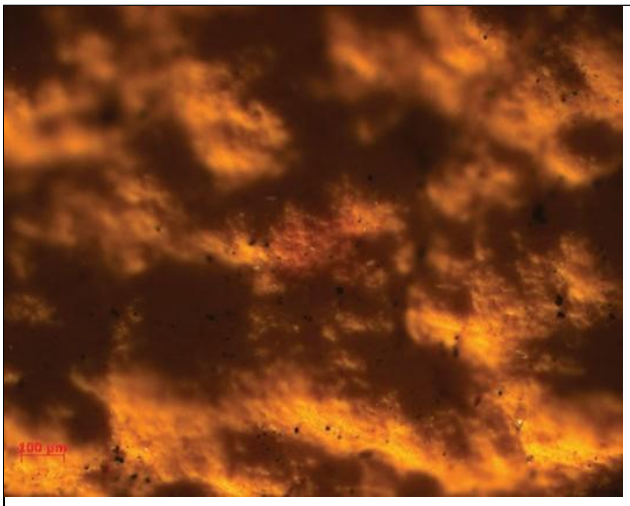


Figure 18 Before cleaning

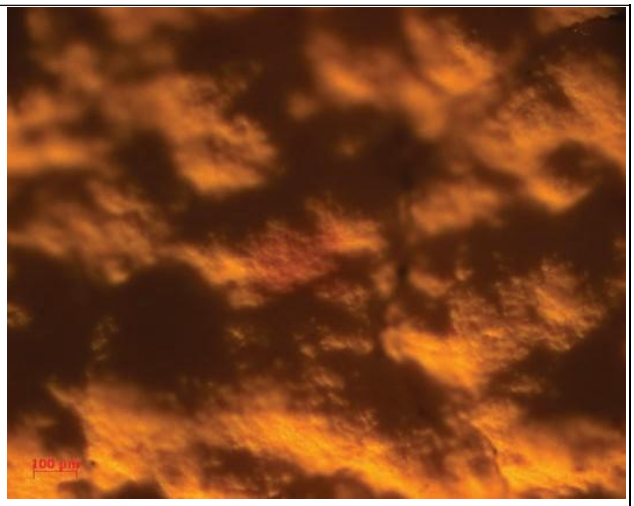


Figure 17 After cleaning

Cadmium yellow gouache sample, (raking) light microscopy at 100× magnification, (left) before and (right) after testing with rinsed polyurethane ether make-up sponge (QVS). The topography is preserved, which is confirmed with SEM observations (Figure 3). Images are taken from the article *"Dry Cleaning Approaches for Unvarnished Paint Surfaces"* (Daudin-Schotte et al., 2013)

The sponge from article research is an organic material, and therefore the result can be taken to account. Since, make-up sponges have a very similar structure from one brand to another, with very narrow capillaries. (Eipper, 2018) Thus, we can conclude that make-up sponges are suitable for precise and light cleaning because research has proved that the makeup sponge has a good affinity to dust agglomeration when it comes to contact with the smooth surface of the paint surface.

6.2 The wet-cleaning methods result

When we mention the wet cleaning treatment, the smalt pigment proved to be water-sensitive to mechanical wet cleaning with a cotton swab and saliva. Consequently, it was necessary to use a cleaning method that did not involve mechanical surface treatment and controlled the amount of water injected into the sensitive colors.

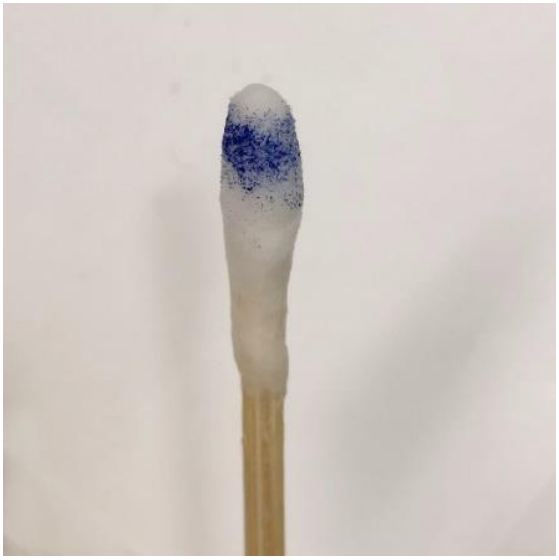


Figure 19 The cotton swab moistened in deionized water after evenly rolled on the pigment smalt layer.

Figure 20 The cotton swab moistened in saliva after evenly rolled on the pigment smalt layer.

The Nanorestore Peggy gels 5 and 6, due to their chemical composition, had lower liquid retention than the HWR and MWR gels. Consequently, this led to a source of trouble that appeared in a non-acceptable amount of pigment pick-up. The common characteristic of all Nanogels is that they are solid gels. That can eliminate mechanical movement and reduce the amount of moisture released on the painting surface. The amount of water exposure to the painting layer is significantly reduced compared to agar-agar gels results (Baglioni P. C., 2015). Nanogels work in such a way that their contaminants are either drawn directly into the gel or can swell the dirt, and then the grime can be removed with a cotton swab. Moreover, the easy and straightforward way of peeling off the gel from the surface ensures that no detectable residues will be left on a substrate surface.

After using HWR and MWR Nanorestore gels®, they indeed showed exceptional results. Besides, the problem is that it is hard to examine this research on the original work. Therefore, it is hard to state if

those gels will work adequately with the integrated dirt on the banner from Kalmar Castle. The rigid gels can have weak adhesion to the surface due to the low viscosity properties, which may decrease cleaning ability.

The situation with the agar-agar gels with different percentage showed even result, where some of the parameters were increasing and simultaneously other decreasing. For example, the swelling issue occurred to a higher degree with a higher percentage even though it has eminent liquid retention. Withal, the application time was extended. Because, as soon as the percentage is elevated, it needs more time to perform a working cleaning action. The agar-agar gels with 2% (w/v) concentration were left with a 60sec period time.

On the other hand, agar-agar with 10 % concentration had to be on the surface for up to 10 min. However, the balance was achieved with the agar-agar gel 6%, which was placed for 60 seconds. It showed an acceptable result without any pigment pick-up as soon as the time was increased up to 3 min. Some visible pigment pick-up was observed on the edges (Fig. 46)

The agar-agar with a 2% percentage had an unclear presentation. The variation of the pick-up amount from a slightly visible to a considerable amount of pigment particles was caused by using different gel sides. The side towards the bottom of the petri dish had more liquid consistency than the side closer to the lock. This problematic case caused an uncertain presentation of the gel. Therefore, it is recommended to blot the gel's side on the filter paper properly. Because agar-agar gels are causing excessive and uncontrolled wetting of the surface.

Among the various hydrogels applied on a substrate, the biggest failure faced the 80xPVAc/Borax gel and Pemulen TR-2 type. The nonacceptable result with a major pigment pick and the non-an easy way of using it during the application, confirmed that those gels are non-applicable for further analyses. The high viscosity of the gel caused a problem while removing the gel from the substrate. It became sticky and left a visible number of residues on the surface, even after cleaning the excess with the cotton swab. The residues were noted with SEM image analyses.

Several problems appeared during the use of the 80%PVAc/Borax gel. One of them was a non-controllable application way. Due to the non-solid consistency, the gel appeared to have a high fluid composition and was attaching to the surface in free form. That might lead to uneven cleaning results on the object. Compared to chemical gels, which can just be applied horizontally, the physical 80%PVAc/Borax gel can be applied vertically.

Also, the preparation of 80%PVAC/Borax was not that easily achievable. One of the problems was that the gel-shaped appearance while diluting the 80%PVAc with Borax was not happening every time. The total fatality was happening multiple times until it was possible to master the excellent preparation result of the gelification process. It turned to be a very time-consuming process, with an unacceptable outcome.

The Pemuel TR-2, compared to 80%PVAc/Borax, had its consistency way more liquidy and had a tenacious quality. It was too sticky to the surface, which led to permeable action onto the surface of a substrate. Many residues occurred in the form of thick irregular layers. The application through Japanese paper and Evolon- CR© with an application time of 30 minutes did not show any good result of the strong absorbancy of the cleaning agent. The surface of the substrate turned to be moderately swelled from the moisture effect.

