An Innovative Heat Transfer Method for Solving Old Mending Glued with Proteinaceous Adhesives in Manuscripts and Rare Books

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1 author:

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An Innovative Heat Transfer Method for Solving Old Mending Glued with Proteinaceous Adhesives in Manuscripts and Rare Books

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Examiner:	Prof. Erwin Emmerling
Supervisors of the Partner Institution:	Dr. Irmhild Ceynowa
	Dr. Thorsten Allscher
	Karin Eckstein, M.A.
Submitted by:	Yuhui Liu
Matriculation Number:	03681673
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Yuhui Liu, Munich, December the 18th 2018.

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Abstract

Old mending in bound manuscripts and rare books can cause distortions on pages or new tears right beside the mends due to their stiffness and inflexibility. Additionally, they may also interfere with the readability of the pages as sometimes they cover text and illustrations. Detaching old mending papers glued with protein-based adhesives often requires a combination of moisture and heat. Nevertheless, not only has a uniform and accurate heat application always been difficult to achieve with the common heating tools, but the accessibility to the working area is also restricted when the mends are glued close to the spine fold of a bound volume.

This study aims to introduce a new heat transfer method to the removal of old mends glued with protein-based adhesives through an innovative heating device – the IMAT heater (Intelligent Mobile Accurate Thermo-Electrical Device). This device is a flexible and ultra-thin heat transfer mat based on carbon nanotubes (CNTs), which was developed by the EU-funded IMAT Research Project. The IMAT heater features a rapid thermal response, a precisely controllable and stable heat regulation as well as a uniform heat distribution during a conservation treatment. Owing to its optional size, air permeability and transparency, different needs of specific applications can be met. Furthermore, due to the slight thickness and the flexibility of the mat, it is considered to be ideal when dealing with old mends glued close to the spine fold of manuscripts and rare books.

Experiments with applications and evaluation of coupling the IMAT heater with various hydrogels and Gore-Tex sandwiches are performed. After the investigation, a considerable temperature-related optimization on conservation treatment utilizing the IMAT heater is verified. An optimal working pattern of combining heat transfer with moisture introduction using the IMAT heater is suggested for the future conservation work. Besides, performance of each treatment variation correlated with different humidification sandwiches and treating temperatures is characterized. Finally, conservation treatments on three historical documents from the collections of the Bavarian State Library are successfully conducted: a medieval manuscript (BSB, Clm 18199), an incunable from the early years of printing (BSB, 2 Inc.ca 1726 a) and a printed book from the 18th century (BSB, Diss. 849 d, 16).

Zusammenfassung

Alte Reparaturen in Handschriften und seltenen Drucken können aufgrund ihrer Versteifung und Inflexibilität im Papier neue Schäden, wie Verwerfungen oder neue Risse direkt neben den Verklebungen, verursachen. Außerdem können sie die Lesbarkeit der Seiten beeinträchtigen, da es vorkommt, dass die Schrift oder Buchillustrationen von den Verklebungen abgedeckt sind. Das Ablösen von alten Verklebungen auf Proteinbasis erfordert häufig eine Kombination aus Feuchtigkeit und Wärme. Allerdings ist nicht nur eine gleichmäßige und präzise Wärmeübertragung mit den traditionellen Wärmemedien immer schwierig zu erreichen, sondern es ist auch die Zugänglichkeit zum Arbeitsbereich eingeschränkt, wenn sich die Verklebungen im Falzbereich eines Buches befinden.

Diese Masterarbeit hat zum Ziel, eine innovative Wärmeübertragungsmethode zum Ablösen von Verklebungen auf Proteinbasis in Handschriften und seltenen Drucken in der Praxis der Papierrestaurierung zu erproben. Zum Einsatz kommt die neue Wärmematte – IMAT Heater (Intelligent Mobile Accurate Thermo-Electrical Device). Bei diesem Gerät handelt es sich um eine flexible und ultradünne Wärmeübertragungsmatte auf Basis von Kohlenstoffnanoröhren (CNTs), die in dem EU-finanzierten IMAT-Projekt entwickelt wurde. Die Innovation der Matte gegenüber anderen Wärmemedien sind die schnelle thermische Reaktion, die präzise steuerbare Wärmeregulierung sowie die stabil bleibende Verteilung der Wärme im Objekt während einer Restaurierungsbehandlung. Durch die optionale Größe, Luftdurchlässigkeit und Transparenz der Matte, können unterschiedliche Anforderungen für spezifische Anwendungen erfüllt werden. Außerdem kann die Matte aufgrund ihrer geringen Dicke und hohen Flexibilität an schwer zugänglichen Stellen im Buch als eine optimale Wärmequelle eingesetzt werden.

In der Masterarbeit werden Versuche mit dem IMAT Heater in Kombination mit verschiedenen Hydrogelen und Gore-Tex-Sandwiches durchgeführt. Durch die Untersuchungen kann eine erhebliche auf der Temperatur basierende Optimierung durch die Anwendung des IMAT Heaters in der Restaurierungsbehandlung verifiziert werden. Für die zukünftige Restaurierung wird ein optimales Vorgehen für die Behandlung mit dem IMAT Heater und Befeuchtungsmaterialien vorgeschlagen. Außerdem wird das Resultat jeder Behandlungsvariation mit unterschiedlichen Befeuchtungssandwiches und Behandlungstemperaturen charakterisiert. Schließlich wird die Restaurierung an drei Büchern aus den Sammlungen der Bayerischen Staatsbibliothek durchgeführt: an einer mittelalterlichen Handschrift (BSB, Clm 18199), einer Inkunabel aus der Frühzeit des Buchdrucks (BSB, 2 Inc.c.a. 1726 a) und an einem Druckwerk des 18. Jahrhunderts (BSB, Diss. 849 d, 16).

Contents

1 Introduction

Old mending can be commonly found in bound manuscripts and rare books, which aimed to rejoin tears and splits on pages, and to reinforce the inner fold of sections or to reinsert loose pages or sections. While some mends remain stable and pose no danger to manuscripts and rare books after centuries, others, nevertheless, can possibly cause severe or potential damages. Due to the aging properties of adhesives, they can become stiff and inflexible which may cause heavy distortions on pages or new tears right beside the mends. Additionally, the mending papers may also interfere with the readability of pages as sometimes they cover text and illustrations. A detachment of these old mends is therefore essential. This thesis focuses on the removal of old repairs glued with protein-based adhesives, which often requires a combination of moisture and heat. Nevertheless, a uniform and accurate heat application has always been difficult to achieve with the prevalent heating tools, and the accessibility to the working area is always restricted when the mending papers are glued in or close to the spine fold of a bound volume. Current limitations may result in an insufficient and inefficient treatment or even other unpredictable outcomes.

With these disadvantages in mind, this study aims to introduce a new heat transfer method to the conservation treatment using an innovative heating device, the IMAT heater (Intelligent Mobile Accurate Thermo-Electrical Device). The IMAT heater is a flexible and ultra-thin heat transfer mat based on carbon nanotubes (CNTs), which was developed by the EU-funded IMAT Research Project (2011–2014). Compared to other heating devices, the IMAT heater features a rapid thermal response, a precisely controllable and stable heat regulation as well as a uniform heat distribution. Heat transfer conducted by the mat allows continuous input of thermal energy, making a precise temperature regulation during a conservation treatment accessible. Furthermore, due to the optional size, the slight thickness and the flexibility of the mat, it is considered to be ideal when dealing with old mends glued close to the spine fold of manuscripts and rare books.

A temperature-related optimization through utilizing the IMAT heater has already be determined in other case studies (Markevicius et al., 2017a, p. 5-9; Markevicius et al., 2017b, pp. 69-71). This project is therefore going to verify the feasibility and advantages of coupling heat transfer with moisture in the removal of old mends glued with proteinaceous adhesives in manuscripts and rare books. The thesis begins with background knowledge of the research, which includes old mending carried out in old volumes, properties of protein-based adhesives, criteria of the conservation treatment and current limitations. Chapter 3 presents a thorough introduction of the sophisticated IMAT heating device as well as the relevant heat transfer theory. Preliminary experiments are carried out in Chapter 4, where the design of mock-ups, approaches of moisture introduction through different humidification sandwiches and selection of an optimal working pattern for combining heat transfer with moisture introduction are demonstrated. Application of the results from the preliminary experiments are presented in Chapter 5, where the heating performance of the IMAT prototypes, the thermal performance of each humidification sandwich as well as the working performance of each treatment variation correlated with different humidification sandwiches and treating temperatures are evaluated. Finally, conservation treatments utilizing this new method of combining heat transfer and moisture are conducted on three historical documents from the collection of the Bavarian State Library (shelfmarks: Clm 18199, 2 Inc.c.a. 1726 a and Diss. 849 d,16).

2 Research Background

2.1 Old Mending in Bound Volumes

In the field of bookbinding, dealing with tears or splits on paper has always been a common work. In the year of 1708, mending technique for optimizing torn pages in bound volumes was already described by Johann Gottfried Zeidler in his book *Buchbinder-Philosophie oder Einleitung in die Buchbinderkunst*:

> Wenn etwas unterm Planiren / oder sonst zerrissen / müssen solche zerrissene Bogen / ehe man sie faltzet / wieder geflickt / oder ergäntzet werden /… Wer nun dergleichen zerrissene Bogen flicken will / der schneidet ein wenig von diesem Mundleim ab / und nimpt es in den Mund / so zergehet es ihm auff der Zungen / zeucht das Zerissene durch den Mund / daß es am ende nur ein wenig naß wird / oder streicht den geweichten Leim drauff / legt das andre Ende dran / daß es nur ein klein wenig übergehet / so daß die Schrifft / Kupfferstich / oder was es ist / nicht verstellt oder verruckt werde / sondern alles zu lesen und zu erkennen sey / drücket es an und streicht es mit dem Falzbein / so ist es gut. Auf dem Rande / oder an den Orten / wo keine Schrifft ist / pflegt man auch wol unterweilen ein Abschnittgen Papier / welches das Zerrissene zusammen hält / auffzulegen / und drüber zu kleiben. (Zeidler, 1708, pp. 35-36)
>
> (English translated by the author: If something is torn by the sizing or elsewise, the torn sheets must be mended or replaced before they are folded… If one wants to mend the torn page, cut off a little bit of mouth glue and take it in your mouth. The glue then melts on your tongue. Pull the torn piece through the tongue that it just gets a little wet at the edges; or brush the softened glue over the torn piece. Place the other edge just a little bit over it, so that the text or engraving or whatever it is, is not misaligned or shifted but able to be read and recognized. Press and stroke it with a fold, then it is good. (If the tear is) on the margins or the places where text does not exist, it is also common to lay and glue a piece of paper onto it, which will hold the torn area together.)

Thon (1856) also mentioned mending technique in his work that the reinforcement of torn areas could be realized by pasting a narrow paper strip with torn edges on the margins of the pages or the areas which were not printed (Thon, 1856, p. 88). Nowadays, old mends glued with different adhesives are frequently to be found in bound manuscripts and rare books.

In the past, various traditional adhesives were used in bookbinding, among which animal glue and wheat starch paste were the most important. As each adhesive possesses specific physical, chemical and mechanical properties, this thesis focuses on the old repairs glued with proteinaceous adhesives.

2.2 Proteinaceous Adhesive and their Properties

Proteinaceous adhesives have been already used since ancient time, among which the adhesives of animal origin – the animal glue – are commonly used in the field of bookbinding. Zeidler (1708) characterized the structure of the glue as "tiny disordered fibers" early in the 18th century (Zeidler, 1708, p. 11), which is nowadays known as collagen. Bücking (1785) mentioned that glue made from alum tanned leather waste or sheep bones was at that time frequently applied in bookbinding (Bücking, 1785, p. 47). Thuma (1949) summarized that glue made from hide, bone and leather waste were applied for gluing covers, leathers, parchments, papers and cardboards as well as for spine lining due to its high adhesive power (Thuma, 1949, pp. 76-78). This chapter will present an overview of the properties of animal glue which are of interest to conservators.

Animal glue is an impure form of gelatin, which is the hydrolytic form of collagen – the major proteinaceous component of mammalian and fish skins, connective tissues and bones (Brandis, 1990, p. 123; Schellmann, 2007, p. 55). Collagen consists of protein molecules, which is a triple-helix wound by three sub-chains and then assembled into an increasingly complex structure (Horie, 2010, p. 229). Collagen is not soluble in cold water, but through a denaturation achieved by hot water extraction, during which the triple-helix-structures are separated into disordered random coils of single protein chains, it can be transformed into soluble gelatin upon cooling (Schellmann, 2007, p. 56; Fig. 2.1).

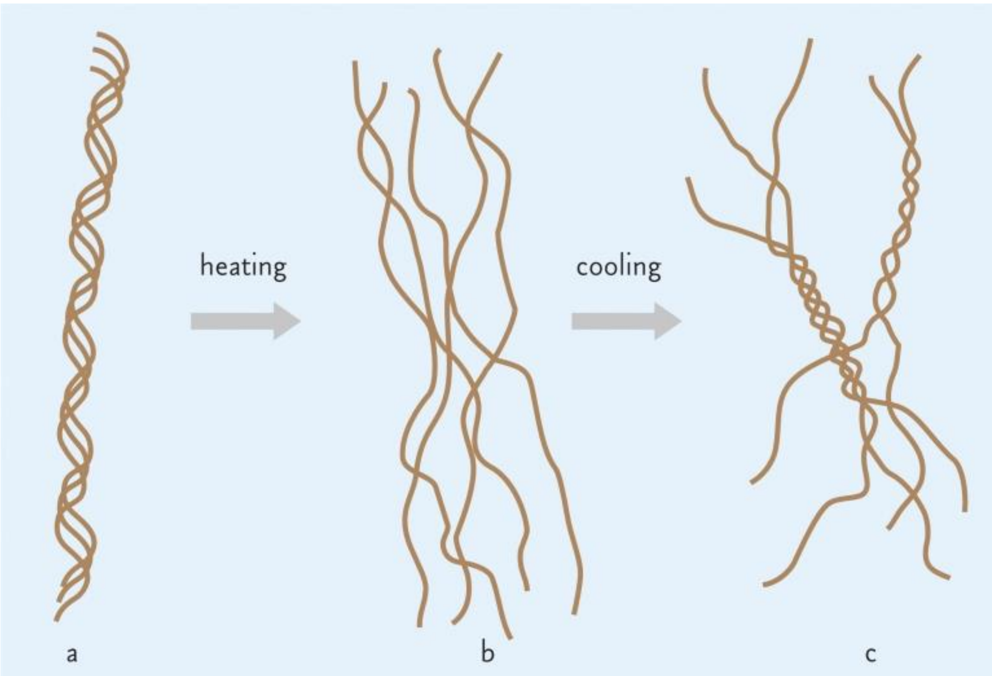


Fig 2.1: Schematic representation of the procedures in the chemical - thermal process steps from collagen (a) through disordered random coils (b) achieved by hot water extraction to soluble gelatine (c). (Source: Gerhard Banik and Irene Brückle, 2018, p.152, ©Gerhard Banik and Irene Brückle)

In general, collagen-based animal glues can be divided into three categories (Ropp, 1951, pp. 49-51; Kolbe, 2001, p. 42; Schellmann, 2007, pp. 55-56): Hide glues are primarily derived from bovine skins and those of small mammals (i.e. rabbit skin glues); bone glues are extracted from fresh bones or ossein from cattle and pigs; fish glues are manufactured from fish swim bladders (isinglass) with higher quality and also from fish skin and bones with lower quality. The content of collagen and its chemical structures vary from different species and even from different parts of the same species. The yield of bone glue is rarely more than 20-25% as the bone contains a large amount of tricalcium phosphate, while animal skin, depending on its quality, can deliver glue at 20-60% of its weight (Greber et al., 1950, pp. 58-59). In comparison, swim bladder is fairly pure collagen. Both hide and bone collagen require either acidic or alkaline pretreatment before hot water extraction, while fish collagen does not need to be pretreated as it contains fewer cross-links. During the first extraction step, denaturation of hide and bone collagen appears, as the extraction conditions become more severe, the cross-linked molecules are degraded resulting in weaker glues with shorter chains (Horie, 2010, p. 230). Thus, glues produced by different procedures from different collagen sources show various properties. Schellmann (2007) summarized the features of various glue types. Generally speaking, hide glue solution has a higher viscosity than bone glue solution; the dried film of the former possesses a higher cohesive and bonding strength than of the latter because bone glue is more strongly denatured. Meanwhile, however, hide glue film owns a lower elasticity than bone glue film. Isinglass from sturgeon swim bladders shows similar tensile strength to that of hide glue, but it is more elastic than hide glue as fish collagen owns a high molecular weight but less inter- and intramolecular bonds (Schellmann, 2007, pp. 58-61). In addition, hide glue and isinglass solutions are acid-free and have a neutral pH from 6.0 to 7.5, while bone glue tends to be more acidic and possesses a pH value between 5 and 7 as it contains free sulfurous and sulfuric acid (Greber et al., 1950, p. 94).

One of the most essential properties of animal glues that interest conservators is their mechanical behavior in different surrounding environments. As gelatin is classified as a gel, it is hydrophilic and can retain water inside its molecule structure. The moisture content of gelatin is in equilibrium to the concentration of water vapor in the ambient environment. Gelatin swells during the increasing of its moisture content and can be liquified when liquid water and a raised temperature are provided (Banik & Brückle, 2018, pp.152-153). Thus, the relative humidity, the contact with liquid water and the temperature in the surrounding environment all significantly affect the mechanical properties of gelatin. Mammal gelatin contains 12-16% of water under normal environment condition (50% RH and room temperature) and 30% of water at 84% RH under room temperature. Its swelling point is at 80% RH under room temperature, but it can already swell at 50% RH when the ambient temperature is 45°C: The dry film turns from a glassy to a rubbery state as the introduction of water allows the gelatin molecules to loosen their helical arrangement in their dry state (Horie, 2010, p. 232, Banik & Brückle, 2018, p.153). If a re-drying process is followed, gelatin molecules undergo another reformation of helical structures, which are not in the same configuration as before (Banik & Brückle, 2018, p.153, Fig. 2.2). Therefore, under fluctuant environmental conditions, the arrangements of the molecule helical structure are continually changed, which leads to a considerable development of internal stresses and strains that affect the glue's elasticity, strength and physical stability (Schellmann, 2007, p. 62). Compared to pure gelatin, the impurity of animal glue may decrease its ability of water absorption.

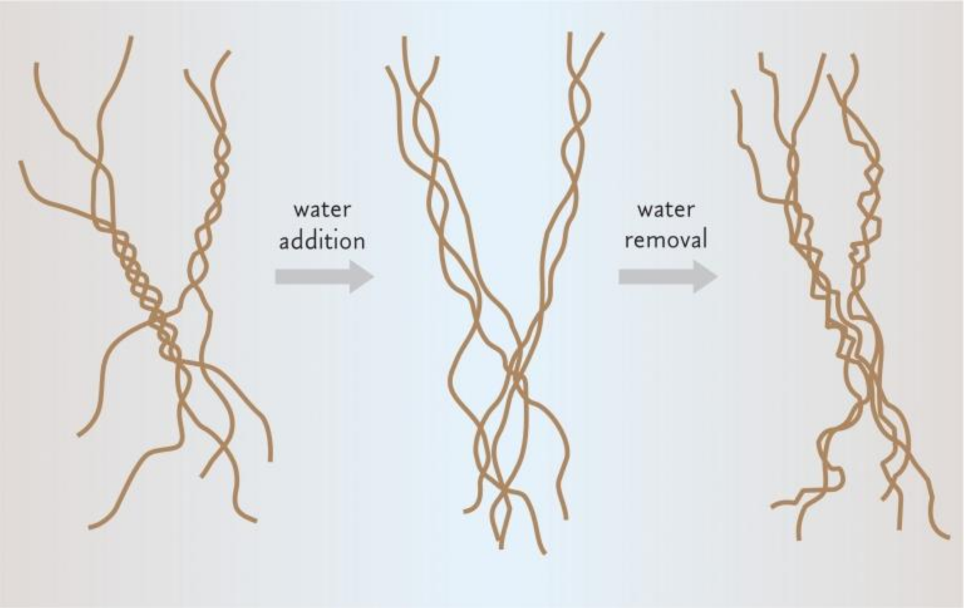


Fig 2.2: Schematic representation of the effect of water addition and removal on the molecular arrangement of gelatin. (Source: Gerhard Banik and Irene Brückle, 2018, p. 153, ©Gerhard Banik and Irene Brückle)

Once animal glue is liquefied, the mechanical properties of the gelatinous glue solution are strongly influenced by its viscosity and the surface tension, which is not only dependent on the type of glue but also on the concentration and the temperature: For a given molecular weight value, the viscosity of the glue solution increases with increasing solution concentration and decreasing temperature, which plays a vital role in the degree of penetration into a substrate (Schellmann, 2007, pp. 57, 60).

Another significant property of animal glue in conservation practice is its aging characteristic. Natural aging may cause a permanent dimensional change as well as an increase of stiffness and brittleness of glue films due to the change of ambient environment condition and the impurity of glue. It may lead to a generation of cross-linking inside the molecular structure of glue due to the presence of metal ions or organic pigments and tannins which increases molecular density and decreases water interaction. It may also result in color changes of glue, among which hide and bone glues are generally more strongly darkened and less transparent than gelatin or isinglass due to their higher impurity content (Schellmann, 2007, pp. 62-63; Banik & Brückle, 2018, p.154).

2.3 Criteria for Conservation Treatment

Although the instructions of mending tears or splits appeared in bound volumes written in old literature (Zeidler, 1708, pp. 35-36; Bücking, 1785, p. 12; Thon, 1856, p. 88) are relative elaborate, when it comes to real practices, it can be far less satisfactory. While some mends can remain stable and pose no danger to manuscripts and rare books after centuries, others, nevertheless, can possibly cause severe or potential damages to historical documents. When the mending papers are glued with protein-based adhesives, the aging of the glue can result in:

- Heavy distortions on pages (Fig. 2.3) due to the strong tension caused by the shrinkage and stiffness of the glue.
- Appearance of new tears right beside the old mends (Fig. 2.4) due to the increased stiffness and inflexibility of the aged adhesives.
- Inconveniency and potential formation of new tears during page turning due to the previous reinforcement in the joint area (Fig 2.5).
- Concealing the original illustrations and texts when the old mending was carried out recklessly (Fig. 2.6).
- A misalignment or shifting of original illustrations and texts when tears were previously not rejoined correctly (Fig 2.7)

Not only has some old mending already caused new damages to originals, but it also interferes with the readability as well as digitization of the pages. As long as an introduction of moisture does not pose a high danger to the area, removal of the old mending papers correlated to the damages listed above is required.

Fig 2.3: Heavy distortions on page are caused by the old mending in the spine fold of the manuscript. (Munich, Bavarian State Library, Clm 18199)

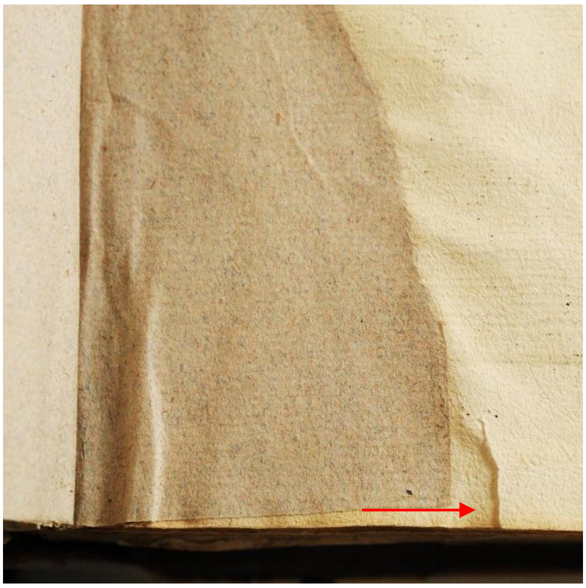


Fig 2.4: A new tear appears right beside the old mending paper. (Munich, Bavarian State Library, 2 Inc.c.a. 1726 a)

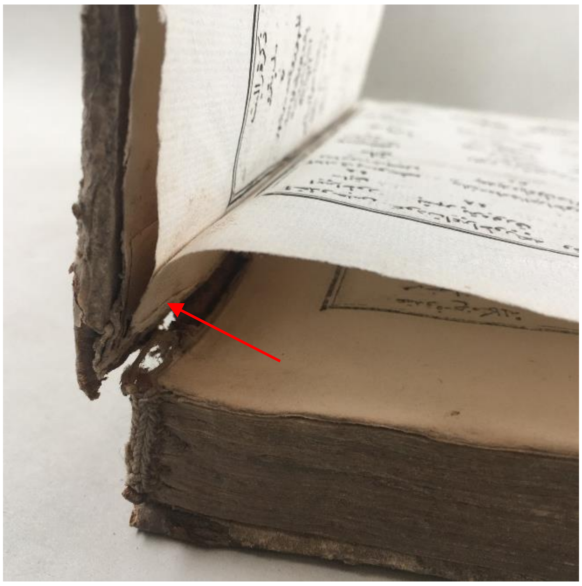


Fig 2.5: Several pages was glued together in the spin fold which interferes with the page turning and causes new tears (Munich, Bavarian State Library, 2 A.or. 363)

Fig 2.6: The old mending paper covers part of the illustration (Munich, Bavarian State Library, Clm 18199)

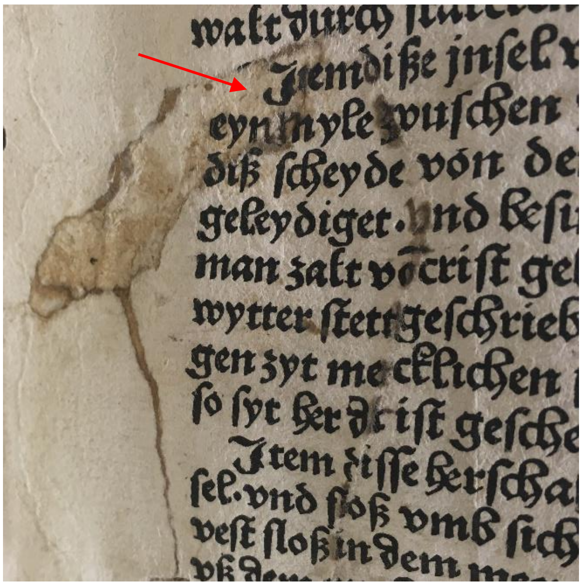


Fig 2.7: The tears through the text were not precisely rejoined by the previous repair (Munich, Bavarian State Library, 2 Inc.c.a. 1726 a)

Since the historical information carried by bookbinding, such as sewing structures and original binding materials, should be retained as much as possible, it is nowadays generally considered that text blocks should not be dismantled during conservation treatments. Therefore, the removal of old mending papers in a bound volume should be carried out *in situ*. Compared to the removal of lining or backing of a single sheet, criteria for detaching old repairs in a bound volume are partly distinct. A treatment will be assessed as successful when it brings about minimal intervention and risk to the original work while achieving the maximum result, namely:

1) Formation of tidelines along the wet-dry boundary and a disparity in color between treated and untreated areas should be avoided. The area to be treated can therefore not be applied an excess amount of water. Tidelines will not only interfere in aesthetic appearance but also cause an inhomogeneous aging process or permanent planar distortions on paper (Banik & Brückle, 2018, p. 383).