Additionally, the Pemulen TR- 2 gel is made with the addition of triethanolamine (TEA), and it can also leave residues, which can provoke future deleterious effects (Burnstock, 1992). This is happening due to the low vapor pressure of the amines such as TEA. That is why Pemulen TR- 2 cannot be applicable for the use of water-sensitive materials and especially unvarnished ones. It can be more useful to apply on the oil paintings with the varnish problems since it has three primary alcohol end groups that can work as a solvent agent in the gel (Sofia Hennen, 2017). On the other hand, the preparation of the gel was easy, and the gelification result was achieved with the first try.

To avoid the residues left from the base used in Pemulen TR- 2, we can use the Mineral alkali as NH_4OH. The research was made by comparing different base materials used together with Pemulen TR- 2. This compound showed promising results when it came to residue criteria and was proved by different authors such as Ahedo Pino, Cantos Martines, and Cremonesi (Ahedo Pino, 2014) (Pino, 2011). Nevertheless, it is a volatile base and can cause some harm to the user because of the mercury and copper parts. Further investigations on Pemulen TR- 2 were abandoned because it can be mechanically weak to be removed without leaving polymer residues.

Concluding the discussion chapter, all of the materials have different properties and are acting differently depending on the task they are facing. One of the hydrogels, gellan gum, was not tested in the research as planned. Due to Covid-19, it was delays and cancelations in postal services, and therefore it was decided to discard it from the list. For future investigation, it will be suggested to try the gellan gum gel on the mockups when the better times arrive.

7. Conclusion

This work has researched various cleaning materials, on the pigment smalt. The problematic material had been identified by being hydrophilic by testing it with swab test moisture in deionized water and saliva. To identify a safe treatment for the banner (KLM 014946), research tested dry-cleaning methods and hydrogels. Their properties were analyzed and discussed, describing their advantages and disadvantages. The result showed that a safe material that does not leave residues and not having pigment pick-up issues was Yellow fiber cloth and hydrogel Nanorestore Gel ® HWR. However, all the materials were tested on the mockup substrates, and the cleaning efficiency was not possible to observe. During the conservation treatment, the Evolon-CR© was tested on the original banner surface during the cleaning. It performed an efficient cleaning of the superficial layers of dirt, combined with a soft brush and vacuum cleaner with – HEPA filter. Whereas, examining the Evolon-CR© on mockups, the paint surface turned sharper and more porous which, caused some fiber residues after usage. While using it on the banner, nothing was detected in the microscope.

Suppose there will be needful in removing the ingrained dirt and performing a partially cleaning treatment. It will be suggested to try out Nanorestore Gel ® HWR and MWR. The cleaning efficiency might be lower in HWR than MWR due to higher liquid retention and more rigid composition, which might not allow close contact with the porous paint layer. Both of the dry hydrogels showed not cause any changes to the surface after accelerating aging. Moreover, no residues were detected in SEM analyses.

The gap in cleaning treatment knowledge with hydrogels on water-sensitive unvarnished tempera pigment was investigated in this work. This study can be used as a stepping stone for future research in this field.

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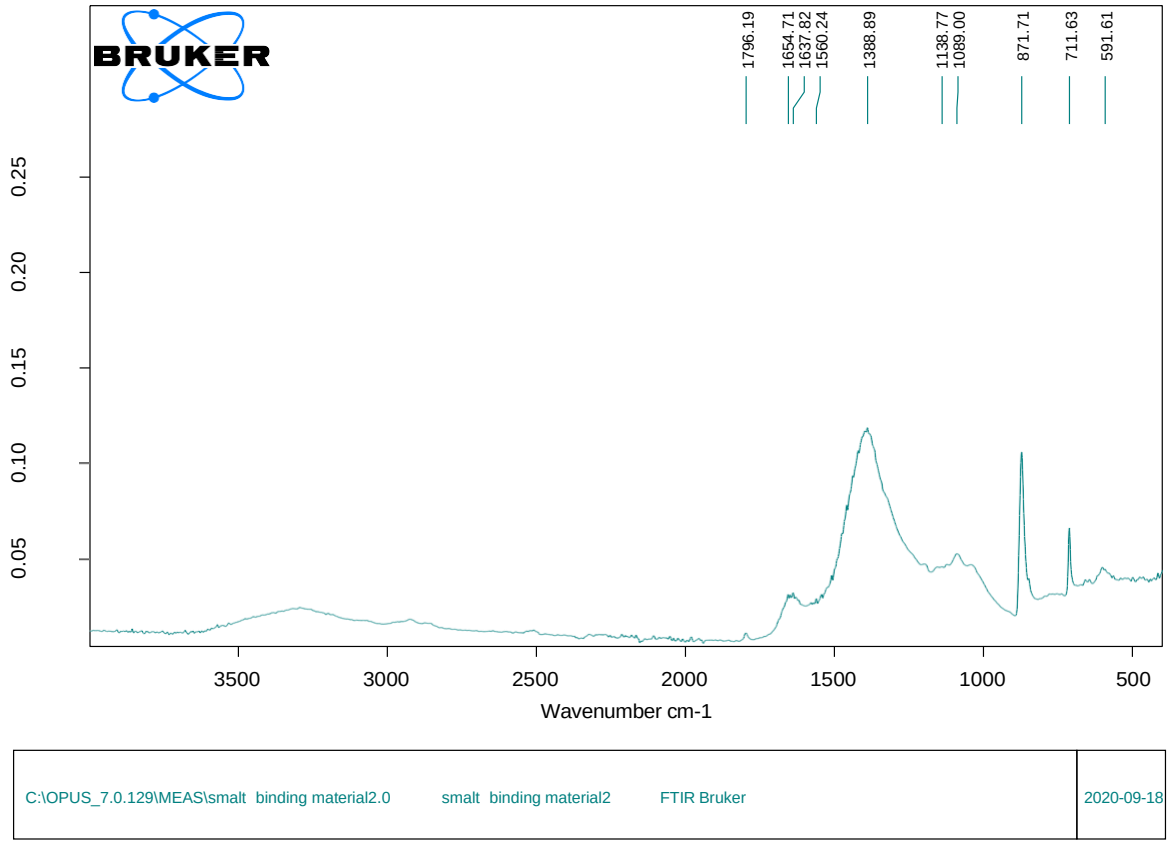
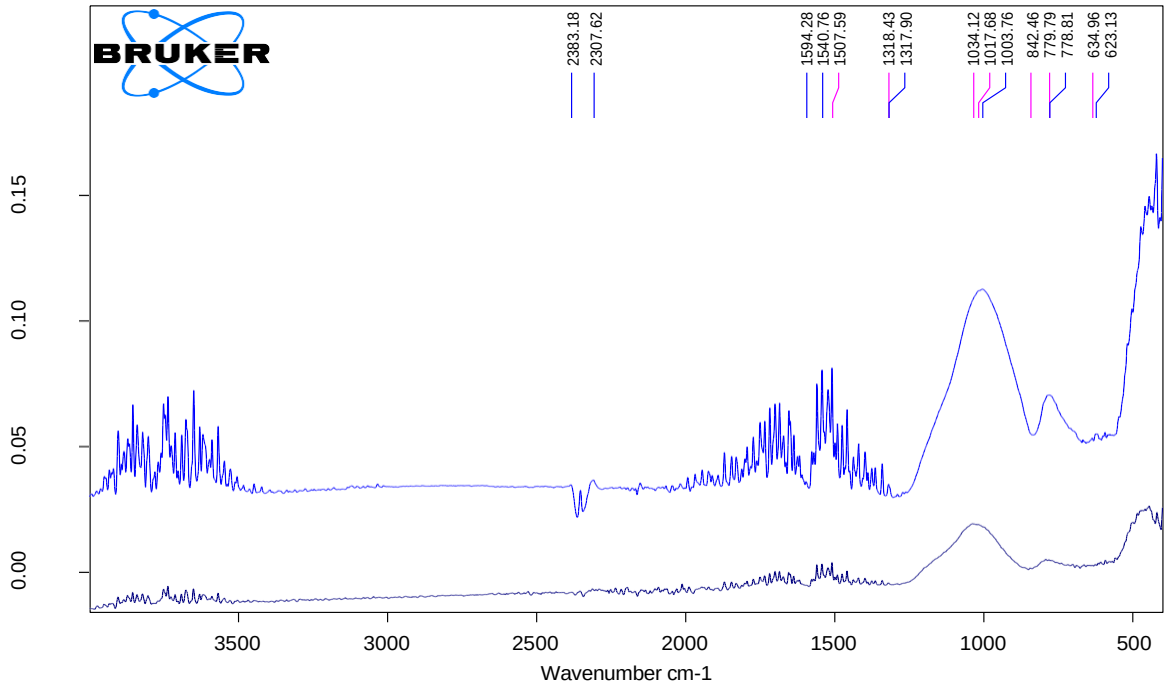
Appendix