2) The treatment should be executed as evenly as possible. During the treatment, protein-based adhesive should swell to a certain degree, which allows a total detachment of the mending papers but prevent the original paper substrates from being penetrated by the adhesive. After the treatment, adhesive residues on the originals should be reduced as much as possible without causing further penetration of glue and additional damages to the fiber or surface structures of the paper substrate. The treated area should regain stability and flexibility, the readability of the page should be improved.

3) The residues of conservation materials should remain as less as possible on the surface of original pages since it is barely possible to spray or rinse the pages with water after the treatment. Residue can only be partly acceptable when the material possesses excellent long-term stability, or the amount of residue is meager, which will not cause more risks or irreversible damages.

4) Due to limited opening angle of a bound volume, the accessibility to the working area is sometimes restricted, primarily when the area to be treated locates in or close to the spine fold. Appropriate thickness and flexibility of the conservation materials applied in the treatment are highly demanded.

Owing to the decreased ability of water absorption of aged animal glue under room temperature, a satisfactory result often cannot be simply achieved only through an introduction of moisture. Under this circumstance, addition of heat or, as a last resort, a corresponding enzyme is required. Since spraying or washing after an enzyme-treatment is recommended in order to ensure no enzymatic residues remain on the paper substrate (Andrews et al., 1992, p. 319; Decoux, 2002, p. 189; Müller, 2016, p. 137), it is skeptical to conduct an enzyme-treatment in a bound volume: A localized washing in bound volumes can only be realized in combination with a suction device. Water can be applied with a brush or by spraying, while the rest of the areas are masked. However, some specific risks or new damages are likely to occur such as the formation of tidelines and planar distortions or disparity in color between treated and untreated areas (Banik & Brückle, 2018, p. 383). Besides, the application of water will damage the initials, illuminations or texts written with red ink. Additionally, protease – the enzyme which hydrolyzes the peptide bonds in proteins – may interfere with the sizing when the paper substrate was initially sized with a protein-based agent (Andrews et al., 1992, pp. 319-320). Therefore, unless 1) the adhesive layer is extremely resistant due to additives or 2) the adhesive has already penetrated the paper substrate in consequence that all other options have been exhausted (Decoux, 2002, p. 189), it is generally preferable to detach old mending with protein-based glue through a localized treatment of combining moisture and heat, which can considerably accelerate loosening entangled molecular network of animal glue during water introduction.

2.4 Current Limitations

During the past decades, numerous researches on investigating different approaches to introduce moisture into the paper as well as theoretical characterization of humidifying, moistening and wetting paper have been carried out. For a localized treatment, water can be introduced into the paper through exposing the paper to an elevated RH level by using a Gore-Tex sandwich or by contact with a water reservoir that possesses a high water-retention power or/and viscosity such as various hydrogels (Singer et al., 1991, pp. 102-104.; Warda et al., 2007, p. 264; Mazzuca et al., 2014, p. 205; Hughes & Sullivan, 2016, p. 32; Banik & Brückle, 2018, pp. 325-317, 369).

However, a uniform and accurate heat transfer resource, from which thermal energy can continuously flow into the system to raise the temperature and keep it constantly, has always been difficult to conduct with the prevalent heating tools currently available (Markevicius et al., 2014, p. 2). Hot/cold gel packs or the traditional large-format heating mats are the common heat resources currently utilized in the paper and book conservation. The hot/cold gel pack can be warmed with a microwave or in a warm water bath before it is applied to artworks. However, the pack cannot be regarded as a constant heat transfer resource since it will not be able to generate energy once it is taken out of the microwave or the warm water bath. Controlling and maintaining the desired temperature precisely during the treatment is scarce to be accomplished. Moreover, the thickness of the pack is also not suitable for a treatment carried out in a book with a limited opening angle (Fig. 2.8). The traditional heating mat is, on the one hand, not suitable for a localized treatment due to its format and thickness, and on the other hand, it always shows an uneven heat distribution and temperature fluctuation. This lack of temperature regulation and the limited accessibility to the working area in bound volumes may lead to insufficient and inefficient removal of old mends or even other unpredictable outcomes during a conservation treatment.

To optimize the heat transfer method, a new heating device, namely an innovative heat transfer mat based on e-textile containing conductive nanomaterials, developed by the EU-funded IMAT project is considered. Thanks to the support from Tomas Markevicius, M.A., one of the co-leaders of the IMAT Research Project, an IMAT prototype console and several mats are provided for this study.

Fig. 2.8: Current localized treatments to introduce heat to the removal of an old mending glued close to the spine fold of a bound volume using a hot/cold gel pack. The heating pack is too thick to insert into the bound volume, which prohibits an accurate and even heat application.

3 Introduction of the IMAT Heater: A New Accurate Heat Transfer Device Based on Conductive Nanomaterials

The IMAT heater, namely the Intelligent Mobile Accurate Thermo-Electrical Device (Olsson et al., 2014), is an innovative heating device in the field of art conservation which realizes a highly accurate heat regulation and distribution utilizing new materials and new technology based on nanomaterials – carbon nanotubes (CNTs) and other conductive nanomaterials. The idea of offering versatility and precise heat application in conservation through a mobile thermal blanket is derived from the research on a flexible silicone rubber thermal blanket dated back to 2003 (Olsson & Markevicius, 2010, pp. 63-67). This sophisticated heating device utilizing nanomaterial is a refined version developed by the Horizon 2020 IMAT Research Project (2011-2014), which involves interdisciplinary cooperation between scientists, electrical engineers and conservators, with the financing under the European Commission's Seventh Framework Program (FP7) (Markevicius et al., 2012, p. 784; Meyer et al., 2013, p. 636). This heating device features a rapid thermal response and a heating range from 20°C to 85°C at 36 V with an accuracy of 0.1 °C (Markevicius et al., 2017a, pp. 2-4). Owing to its optional size, costumer-designed air permeability and transparency as well as its slight thickness and high flexibility revealed in the previous researches, the IMAT heater is considered to replace other traditional heating devices to overcome the current limitations described in the previous chapter. The first part of this chapter presents a theoretical background of the basic material – carbon nanotubes – and the design concept of this innovative heater. In the second part, a critical discussion on how to realize a uniform and precise heat application concretely during conservation praxis will be carried out.

3.1 Carbon Nanotubes and the Design Concept of the IMAT Heater

Carbon nanotubes (CNTs) can be visualized as molecular scale sheets of graphite rolled up to make a tube, which belongs to carbon allotrope family falling between fullerenes and graphite. CNTs are often divided into two overall categories (Fig. 3.1 and 3.2): single-walled carbon nanotubes (SWCNTs) consist of single rolls of graphene, while multi-walled carbon nanotubes (MWCNTs) are simply composed of two or more concentric SWCNTs (Thostenson et al., 2001, p. 1900). CNTs reveal numerous outstanding features: besides lightweight, they possess an electrical conductivity similar to copper, a thermal conductivity similar to diamond and an E-modulus 10 times greater than steel (Meyer et al., 2013, p. 633; Markevicius et al., 2014, p. 2). With their additional low thermal mass and sheet resistance, CNTs are regarded as an ideal material for achieving efficient, even and steady heat transfer. Compared to traditional materials, CNTs can significantly accelerate the time reaching a target temperature and maintain the temperature constantly due to their rapid thermal response, even over large surface areas. Moreover, conductive films made by carbon nanotubes or other conductive nanomaterials like metal nanowires are measured only around 50-100 nanometers thick, and they also contain a considerable transparency (Markevicius et al., 2014, p. 3; Markevicius et al., 2017b, p. 68).

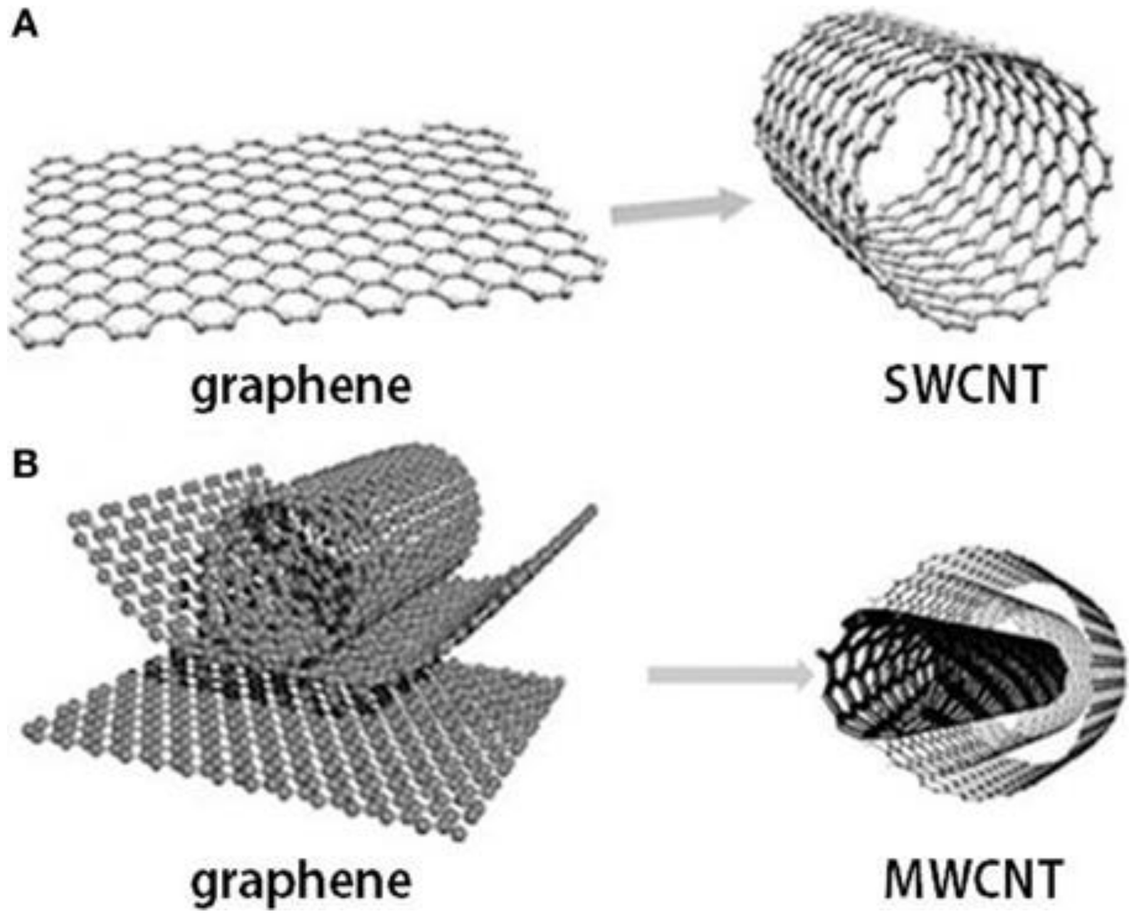


Fig. 3.1: Graphene and carbon nanotubes as (A) single wall carbon nanotube (SWCNT) and (B) multi-wall carbon nanotube (MWCNT) structures (Source: Vidu et al., 2014, p. 3).

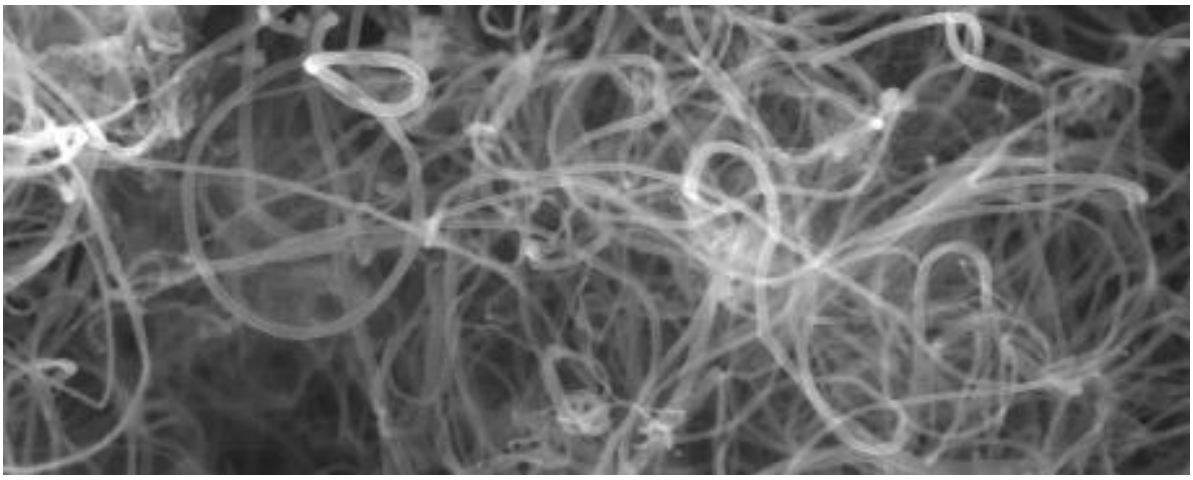


Fig. 3.2: SEM image of multi wall carbon nanotubes bundles (MWCNT). (Source: Markevicius et al., 2012, p. 787)

On account of the magnificent properties of CNTs described above, the IMAT Project devoted to utilizing carbon nanotubes for the design of a new highly accurate mobile device that can apply mild heating in art conservation – in the form of a lightweight, flexible and eventually transparent or breathable film-like mat (Meyer et al., 2013, p. 636). Schematic drawing of the CNTs-based mat design concept is shown in Fig. 3.3. In principle, the mat is designed with parallel multiple electrodes, consists of a selected substrate such as a plastic film or an ultra-thin translucent textile. The substrate is covered firstly with a heating layer with a CNT film and then finished with laminate layers. The laminate layers can protect the CNT coating, bring about an electrical insulation and offer different desirable surface properties at the same time. When voltage is applied, the current is uniformly distributed over the conductive layer of the deposited nanomaterial and heat is generated evenly over the entire surface (IMAT concept design, n.d.; Markevicius et al., 2014, p. 4).