ATR-FTIR Analyses



Resolution	4 cm-1
Scans	100
Range	4000-400 cm
Detection	RT-DLaTGS detector

Figure 21 ATR-FTIR of Blue pigment sample taken from the KLM 014946 object



C:\OPUS_7.0.129\MEAS\smalt grain.0	smalt grain	FTIR Bruker	2020-09-18
C:\OPUS_7.0.129\MEAS\smalt fine.0	smalt fine	FTIR Bruker	2020-09-18

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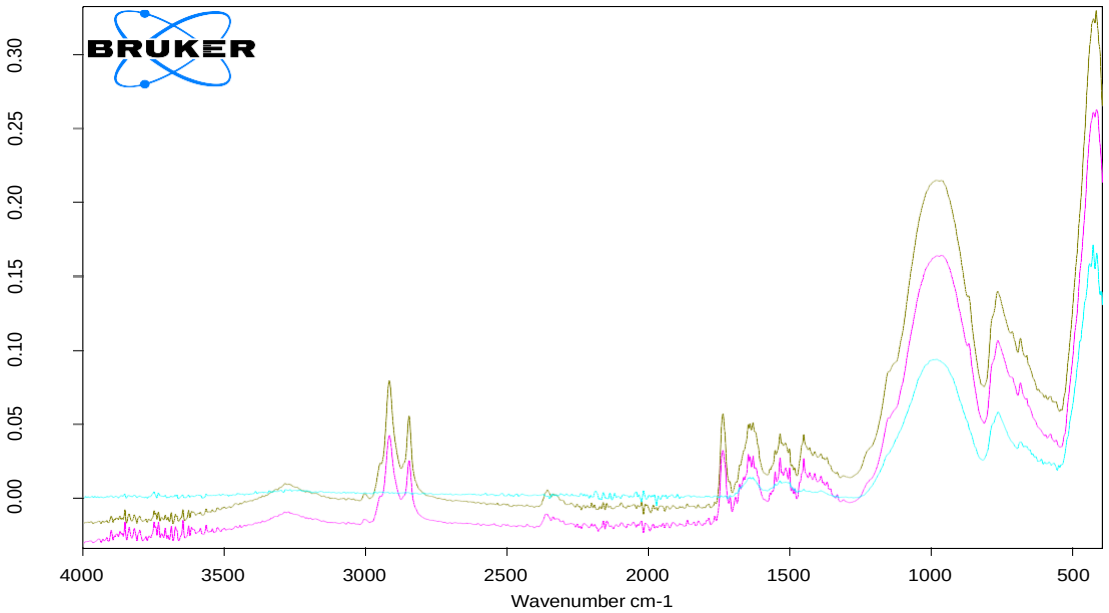
Figure 22Blue pure pigment Smalt taken for the comparative analyses



C:\OPUS_7.0.129\MEAS\Smalt with egg white only pigment.0	Smalt with egg white only pigment	Bruker	2020-10-19
C:\OPUS_7.0.129\MEAS\Smalt with whole egg only pigment.0	Smalt with whole egg only pigment	Bruker	2020-10-19
C:\OPUS_7.0.129\MEAS\Smalt with egg yolk only pigment.0	Smalt with egg yolk only pigment	Bruker	2020-10-19

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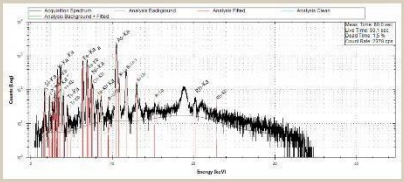
Figure 23 The comparative FTIR- analyses to detect binding media in mock - up samples.

XRF- analyses

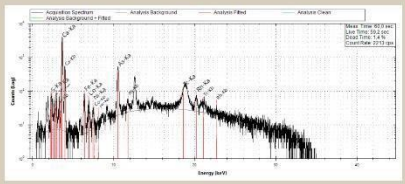
Blue “1”



Analysis Results:

Element	Concentration	Error
Si	61,19%	±4,68%
Ca	12,67%	±1,66%
K	12,37%	±2,04%
S	7,86%	±7,84%
As	2,23%	±0,64%
Fe	1,39%	±1,36%
Co	1,3%	±1,28%
Bi	0,43%	±2,09%
Ni	0,38%	±2,22%
Ti	0,14%	±8,68%
Zn	0,04%	±5,8%

Blue “2”



Analysis Results:

Element	Concentration	Error
Ca	91,4%	±0,56%
S	4,28%	±8,91%
K	1,46%	±4,47%
As	1,44%	±1,24%
Tc	0,64%	±2,11%
Fe	0,49%	±3,68%
Co	0,18%	±6,32%
Ni	0,11%	±6,21%

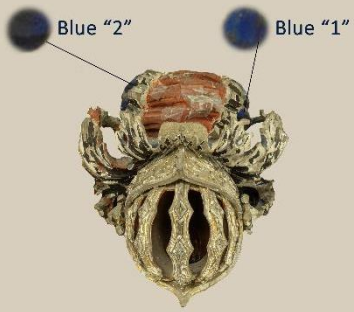


Figure 24 XRF- analyses of the blue pigment

Optical Microscopy

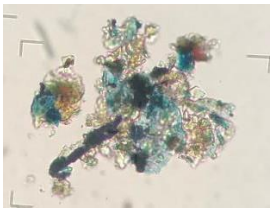


Figure 28 Microsample image

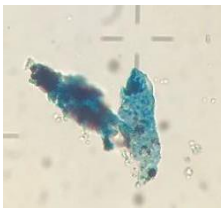


Figure 27 Microsample image

Figure 26 Microsample image

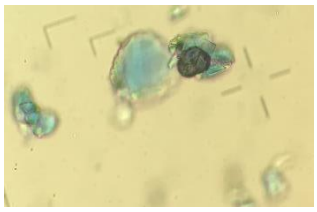


Figure 25 Microsample image

Microscope photo

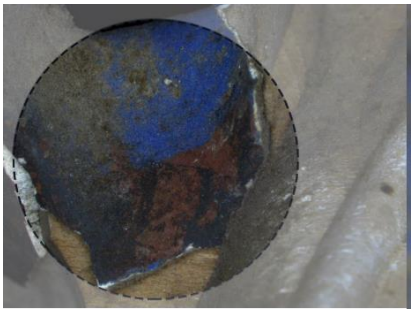


Figure 29 Photo made with microscope Leica, shows blue paint under the dust layer.

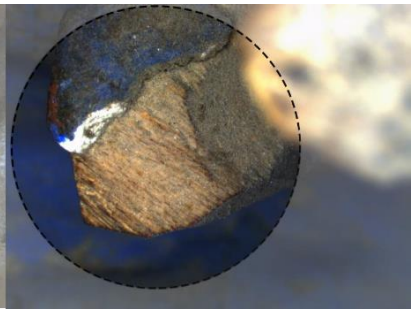


Figure 30 Photo made with microscope Leica, shows a thick ground layer with a thin blue paint application

Cross -section

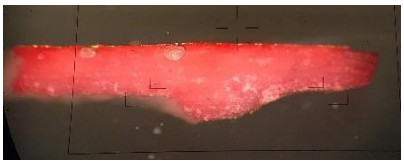


Figure 31 Before Staining

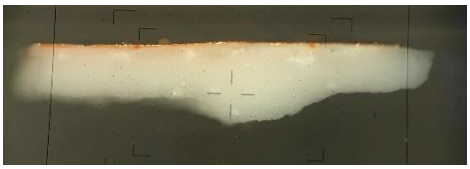


Figure 32 After staining with Ponceau S

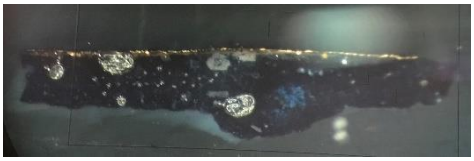


Figure 33 After Staining with Sudan Black

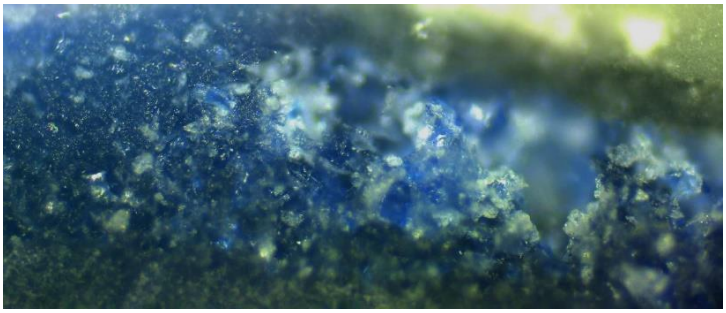


Figure 36 Cross-section pigment Smalt

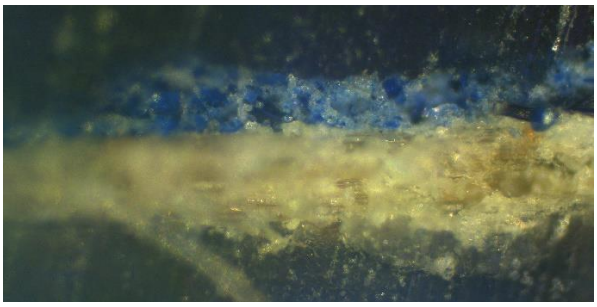
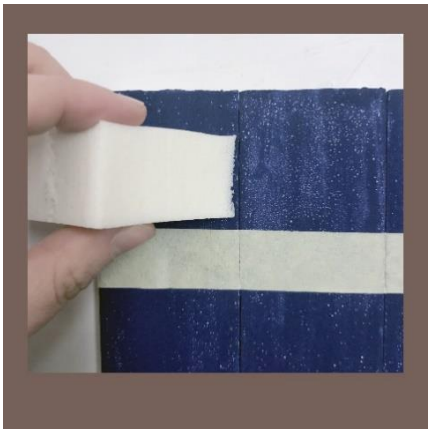


Figure 35 Cross-section Pigment Smalt

Figure 34 Drawing of the blue paint cross-section. 1. Wooden surface 2. Ground layer 3. Smalt pigment



The Table of 32 Samples taken to test Cleaning methods

Dry-Cleaning systems	Application Characteristics	Observation	Residues
Yellow micro-fiber cloth	The fiber cloth was gently applied to the substrate. And removed right after.	The cleaning performance was easy, the light application had a negligible amount of pigment particle. This happened just in the area where the light pressure was used.	None
Evolon-CR	The non-woven textile was applied gently and kept in place with light pressure from the brush above.	The use of Evolon-CR performed with a good result. No particles were observed on the surface.	A small amount of non-woven parts were attached to the substrate due to sharp particles from the glass contained in pigment Smalt.
Make-up sponge	The sponge was used as an eraser with a one-way removal direction.	The use of the sponge was soft and delicate in use. A very slight amount of pigment got attached to the sponge's porous surface right on edge, where more pressure was applied.	None
White Akapad sponge	The sponge was used as an eraser, applied with one-way move direction.	The use of the Akapad sponge was hard to apply due to its porous characteristics. A small amount of pigment got attached to the cleaning agent.	Due to its textured surface, a significant number of residues in form of white porous fragments of the sponge got attached to the substrate.

Wet-Cleaning systems	Tailored options	Time Application	Application characteristics	Observation	Removal
Aqueous media	Deionized water		A cotton swab was moistened in deionized water and rolled in one direction over the substrate.	A major amount of pigment particles was attached to the cotton swab. The deionized water was very harsh in use.	
Enzyme solution	Saliva		A cotton swab was moistened in saliva and rolled in one direction over the substrate.	A significant amount of pigment particles was attached to the cotton swab. Uneven distribution of the solution.	
Nanorestore Gels	HWR (Max dry)	30 sec 1 min	All the gels were blotted in a filter paper on each side, it was applied on the surface with a light pressure to remove air in between.	A negligible, near to the not visible amount of pigment particles were observed on the cleaning agent. The 2 min application had more pigment	The gels were removed with the pincette, without using any mechanical action.

				pickup from the substrate.	
	MWR (Extra Dry)	30 sec 1 min		A slight amount of pigment pick-up was observed on the cleaning agent.	
	Peggy Gel 6	30 sec 1 min		A major amount of pigment pick-up was detected, which was distributed all over the gel.	
	Peggy Gel 5	30 sec 1 min		A marked amount of pigment pick-up was detected, which was partially distributed on the gel surface.	
	Peggy Gum 6		The gum was used as an ultra-delicate	A major amount of pigment pick-	

			eraser on the substrate.	up was taken during the cleaning application	
	Peggy Gum 5			A marked amount of pigment pick-up happened during the application.	
Polysaccharide-based gel	Agar-agar (2% w/w)	30 sec 1 min	The gel was cut in a square shape to fit in the 4x4 cm substrate sample area. Before applying the gel, it was blotted on two sides with filter paper.	The gel had a slight pick-up, very important to remove moisture excess properly before use. Because this can have a big effect on the result.	The hydrogel was easily removed with a pallet knife and the hand.
	Agar-agar (4% w/w)	30 sec 1 min		It was a negligible amount of pigment particles attached to the cleaning agent. The result was better with -30	

				sec time application.	
	Agar-agar (5% w/w)	1 min		Each sample showed a different result but compared it with others, it also had a noticeable amount of pigment particles removal.	
	Agar-agar (6% w/w)	1 min 3 min		A negligible amount of pigment was found after 1 min of application. The time application was increased. The visible amount of pigment was seen after 3 min.	
	Agar-agar (8% w/w)	3 min 7min		The application of Agar-agar gel with 3 min	

				time performed an excellent result. The time was increased by 7 min. Partially on the borderlines some minor amount of the pigment particles were attached to the hydrogel.	
	Agar-agar (10 % w/w)	5 min 7 min 10 min		The Agar-agar (10%w/w) had a good performance, with a minimal amount of pigment particles founded partially on the borderline edges.	
Hydrogel	Partially hydrolysed 80% PVAc-borax (2%:1%w/w)	The application time was between 10-30 sek.	Applied with a pallet knife, the gel was spread by its force over the	The gel was interacting with the porous texture of the	The removal of the Hydrogel was not

			substrate surface.	substrate. This led to an extreme pick-up of the pigment.	easy. The excess of the gel was cleaned out with a dry cotton swab.
	Partially hydrolysed 80% PVAc-borax (4%:1%w/w)	The application time was between 10-30 sek.		The gel had a harder and more rigid form compared to the (2%:1%w/w) concentration. The pigment removal from the substrate was on the major level.	
Polyacrylic gel	Pemulen-TR	10 sek	Applied with the wooden spatula, spread over the substrate surface.	The polyacrylic gel went deeply into the texture of the substrate. The pigment was unevenly picked up invisible clusters.	The removal of the gel was hard. It was sticky and stayed in the surface. Removed with a dry cotton swab, with

					the several applications.
		30 min	Applied with the wooden spatula with the Evolon-CR and Japanese paper as a barrier for the substrate.	The surface was moistened with the gel through the barrier film. The slight pigment peel of effect appeared with both methods used.	The removal of the gel was easy, by peeling off the film from the substrate.