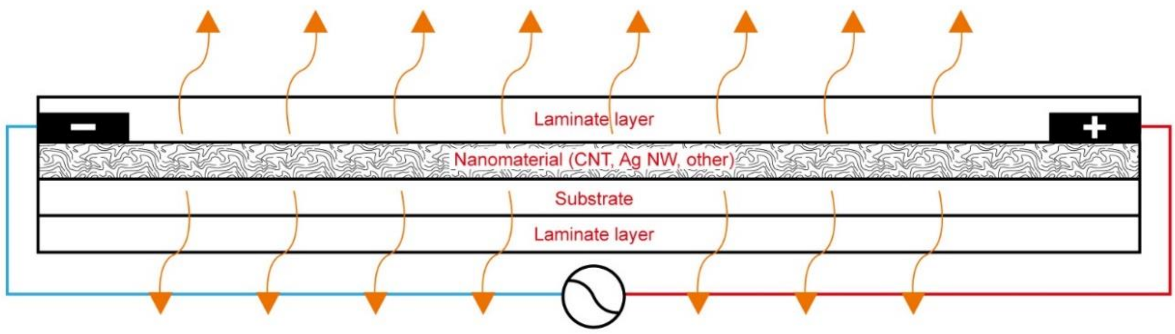


Fig. 3.3: Schematic drawing of IMAT heater cross section (Source: Markevicius et al., 2012, p. 788).

Based on this design concept, the IMAT mat is devised generally in three distinct types to meet specific needs of different applications:

1) IMAT-S or "standard": IMAT-S has a soft and non-tack surface which is opaque and nonbreathable. This type is designed for a thermal treatment where visibility and breathability are not required. The substrate of the IMAT-S is composed of a transparent polyethylene terephthalate (PET) film; two copper electrodes are glued onto one side of it; the PET substrate is then coated with the Carbo-e-Therm by spraying and then coated with a soft-touch protective silicone layer. (Meyer et al., 2013, p. 642; Markevicius et al., 2014, pp. 5-6; IMAT application in art conservation, n.d.).
2) IMAT-B or "breathable": IMAT-B is permeable to airflow and water vapors. IMAT-B is manufactured in three different types, two of them consist of a substrate made by a weave polyester textile coated with Carbo-e-Therm and CarboImpreg, while the third type is composed of a PET-based woven fabric with electrically conductive filaments in a dense pitch. The CNTs-textile can also be transparent if coated with silver nanowire or single walled CNTs and semi-transparent if coated with multi-walled CNTs (Meyer et al., 2013, p. 642; Markevicius et al., 2014, pp. 7-8).
3) IMAT-T or "transparent": IMAT-T is transparent or translucent, whose material is largely based on SANTETM EMI Shielding Film and other high-performance transparent film

heater based on a hybrid of carbon nanotubes and silver nanowires (Markevicius et al., 2014, p. 8).

All types of the IMAT mats are portable, mobile and available in different sizes, which permits a heat application for different target areas. Three prototype mats with various sizes, air permeability and transparency are provided for this study, which are presented in Fig. 3.4. Characteristics of each mat are observed and described in Chapter 5.2.1. Furthermore, due to the slight thickness and the flexibility of the mat, it can easily be arranged according to each specific demand during conservation treatment. In the case of this research, one can readily insert a mat to the spine fold of a bound volume, even if its opening angle is around or less than 90° (Fig. 3.5 b). The working area is therefore much easier to be accessed than using a gel pack (Fig. 3.5 a).

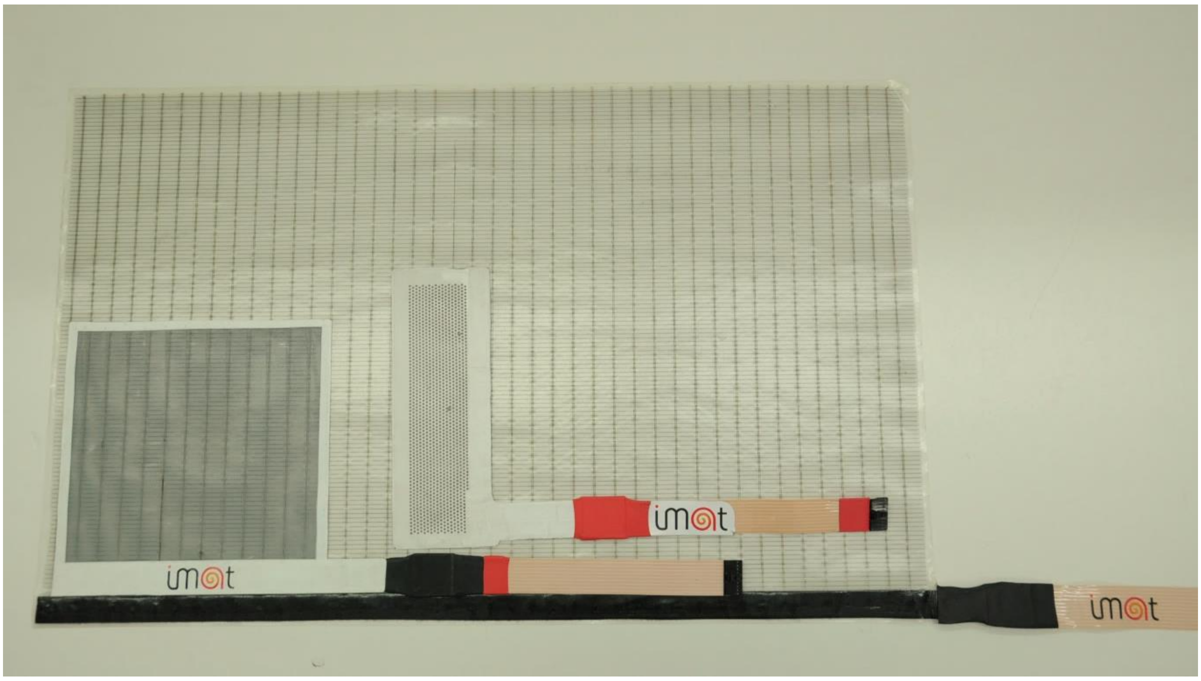


Fig. 3.4: Overview of the three prototypes utilized in this study of varying sizes, with different air permeability and transparency.

To regulate a precise and stable temperature application, the CNT-based mats are associated with a corresponding control unit (console) with a flat cable, and together they compose the final version of the IMAT heating device (Fig. 3.6). The IMAT console, which includes an IMAT Power Box, an IMAT Control Unit with a digital touch screen and an IMAT thermocouple (TC) Unit, is responsible for the temperature regulation as well as the accuracy and steadiness of the heating process. The IMAT Power Box is composed of a voltage power supply and a IMAT Main Board; the IMAT TC Unit is equipped with a T-type thermocouple laminated with an electrostatic film and it measures the temperature of the heating mat locally as a sensor; and the IMAT Control Unit allows the target temperature as well as the heating or cooling time to be set manually or programmed (Markevicius et al., 2014, pp. 9-10). When a desired temperature is set by the Control Unit, the TC Unit measures the temperature of the mat and transmits the data via Bluetooth to the IMAT Main Board. The IMAT Power Box then analyses the data coming from the TC Unit 40 times per second and coordinates the temperature through the classical approach of PID-PWM regulation. The temperature can thus remain constantly with an accuracy of 0.1°C (Markevicius et al., 2017a, p. 4; Markevicius et al., 2017b, p. 68.).

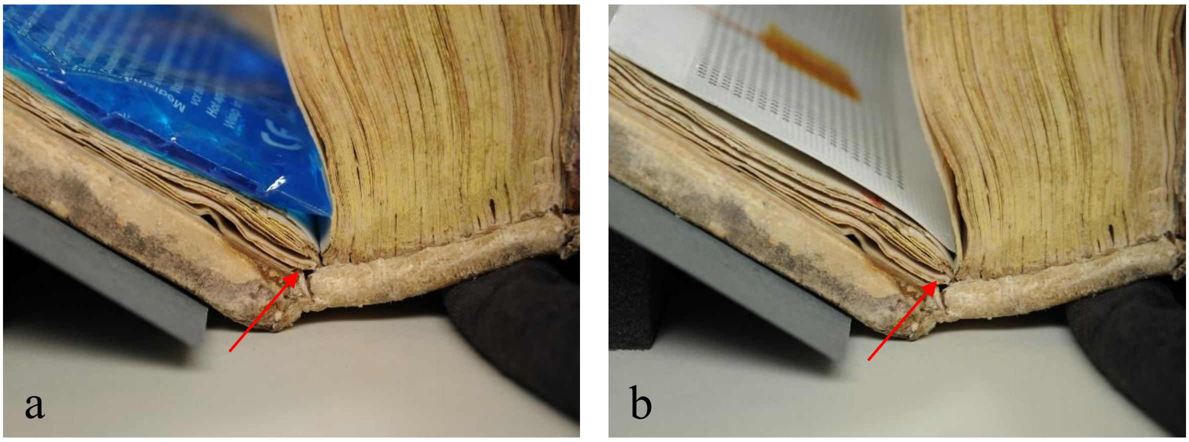


Fig. 3.5: Comparison of the thickness of a gel pad (a) and an IMAT mat (b) during heat application. The arrangement with the IMAT mat presents a much better result.

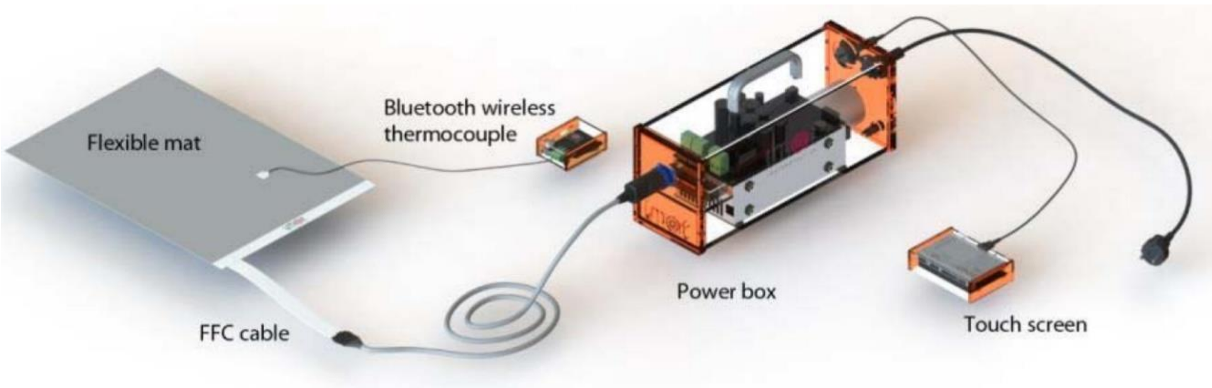


Fig. 3.6: Conceptual design of the overall IMAT architecture (Source: Markevicius et al., 2014, p. 4).

As for the prototype console applied in this study (Fig. 3.7), the IMAT power box and the IMAT Control Unit are equipped together while an OMEGA T-type mini SMP spool caddy thermocouples with 1m 40 AWG PFA insulated wire is utilized to transmit the temperature data, which functions similarly as the IMAT TC Unit. The thermocouple is adhered to a mat with a piece of polyimide high temperature resistant tape and its connector is inserted to the console. This IMAT prototype operates with a universal 110-230 V input and 36 V output. A precise and steady heating can be achieved through the whole device (Fig. 3.8).

To avoid confusion, the term “IMAT heater” in the following chapters refers to a combination of “IMAT mat” and “IMAT console.”