Micro images of the analyses

Figure 37 Micro images of dry-cleaning methods

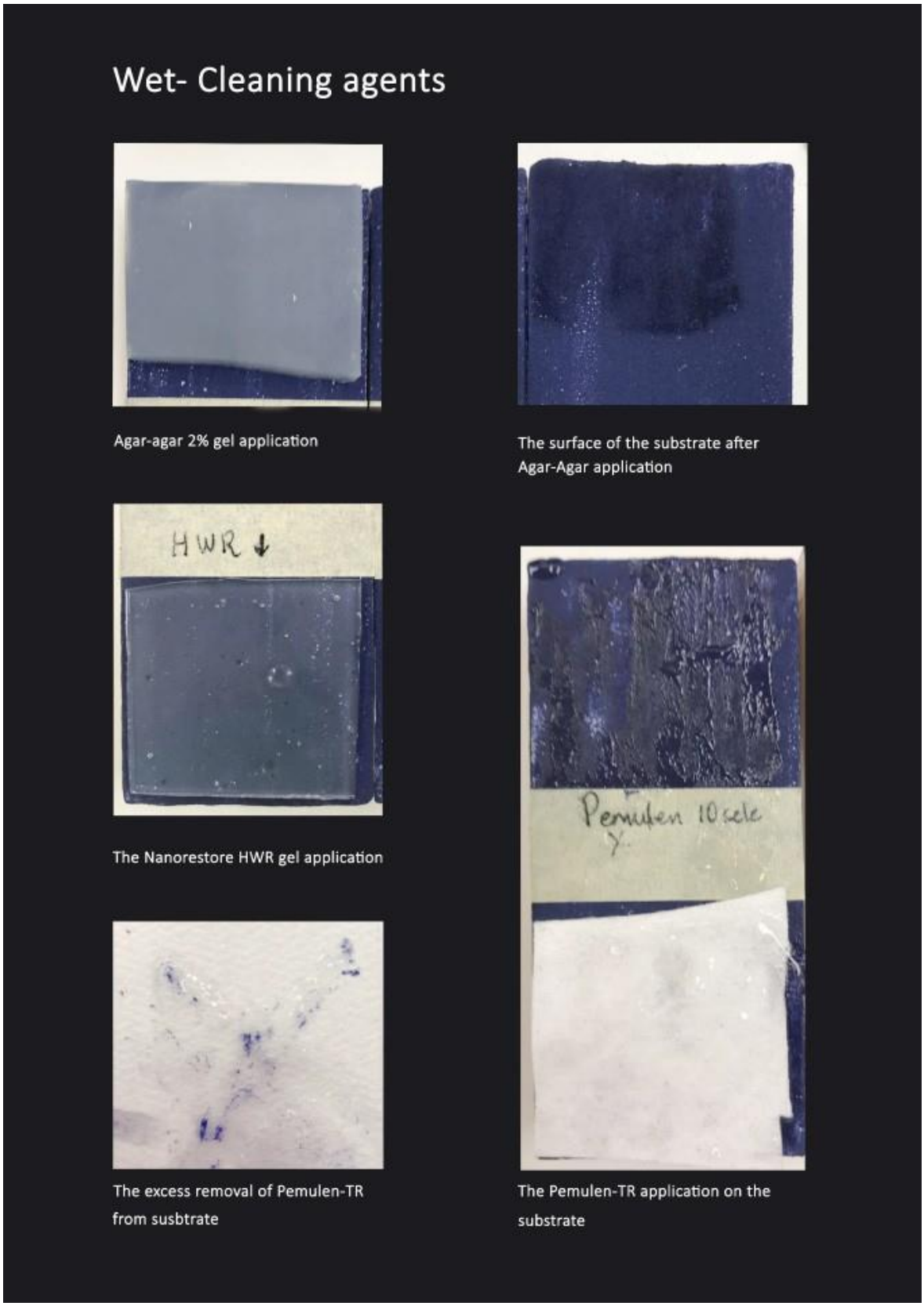


Figure 38 Micro images of wet- cleaning materials

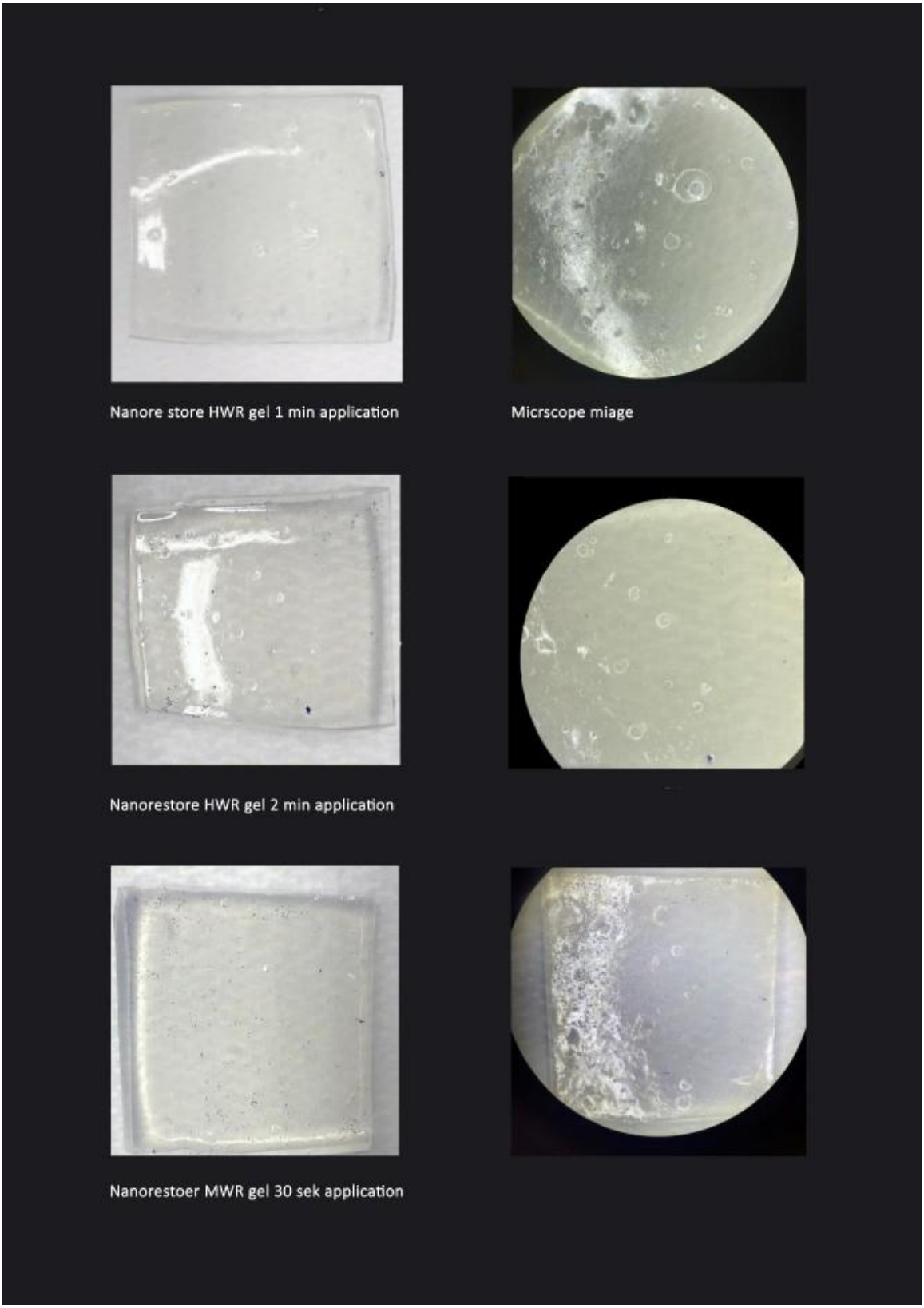