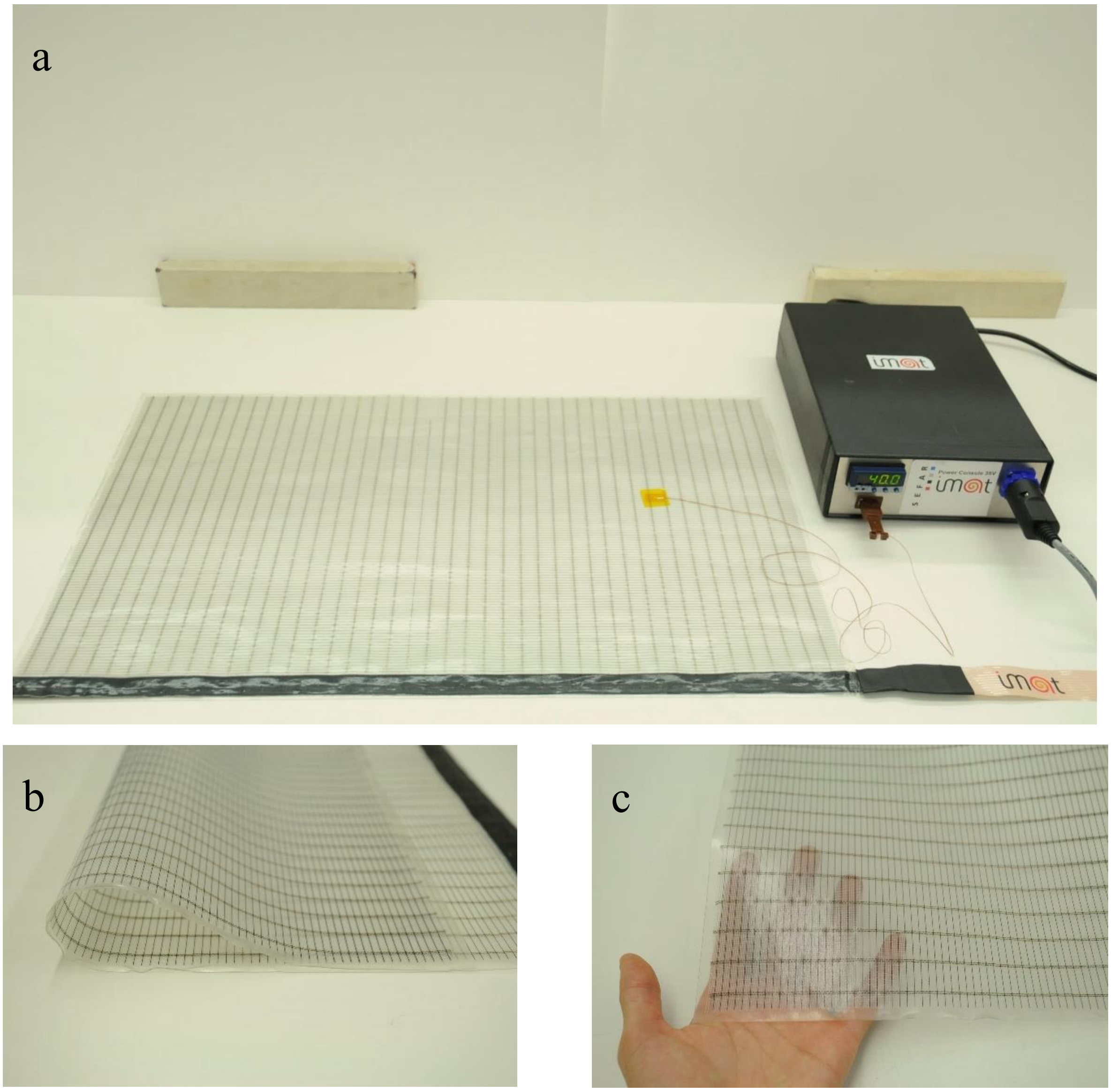


Fig. 3.7: The IMAT prototype equipped with a console, a T-type thermocouple and a large mat (a). The mat shows a considerable flexibility (b) and transparency (c).

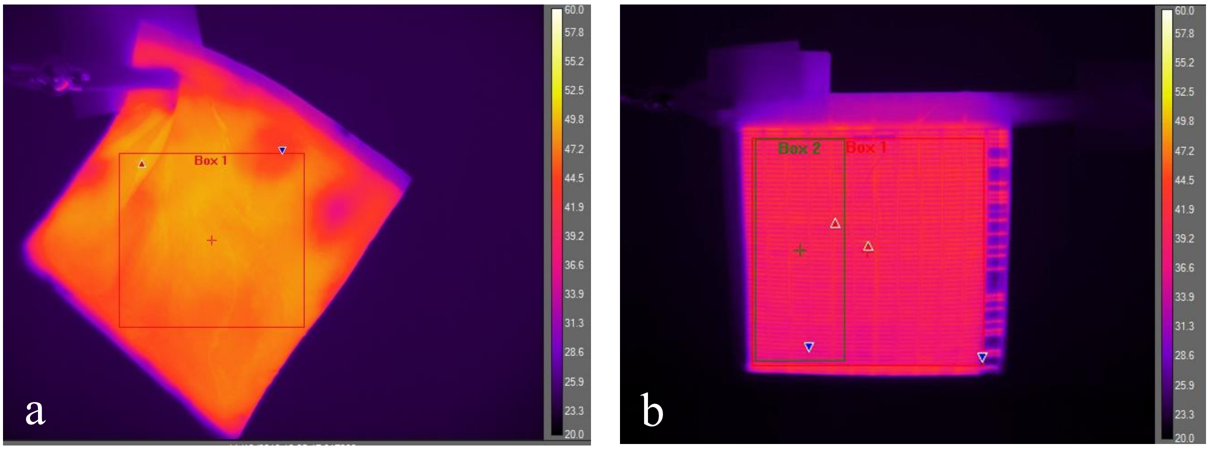


Fig. 3.8: Comparison of the heat distribution of a gel pad (a) and an IMAT mat (b). The IMAT mat demonstrates a more uniform heat distribution.

3.2 Critical Discussion of "a Uniform and Accurate Heat Application" in Praxis

Thanks to its unique features, the IMAT heater seems to meet all the demands for accomplishing a precise heat transfer during a localized treatment in book conservation. Nevertheless, theoretical conclusions are sometimes not directly applicable in real praxis and field works. A continuous energy resource with a rapid heat response and ultra-sensitive temperature regulation is not the only factors that determine the performance of a heat transfer process. One should pay attention to all the thermal parameters involved in the process as well, such as the heat capacity of different objects, the thermal conductivity and density of different materials.

To contribute a better explanation, several terms in the thermal science should be clarified:

- *System*: "A macroscopic unit of particular interest, especially one whose thermal properties are under investigation" (Wasserman, 2012, p. 3). In the case of applying heat through the IMAT heater, "system" should refer to the IMAT mat and all the materials which need to be heated during the treatment, such as the object to be treated and conservation materials.

- *Surroundings*: "Everything physical that is not the system or which lies outside the system's boundaries is regarded as surroundings" (Wasserman, 2012, p. 3). In the case of applying heat through the IMAT heater, "surroundings" includes air, all objects which have direct contact with the system and the IMAT console that supplies voltage power to the system.

- *Thermal variables*: "A set of macroscopic variables that describe the state of the system" (Wasserman, 2012, p. 3). In the case of applying heat through the IMAT heater, thermal variables mostly refer to the temperature of the system.

- *Thermal equilibrium*: "The final state attained in which thermal state variables that describe the macroscopic system no longer change in time" (Wasserman, 2012, p. 3). In the case of applying heat through the IMAT heater, thermal equilibrium refers to the temperature of the system does not change any more.

- *Heat capacity and specific heat*: The heat capacity of a system is defined as the limiting ratio of the heat introduced reversibly into the system divided by the temperature rise, while the specific heat is the heat capacity per unit mass (Rex & Finn, 2017, p. 49). The heat capacity and the specific heat are thermal equilibrium properties (Kaviany, 2011, p. 163).

- *Conduction heat transfer*: Thermal energy transports within a medium or among neighboring media by molecular interaction resulting from a spatial variation in temperature (Kaviany, 2011, p. 3). Heat transfer during the heating through the IMAT heater occurs mostly in the form of conduction.

- *Thermal conductivity*: Thermal conductivity is the ability of a medium to transfer heat per unit of time and area without any net motion and in the presence of a unit temperature difference over a unit length within the medium. In contrast to the heat capacity, the thermal conductivity is a nonequilibrium property, which depends on the ability of micro heat carriers of heat to travel to exchange this heat. The ability to transfer heat by conduction is related to the ability of molecules (for gases), electrons and holes (for metallic and semimetallic liquids and solids), phonons (for all liquids and solids, but dominant in nonmetals) to store/release thermal energy (i.e., heat capacity), and the ability of electrons, phonons and molecules to travel a distance before losing their energy (Kaviany, 2011, pp. 163-164).

During a heat transfer process, the IMAT console continuously provides electric energy to the system. This electric energy is first transferred to thermal energy through the mat and then flows through conduction into all materials in the system. The state of the system will be changed from the previous thermal equilibrium state (before heating) to a new thermal equilibrium state (after heating) with a temperature difference.

Two equations are therefore important in a heat transfer process. Equation 3.1 shows that the relationship between increased temperature ΔT of a sample of mass m and specific heat c through input of energy Q. Equation 3.2, namely the heat equation in an isotropic and homogeneous medium in a 3-dimensional space[1], demonstrates that the rate of change of temperature $(\frac{\partial T}{\partial t})$ at a point (x, y, z) over time depends on the thermal conductivity (λ), the density (ρ) and the specific heat (c) of the involved materials.

$$\Delta T = \frac{Q}{mc} \tag{3.1}$$

$$\frac{\partial T}{\partial t} = \frac{\lambda}{\rho \cdot c}\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}\right) \tag{3.2}$$

Therefore, the increase of temperature of an object, which possesses a higher heat capacity, is less than the increase of temperature of another object owns a lower heat capacity, when both

[1] In reality, however, what conservators deal with during a treatment are normally non-homogeneous anisotropic media, of which the heat flow equation is more complicated. Nevertheless, since this thesis is not going to calculate the time derivative of the temperature at a specific point, but rather to provide a general understanding of the thermal parameters that influence a heat transfer process, Equation 3.2 is presented here to simplify the explanation.

are provided a same amount of energy. When the system contains only an IMAT mat, the time before a target temperature is reached is quite short, as the CNTs has an extremely high thermal conductivity and the mat possesses a low heat capacity. However, when more materials adjoin the mat, the thermal conductivity, the density and the heat capacity of the whole system will be changed, which as a result, strongly affects the thermal response of the system. Therefore, a thermal gradient occurs before a target temperature is reached cannot be ignored (Markevicius et al., 2014, p. 11; Fig. 3.9). Meanwhile, the thermal parameters of the surroundings play a vital role: the thermal energy may flow out of the system, which affects the final thermal equilibrium state of the system (Fig. 3.10). Additionally, if different parts of the mat have contact with different materials at the same time, which have diverse thermal conductivities, densities and heat capacities, it is impossible for all the materials to reach a desired temperature simultaneously (Fig. 3.11). The first two examples shown by Fig 3.9 and Fig. 3.10 are relevant to all conservation treatments using the IMAT heater to introduce thermal energy, while the example shown by Fig. 3.10 should be considered specifically when the area to be treated is smaller than the mat. Thus, conservators should be aware that a "delayed" temperature regulation cannot be completely avoided by using the super-sensitive IMAT heater, and an "uneven heat distribution" can also possibly occur when the heat transfer condition is not ideally created.

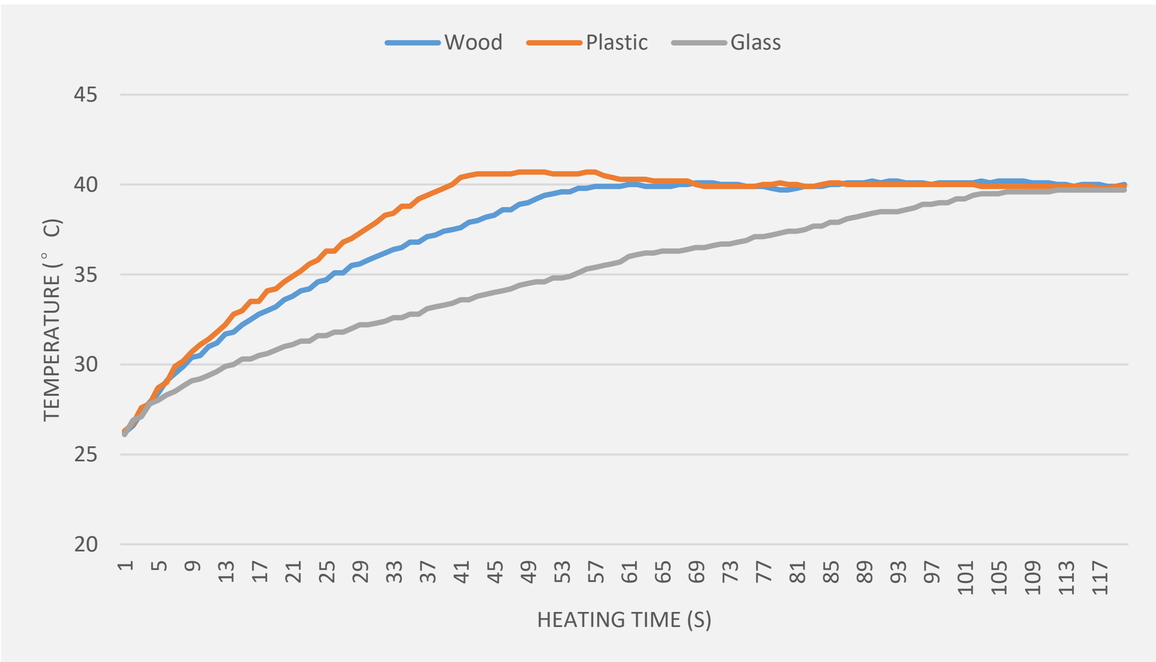


Fig. 3.9: Temperature trends in 2 minutes at a selected point of an IMAT prototype coupled with respectively, a wooden desk, a plastic tray and a glass plate.