Figure 39 Micro images of Nanorestore Gels HWR and MWR

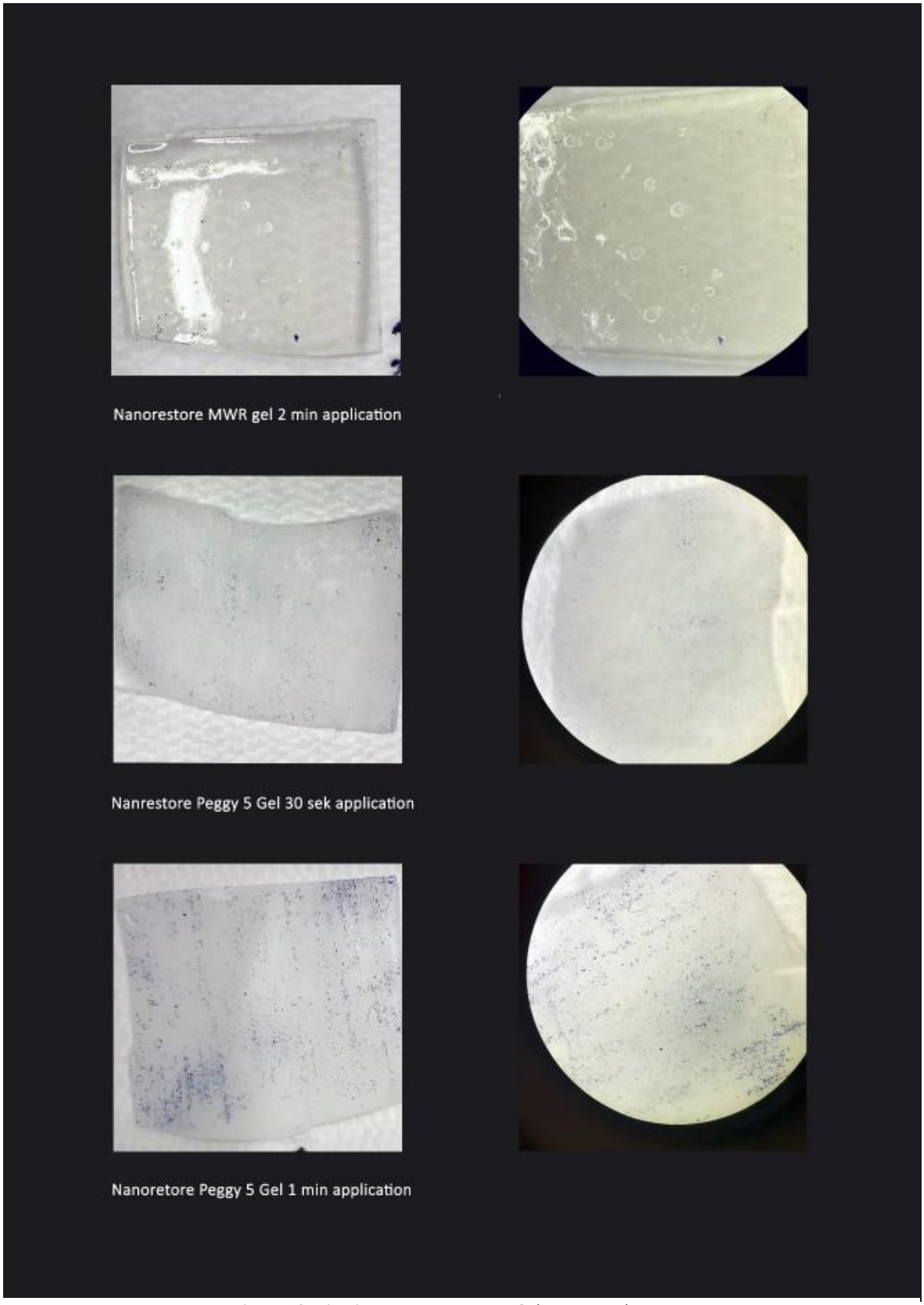


Figure 40 Microimages Nanorestore Gels MWR and Peggy 5

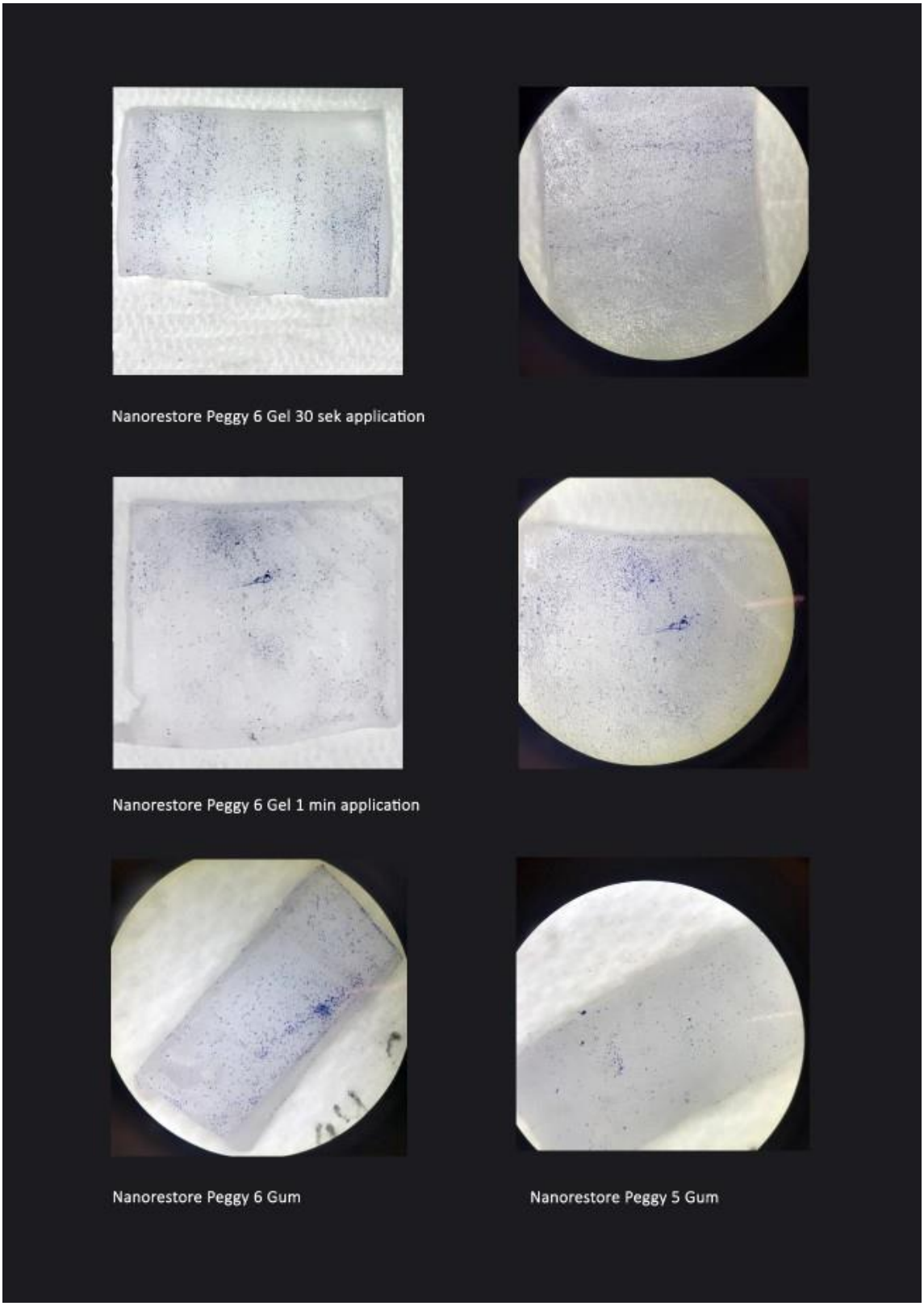


Figure 41 Micro images Peggy 6 Gel and Gum