Another significant macroscopic expression of the thermal factors mentioned above is the rate of conduction heat transfer inside a system. In an ideal condition, where the rate of heat transfer reaches 100%, the treated objects will be heated to the same temperature as the mat, namely the target temperature set by the IMAT console. Nevertheless, one should always bear in mind that the rate of conduction heat transfer cannot reach 100%. Heat loss always occurs in practical application, which depends crucially on, for instance, the thermal conductivity of the materials, through which thermal energy flows, and the distance that the heat must be conducted. During the treatment, if the mat does not adhere as much as possible to an object, the presence of air pockets between the mat and the object can lead to an uneven heating process as thermal energy at some spots does not directly transport from the mat to the object (Markevicius et al., 2014, pp. 10-11). The air pockets in between insulate a further penetration of heat due to the low thermal conductivity value of the air and thus interfere a uniform heat distribution on the object surface. Besides, when thermal energy should transport through several media before reaching the target object during a treatment, it is possible that thermal energy does not completely flow to the object since some electrons, phonons and molecule in the media have already lost their energy before they reach the target object. Materials as well as thickness of the "barrier" media play an important role in a heat transfer process, which should always be considered in conservation treatments.

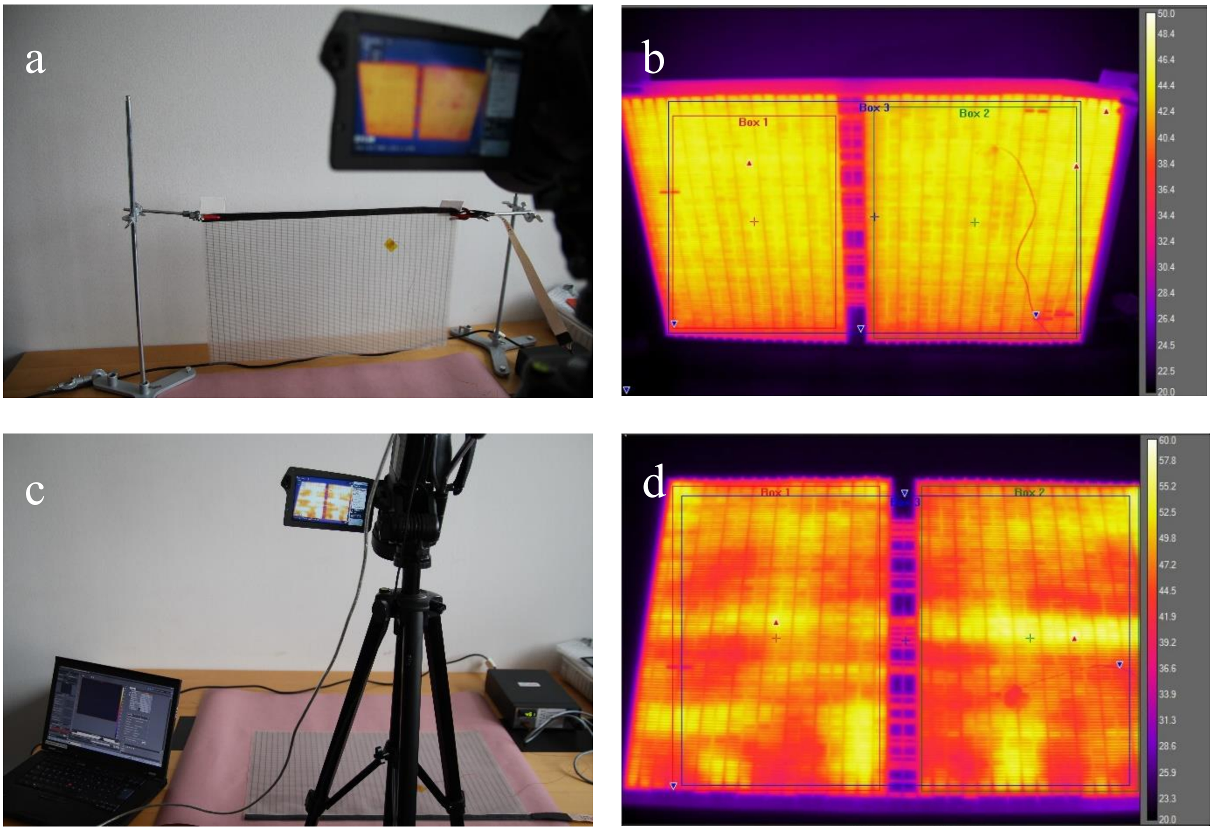


Fig. 3.10: Thermographic experimental setups and images obtained for an IMAT prototype when it was hanged in the air (a, b) and placed on a paper support with not perfect adherence (c, d). When only the mat was counted as "system", air and the paper support was counted as "surrounding" elements, thermal energy partly flowed out of the system during heating where the mat has contact with the paper support. which results in an ununiform heat distribution final thermal equilibrium state of the system.

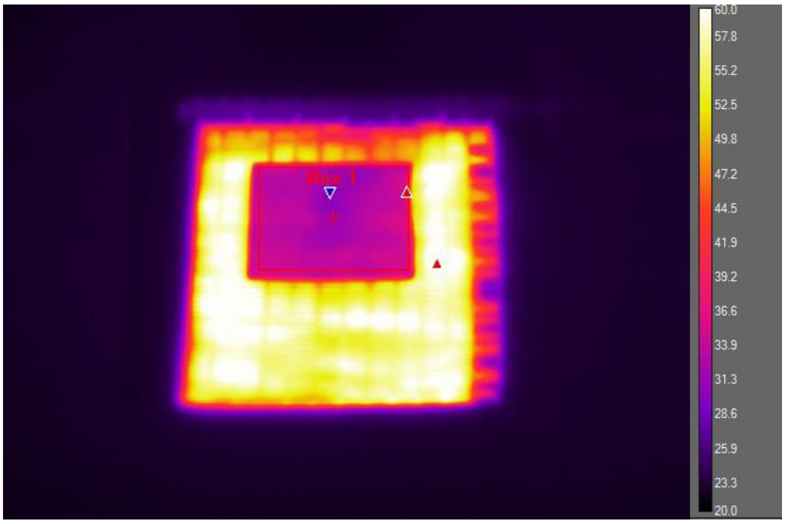


Fig. 3.11: Heat distribution of an IMAT prototype locally coupled with a sheet of agarose gel. During the heating process, the temperature where the mat has contact with the gel was lower than where the mat only touches the air.

According to the thermal parameters described above, although the IMAT heater provides a much better heating resource than other traditional heating devices, the uniform heat distribution and the precise heat regulation generated by the IMAT heater cannot absolutely guarantee an ideal heat application on artworks. During a heat application for each specific treatment, it is always necessary to determine, which materials belong to "system" – the mat and the materials need to be heated – and which materials belong to "surroundings" – the console and all materials that do not need to be heated but still have contact with the system. Then one should consider the thermal parameters inside the system while minimizing the loss of thermal energy through the surroundings to achieve an ideal heat transfer condition. One should always bear in mind: it is the thermal energy in the system that is increased by the IMAT heater but not the temperature, which is just an expression of the changes of energy in the system. The IMAT console is not a thermometer. The temperature it presents always refers to the temperature where the thermocouple is placed but never refers to the temperature of the whole mat or the temperature of the treated object. To summarized, creating a heat transfer condition as ideal as possible is exactly important as the performance and properties of the applied heating device.

Based on this critical discussion, experiments on different working patterns to introduce heat through the IMAT heater as well as observations on different heating processes of different humidification sandwiches will be carried out in the following chapters.

4 Preliminary Experiments

Before investigating the feasibility and advantages of coupling heat transfer with moisture, several fundamental questions should be clarified: What object should be treated? How should moisture transfer into the object? How should moisture in combination with thermal energy be introduced into the object? To answer these questions and give a preconception to the design of the main investigation series (Chapter 5), preliminary experiments were carried out to achieve the following goals:

1) Designing appropriate mock-ups to simulate old mends in bound volumes, which will be applied in both the preliminary experiments and the main investigation.

2) Evaluating and selecting appropriate methods and materials for the introduction of moisture into the mending paper, which will be further characterized in the main investigation.

3) Evaluating and selecting an optimal working pattern for coupling heat transfer with moisture introduction, which will be utilized in the main investigation.

4.1 Design of Mock-ups

Experiments on selecting appropriate and representative paper substrates, proteinaceous adhesives, mending papers as well as condition of artificial aging were carried out.

Six papers with various raw materials, thickness and surface characteristics were considered:

- Anton Glaser Nr. 2058 (50 g/m², sized, slightly textured with a matt surface, handmade cotton-linen-Manila hemp rag paper, acid-free)
- Anton Glaser Nr. 2061 (120 g/m², sized, slightly textured with a matt surface, handmade cotton-linen-Manila hemp rag paper, acid-free)
- Anton Glaser Nr. 2062 (80 g/m², sized, slightly textured with a matt surface, handmade cotton-linen-Manila hemp rag paper, acid-free)
- ZERKALL-BÜTTEN Nr. 8181/2 (110 g/m², sized, slightly textured with half-matt surface, machine-made, rag-containing, acid-free)
- An old typing paper (undated, calendered, machine-made, wood-pulp-containing, acid, already aged and yellowed)
- An old wood pulp paper with a printed map (undated, calendered, machine-made, wood-pulp-containing, acid, already aged, yellowed and brittle).

As simulation of old mending papers, rag papers (Anton Glaser Nr. 2061 and Nr. 2062) and wood pulp papers were considered respectively as possible mending papers used before and after the industrial revolution. Based on the different properties of various animal glues described in Chapter 2.2, hide glue and bone glue were chosen as adhesives for the mock-ups. Samples were prepared in two different models as shown in Fig. 4.1.

According to previous literatures (Coerdt, 2007, p. 193; Schellmann, 2007, pp. 62-63), an artificial aging with a fluctuating RH condition was assumed to be a realistic and efficient aging environment for protein-based adhesives. The samples were therefore aged for 14 days in an environmental aging chamber under the condition of 65 °C as well as a cycling humidity of 35% and 80% which changed every 3 hours.

The preliminary experiments on mock-ups design showed positive results that the condition of the samples after accelerated aging approximated the damages caused by the old mending in bound manuscripts and rare books: areas where the mending papers existed became stiffer accompanied by strong distortions; the ability of water absorption of proteinaceous adhesives was obviously decreased. Among all samples, the rag paper (80 g/m²) was considered to represent the paper commonly found in manuscripts and rare books, the old wood pulp paper with a printed map which possesses a considerable brittleness and fragility was regarded as a great simulation of a strongly degraded paper substrate.

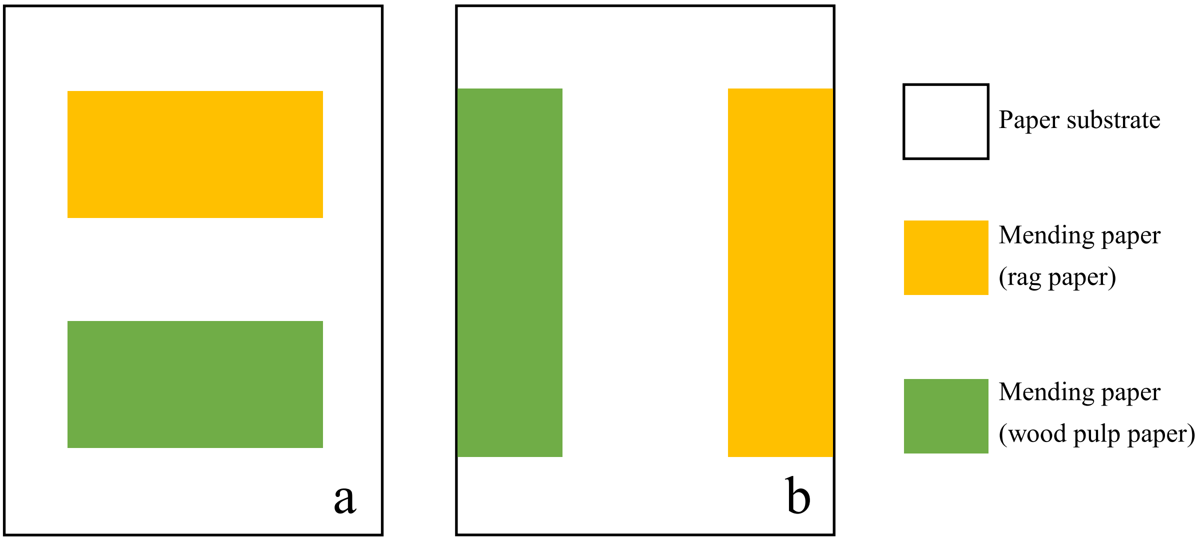


Fig. 4.1: Schematic diagrams of two models of samples prepared for preliminary experiment.

Therefore, for the mock-ups applied in the main investigation, the rag paper with a weight of 80 g/m² and the old wood pulp paper (Fig. 4.2 and 4.3) are selected as paper substrates; the rage paper with a weight of 120 g/m² and the old typing paper (Fig. 4.4 and 4.5) are selected as mending papers; hide glue and bone glue (Fig. 4.6) are selected as adhesives and the environment of artificial aging was chosen under the condition of 65 °C as well as a cycling humidity of 35% and 80% which changed every 3 hours. The mending papers were glued onto the paper substrate according to model b presented in Fig. 4.1. The final design of mock-ups is shown in Fig. 4.7.

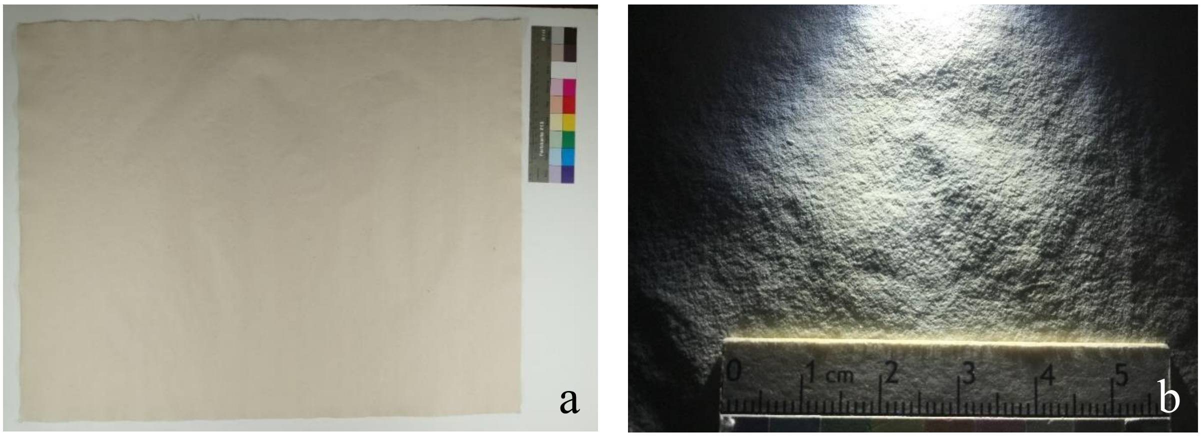


Fig. 4.2: Selected paper for the substrate of the mock-ups: Overview (a) and the surface texture captured with a raking light (b) of the Anton Glaser Nr. 2062 with a weight of 80 g/m².

Fig. 4.3: Selected paper for the substrate of the mock-ups: Overview (a) and the surface texture captured with a raking light (b) of the old wood pulp paper with a printed map.

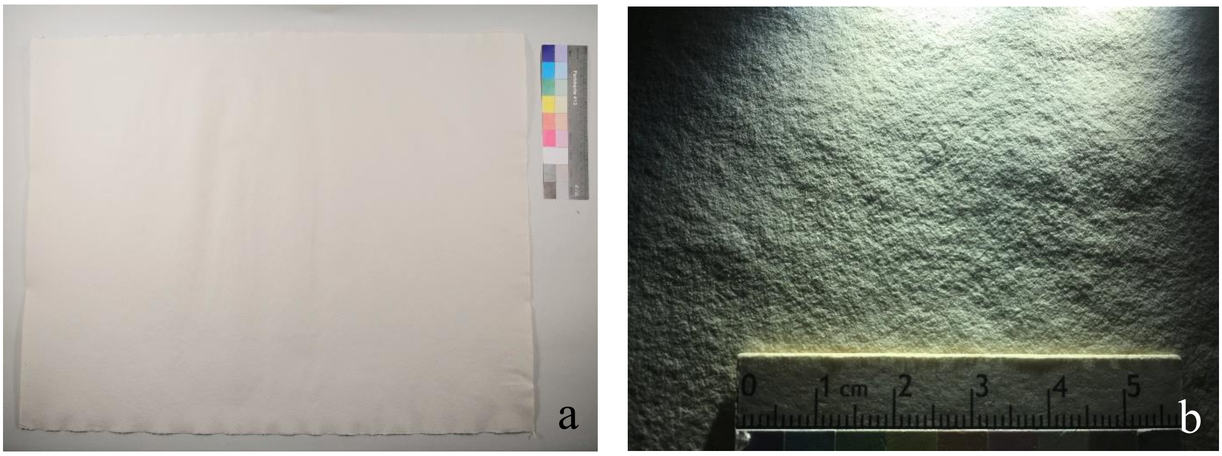


Fig. 4.4: Selected paper for the mending paper of the mock-ups: Overview (a) and the surface texture captured with a raking light (b) of the Anton Glaser Nr. 2061 with a weight of 120 g/m².

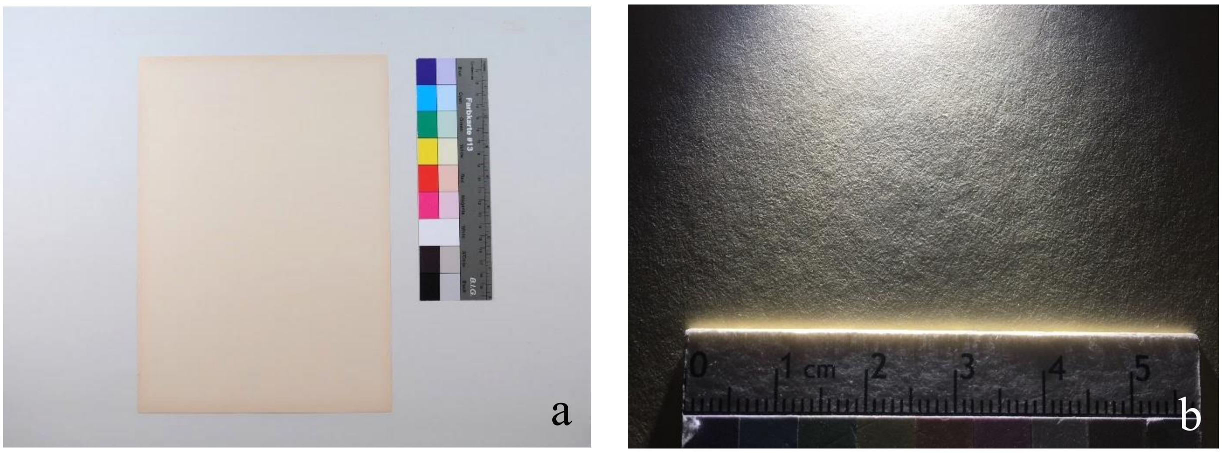


Fig. 4.5: Selected paper for the mending paper of the mock-ups: Overview (a) and the surface texture captured with a raking light (b) of the old typing paper.

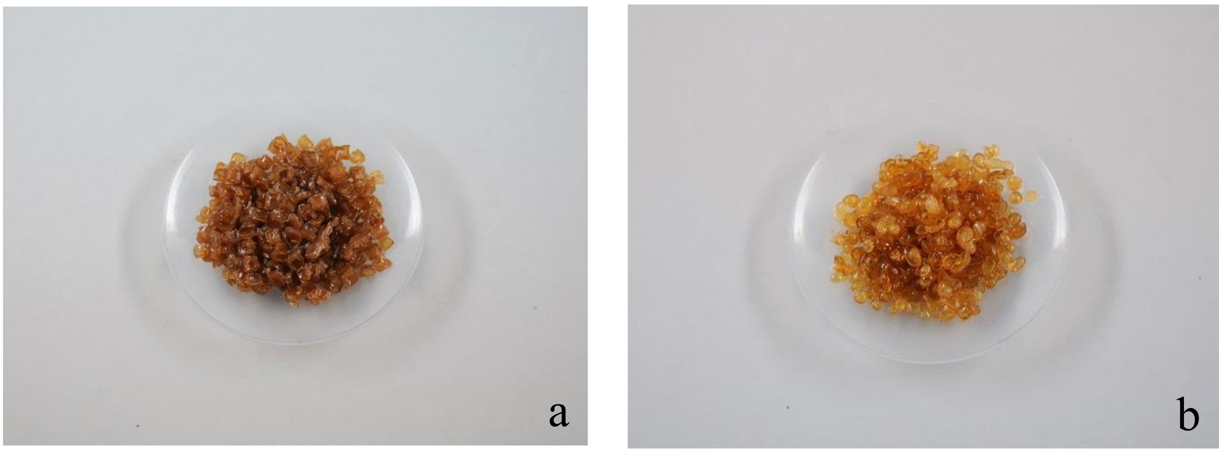


Fig. 4.6: Selected animal glues for the adhesive of the mock-ups: hide glue (a) and bone glue (b).

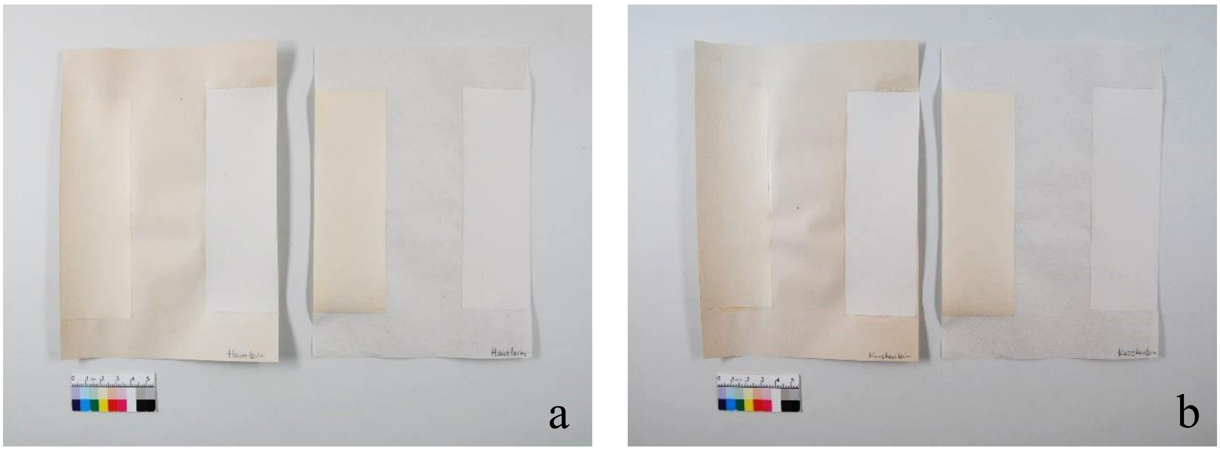


Fig. 4.7: Final design of the mock-ups for the main experiment: (a) Rag paper as substrate (left) and wood pulp paper as substrate (right), mending papers made of the old typing paper (left stripes) and the thick rag paper (right stripes), glued with hide glue. (b) Rag paper as substrate (left) and wood pulp paper as substrate (right), mending papers made of the old typing paper (left stripes) and the thick rag paper (right stripes), glued with bone glue.

4.2 Methods for the Introduction of Water into Paper

4.2.1 Relevant Mechanisms

Before different materials for introducing moisture into paper are evaluated and selected, it is necessary to clarify some terminologies and the mechanisms during the introduction of water into paper, which involves the interaction of paper with water vapor, liquid water, as well as the mechanisms of water migration in paper (Banik & Brückle, 2018, pp. 304, 316).

4.2.1.1 The Interaction of Paper and Water Vapor

The dominated factor in the interaction of paper and water vapor is the *equilibrium moisture content (EMC)*, which is a characteristic moisture content value of a humidify-sensitive material for a particular level of RH at a given temperature (Stolow, 1979, p. 18). Fig. 4.8 shows the relationship between RH, temperature and EMC of cotton, which indicates the maximal amount of water absorbed by the cellulose-based material at a particular RH and temperature (Banik & Brückle, 2018, p. 311). The EMC of cellulose rises with increasing RH and the increase becomes drastic as from 80% RH, while the EMC decreases slightly with increasing temperature. Therefore, when a dry paper (which possesses a low EMC) is placed under a high RH condition (Fig. 4.9 a), the paper will absorb water vapor from the air to establish a new and higher EMC (Fig. 4.9 b). When the new equilibrium has been approached, the absorption of water comes to an end and the exchange of water between the paper and the air is equal (Fig. 4.9 c). If the RH condition is decreased, the paper then releases water to the air to establish another lower EMC until the equilibrium is arrived (Fig. 4.9 d). The introduction of water into paper is realized by exposing paper to a high RH (Banik & Brückle, 2018, pp. 311-312).

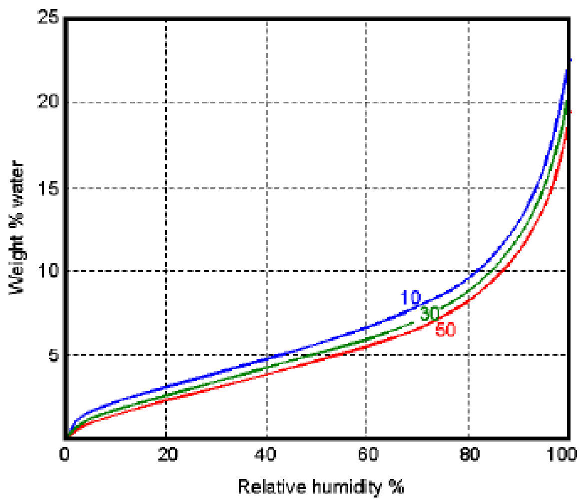


Fig. 4.8: Absorption isotherms for cotton at three different temperatures. (Source: Padfield & Larsen, 2007, p. 216)

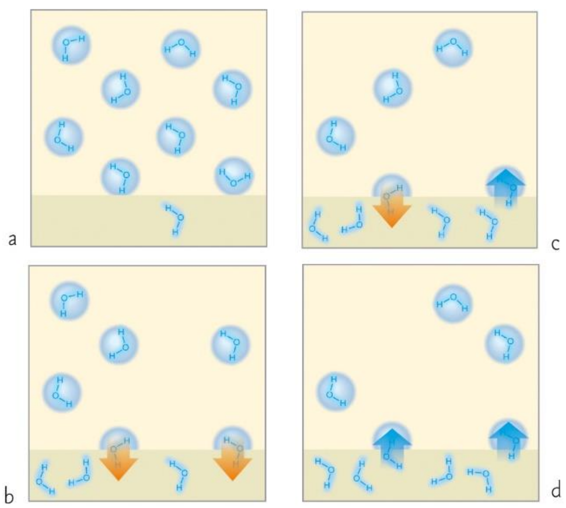


Fig. 4.9: Interaction of paper and water vapor in a confined space. (Source: Gerhard Banik and Irene Brückle, 2018, p. 311, ©Gerhard Banik and Irene Brückle)

4.2.1.2 The Interaction of Paper and Liquid Water

When water is introduced into paper in liquid form, the microscopic mechanism of the process involves *wetting* and *absorption*; the former refers to a surface interaction between the liquid water and solid paper, and the latter concerns the penetration of water into porous paper (Banik & Brückle, 2018, p. 312). Both of the mechanisms involve several forces, among which hydrogen bonding dominates. The degree of wetting and absorption depends on the interrelation of the forces – the forces of adhesion applied by the paper surface to adhere water molecules and the opposite forces of cohesion within liquid water – at equilibrium (Banik & Brückle, 2018, p. 312). *Contact angle* is therefore a significant factor in both wetting and absorption, which is strongly dependent on the surface tension of water, and the surface characteristics of paper and walls of its interior pores, i.e. whether hydrophilic or hydrophobic. Additionally, the absorption of water (the penetration of water into paper) is influenced by *capillary pressure* between air, water and the walls of paper pores, *viscosity* of water as well as *other applied forces* like gravity or partial vacuum applied in conservation treatments (Juncker, 2002, pp. 21-27; Banik & Brückle, 2018, pp. 368-370). Among these factors, viscosity of water and capillary pressure are also strongly affected by *temperature*. With an increased temperature, viscosity of water decreases which leads to an increase of water flow; whereas the surface tension of water decreases and results in a decreased capillary pressure (Banik & Brückle, 2018, pp. 27-31, 370).