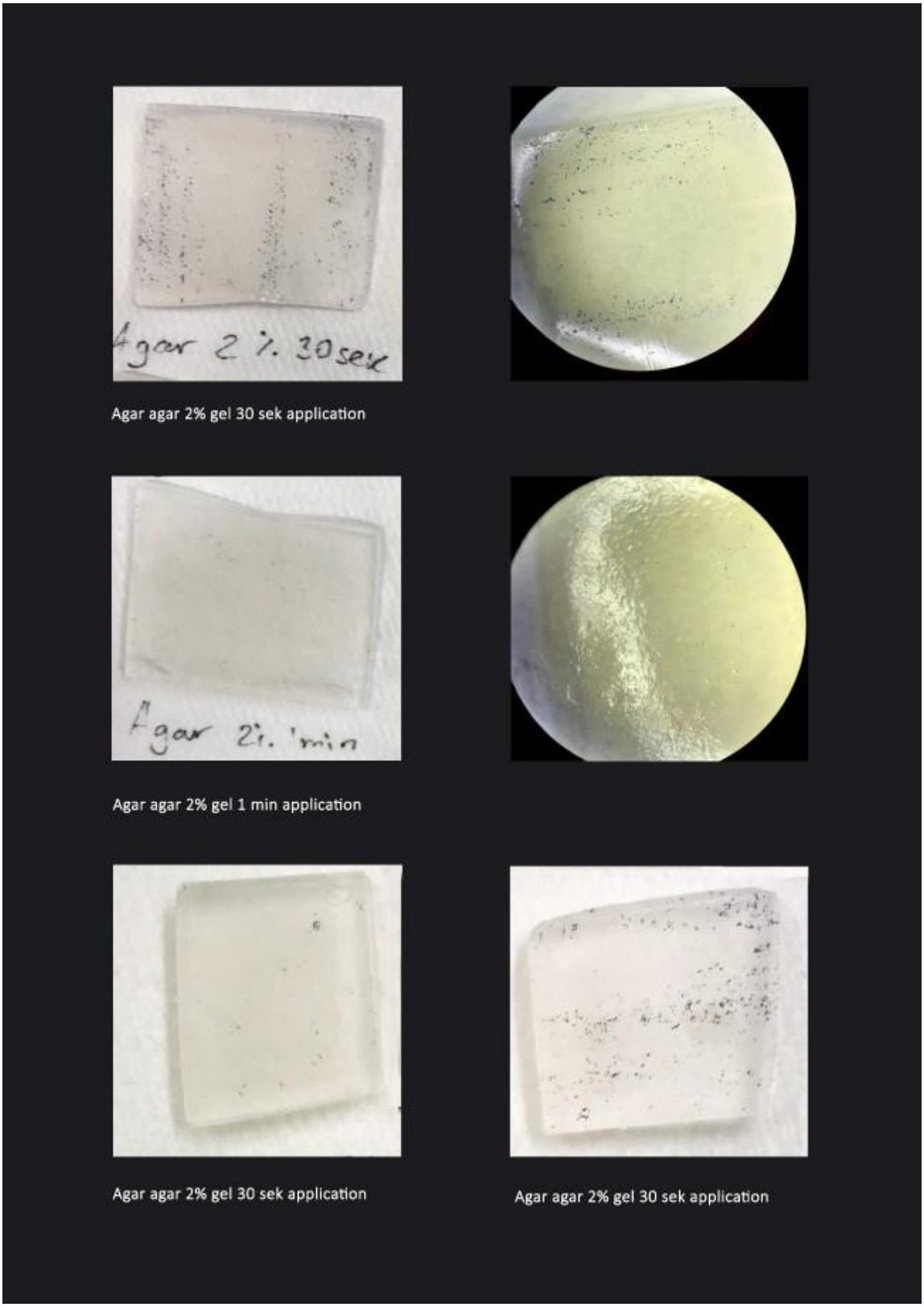


Figure 42 Micro images of Agar - agar gel 2 %

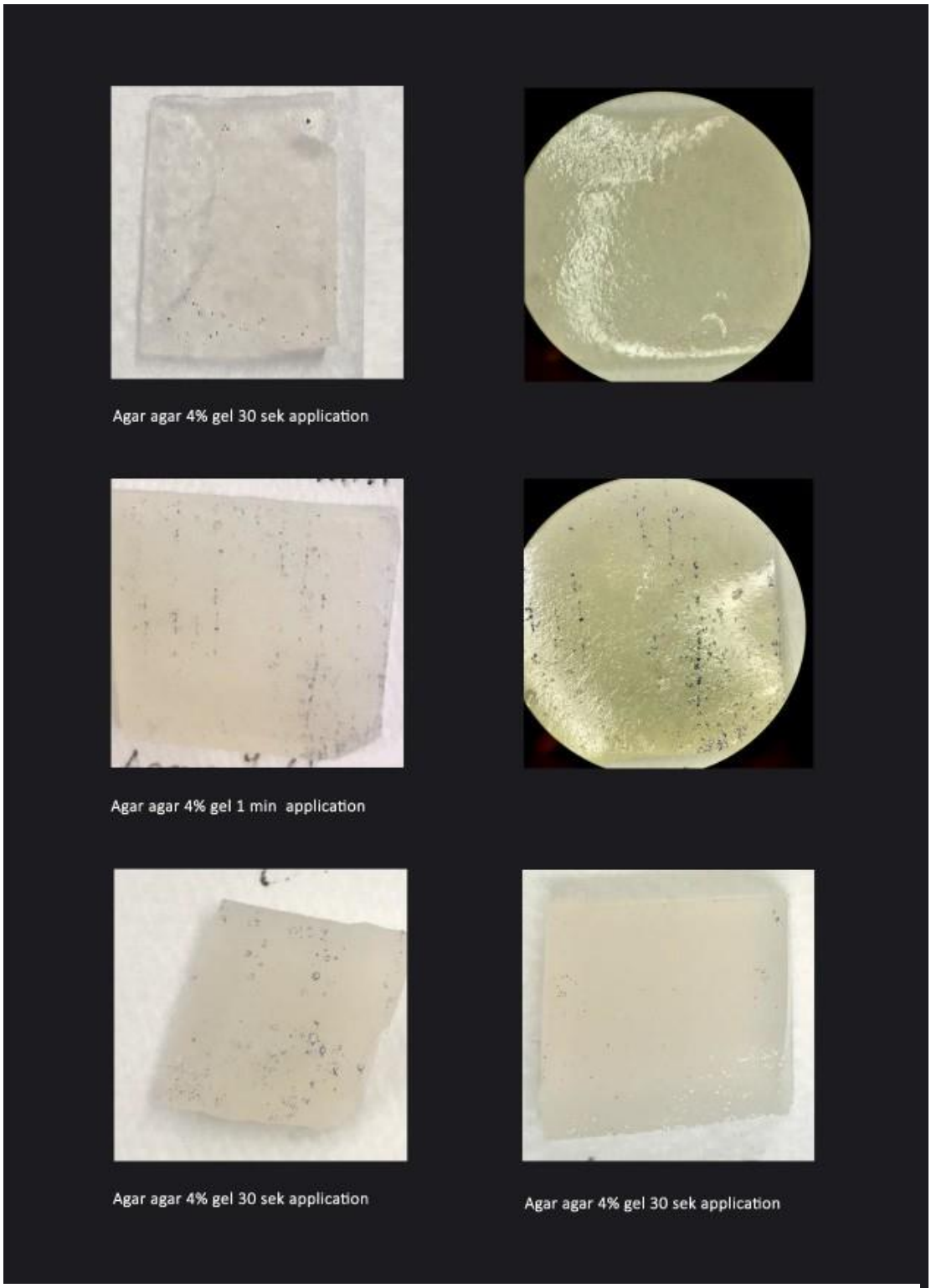


Figure 43 Micro images Agar-agar gel 4%

Figure 44 Micro images Agar- agar gel 5%, 6%

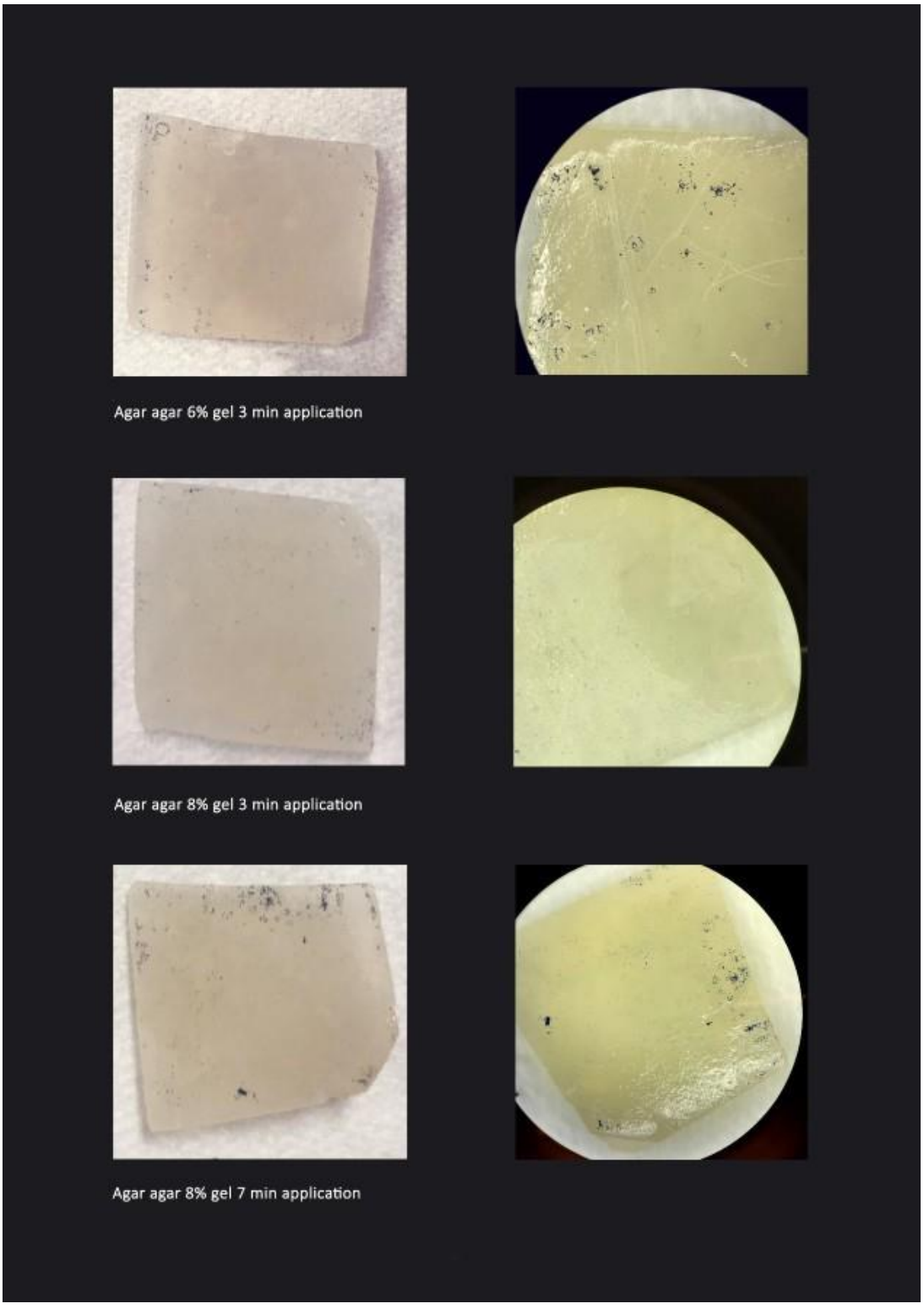


Figure 45 Micro images Agar - agar gel 6%, 8%

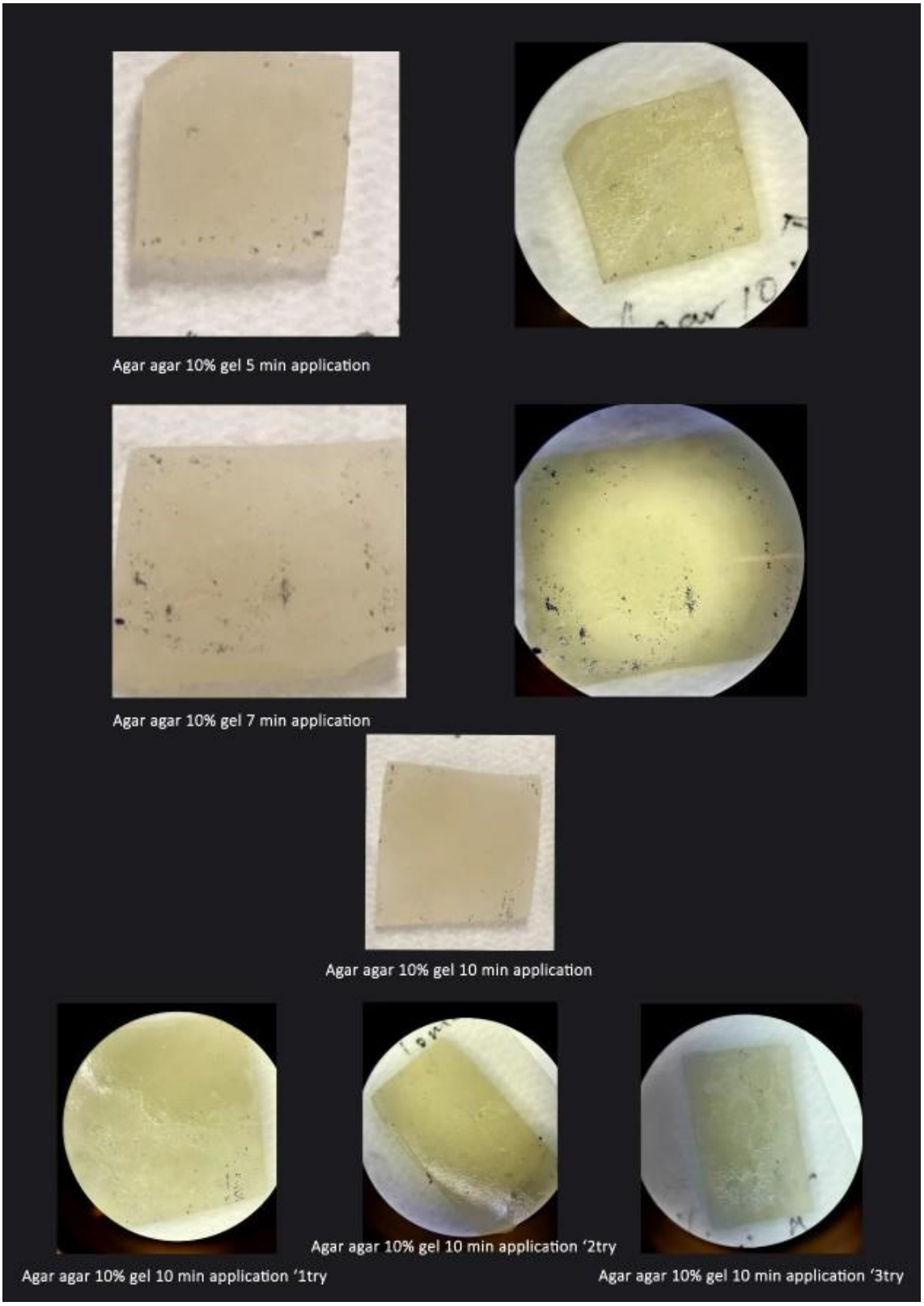


Figure 46 Micro images Agar - agar gel 10 %

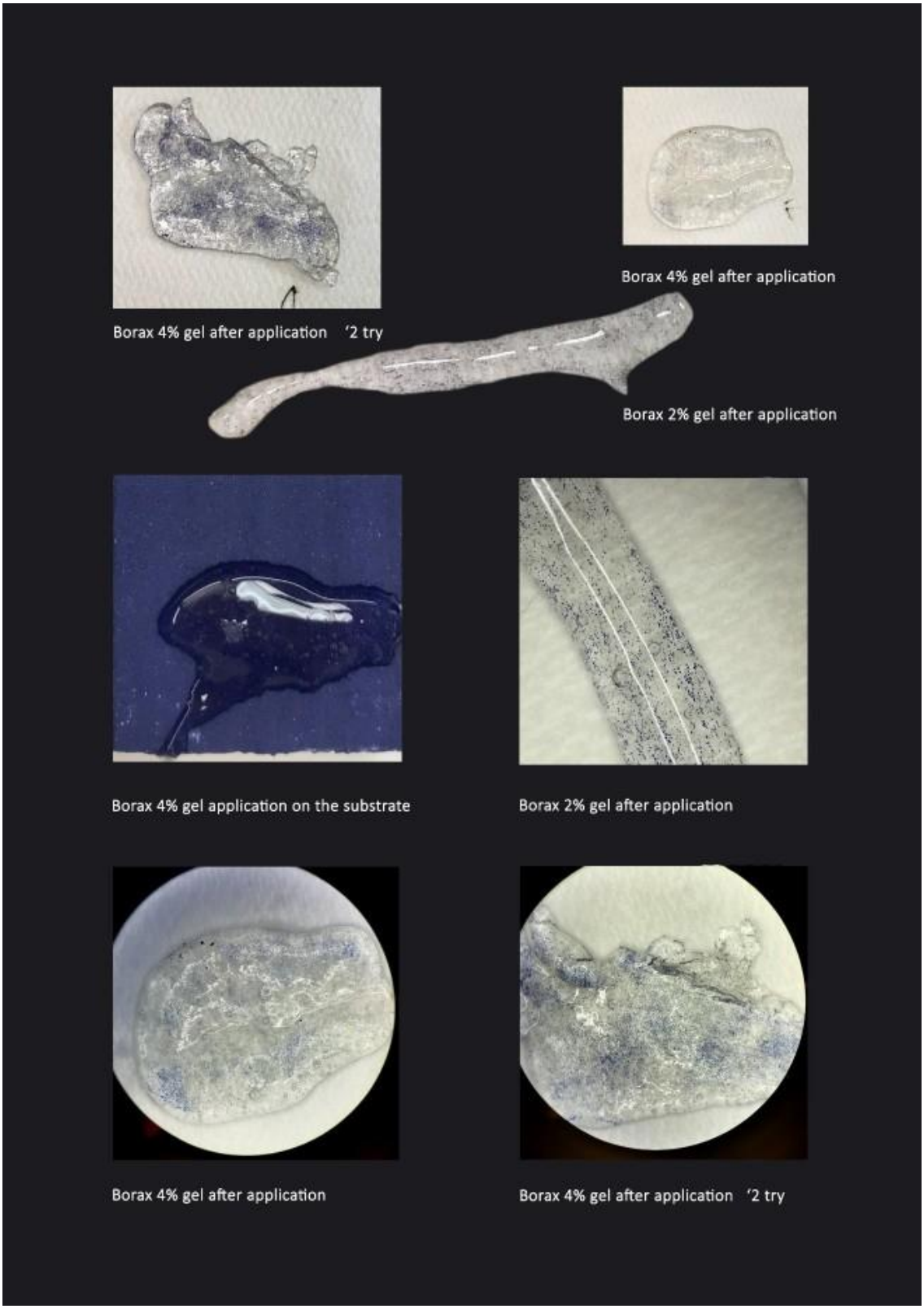


Figure 47 Micro images of 80PVAc/Borax 4 % gel