4.2.1.3 Mechanisms of Water Migration in Paper

Water transport mechanisms in paper can be divided into: gas diffusion, Knudsen diffusion, surface diffusion, bulk-solid diffusion and capillary transport (Liang et al., 1990, p. 642; Nilsson et al., 1993, p. 1206).

Gas and Knudsen diffusion occur when water molecules in the gas phase operating in paper pores. Gas diffusion occurs throughout the process of water introduction into paper as long as open pores exist in fiber matrix. This mechanism depends only on temperature: Through a thermal energy input, the rate of gas diffusion increases due to enhanced molecular mobility (Liang et al., 1990, p. 642, Banik & Brückle 2018, pp. 316-317).

Surface diffusion, bulk-solid diffusion and capillary transport involve transport of water in the condensed state as absorbed water or capillary water (Liang et al., 1990, p. 642). Surface diffusion occurs when absorbed water has accumulated on the fiber surface, and bulk-solid diffusion occurs when absorbed water has accumulated within amorphous areas of fibrils and transports within the fiber cell wall. Both of them increase with increasing RH inside the fiber cell wall (Nilsson et al., 1993, p. 1206; Banik & Brückle, 2018, pp. 317-318). Capillary transport occurs only when pores are filled with water and capillary water has accumulated by interfiber pores. When not only small pores but also large pores are saturated with water, paper is fully wetted, and looks dark and translucent. Cellulose degradation products and other soluble compounds in paper can be transported from inter- and intrafiber pores to the paper surface, which can lead to tideline formation on paper (Banik & Brückle, 2018, pp. 92-93, 318-319).

During the water introduction, different mechanisms occur simultaneously in paper (Fig. 4.10). When water is introduced in gas phase by a high RH range in the ambient environment, paper will absorb water vapor from the air to establish a new and higher EMC, and the RH inside the fiber wall increases. Capillary transport can therefore occur at high RH range, but the paper cannot be fully saturated by water. The reason is that only very small pores are able to hold capillary water stably inside the pores, while large pores cannot be filled with water (Banik & Brückle, 2018, p. 93). When water is introduced in liquid phase, it is imbibed into paper firstly through capillary action. In the case of unsized paper, liquid water penetrates rapidly into pores by capillary transport, while water vapor moves before liquid water into the pores and the fiber interior by bulk-solid diffusion. In the case of sized paper, the fiber walls in the sizing layer do not wet, but water vapor can travel into the pores by gas diffusion, surface diffusion and bulk-solid diffusion (Banik & Brückle, 2018, p. 319). Since not all fibers in paper are completely sized, a full saturation of water is only a matter of time when water is introduced by liquid water.

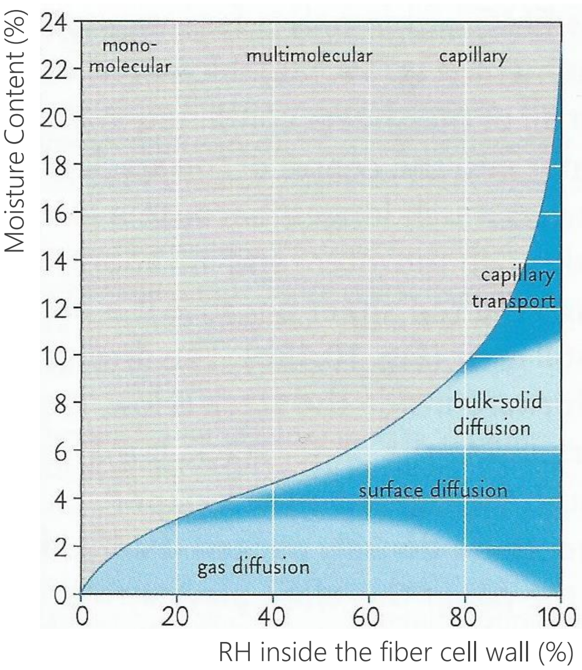


Fig. 4.10: Different mechanisms of water transport in relation to paper water content at 20 °C, fiber condition from dry to fully wetted. (Source: Gerhard Banik and Irene Brückle, 2018, p. 319, ©Gerhard Banik and Irene Brückle).

4.2.1.4 Humidified, Moistened and Wetted

Aqueous conservation treatments of paper, ranging from humidification to washing, arrange different stages of water accumulation inside the paper depending on the aims and requirements of each individual treatment. In order to make the terminologies clear, which will be used in following chapters, description of paper condition after the introduction of water can be divided into three groups regarding the approximate water content of paper (Fig. 4.11): *Humidification* treatment achieves water content of paper in the range of 8-24%, which can be further devided to two descriptions of paper condition, namely the paper is *humidified*

(8-12% moisture content) and *moistened* (12-24% moisture content). The moistened paper can be further introduced more water through misting or a contact with bulk water until the paper is fully *wetted* (above 24% moisture content). During the process, water accumulates firstly within fibers (stage 1 and 2), then begins to fill the paper pores (stage 3 to 5) until the pores are fully saturated by water (stage 6) (Banik & Brückle, 2018, p. 323).

Based on the criteria for localized aqueous treatment (see Chapter 2.3), neither tideline-formation nor penetration of animal glue into paper substrate after the treatment is allowed. Area to be treated cannot be applied with too much water as all pores of paper are fully saturated. Therefore, the introduction of water in this study should be defined as **humidification**. Since the measurement of the EMC during treatment is hardly to be conducted, it is difficult to differentiate “humidified” or “moistened”. To avoid confusion, the terminology used in the further chapters will be uniformly defined as **humidified**.

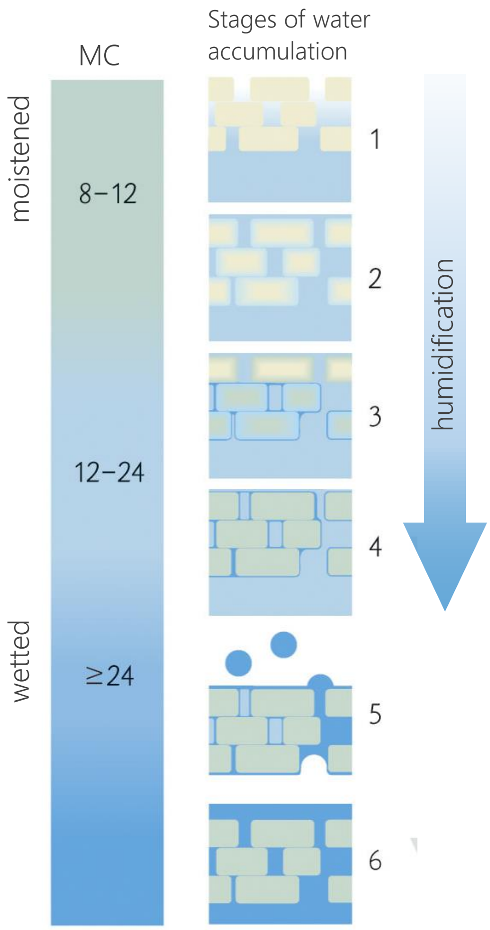


Fig. 4.11: Description of paper condition after the introduction of water regarding the water content of paper (Source: Gerhard Banik and Irene Brückle, 2018, p. 323, ©Gerhard Banik and Irene Brückle)

4.2.2 Humidifying at a Locally Elevated RH Condition – Gore-Tex Sandwich

Target humidification can be achieved by locally increasing the RH levels, through which water is introduced into paper and adhesive in gas phase. The RH levels can be locally elevated by combining blotting paper with Gore-Tex® membrane, the so-called Gore-Tex sandwich, which has been used in conservation since the mid-eighties (Singer et al., 1991, p. 102). Gore-Tex® is a stretchy, microporous membrane composed of expanded PTFE which is air permeable, hydrophobic, weather durable and functions over a wide temperature range. Various different materials under the name Gore-Tex are commercially available, among which a special form of Gore-Tex® is used in conservation: a nonwoven fabric bonded to a thin film of Gore-Tex®, with no colorants or additional adhesives (Purinton & Filter, 1992).

Thanks to the micro pores in Gore-Tex® membrane, which are large enough for water vapor but too small for water droplets to pass through, Gore-Tex sandwich is generally regarded as a low-risk and controllable humidification system in paper conservation. Various applications, such as humidifying objects, removing backings or linings, solving local adhesives etc., benefit hugely from Gore-Tex sandwich since different constructions of the sandwiches can be conducted to meet specific requirements for each application (Singer et al. 1991, pp. 104-110). For a localized removal of mending papers in bound volumes, Gore-Tex sandwich is normally constructed as:

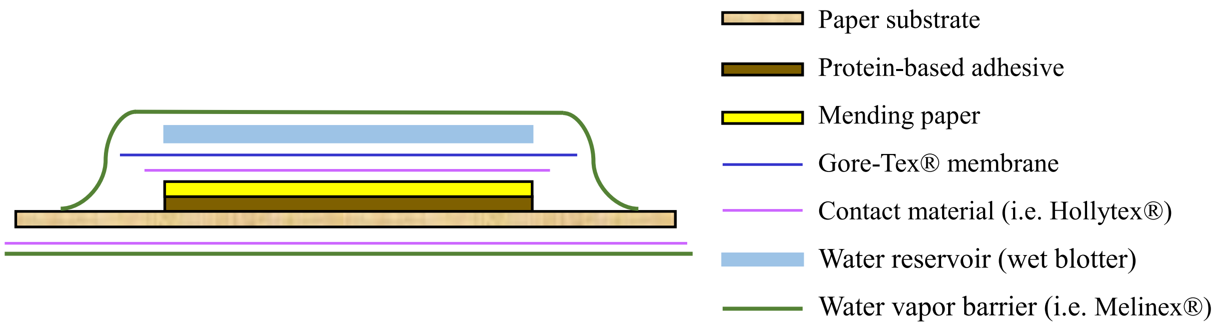


Fig. 4.12: Schematic diagram of Gore-Tex sandwich for removing a mending paper.

The introduction of moisture using Gore-Tex sandwich is achieved by placing the mend in a space with a high RH level. The Gore-Tex® membrane protects the mend from having direct contact with liquid water in the water reservoir – normally a wet blotter – and at the same time exposes the mend to the water vapor transmitted through it. Due to the small air space in the sandwich compared to the surface of water reservoir, the RH between Gore-Tex and the mend can reach to a level close to 100% within minutes (Banik & Brückle, 2018, p. 327). The water vapor from the sandwich travels through the mending paper, the adhesive layer and finally the paper substrate. This humidification treatment should proceed until the protein-based adhesive swells sufficiently that the mending paper can be readily removed from the paper substrate with a spatula.

Since the water is introduced in gas phase during the humidification treatment, generally there is barely no risk of formation of tideline or severe distortion on the paper substrate, regardless of the heat is applied or not. However, the humidification by Gore-Tex sandwich generally lasts long, from few hours to more than ten hours until the glue layer absorbs enough moisture (Singer et al., 1991, p. 105). Heat application can distinctly accelerate the swelling time of the protein-based adhesive (Singer et al., 1991, p. 106).

4.2.3 Humidifying by Materials with High Water Retention Power – Hydrogels

As described in Chapter 2.3, 4.2.1.3 and 4.2.1.4, direct contact with liquid water presents several disadvantages such as tideline formation, alteration the surface texture of paper as well as distortion, deformation and disparity of the treated area. However, if a water reservoir possesses a high water retention power, through which the rate of moisture penetration into paper sheet can be significantly delayed, they can possibly be suitable for the localized introduction of water into paper (Warda et al., 2007, p. 264; Mazzuca et al., 2014, p. 205). Hydrogels are typical materials which obtain these properties.

Hydrogels are polymers with three-dimensional (3D) network structure possessing the ability to absorb and retain a large fraction of water in their interstitial structures. While touching water, hydrogels continue to absorb and swell to form relatively stable space lattice or network pores because of the presence of hydrophilic groups. Due to their physical or chemical crosslinking within the polymer chains, hydrogels can hold an unaltered 3D structure during swelling without completely dissolved in water (Faroongsarng & Sukonrat, 2008, p.152; Kabir et al., 2018, p. 154). Water absorbed in hydrogels presents special thermodynamic properties and can be classified into three types: (i) non-freezable bound water, which is non-crystallizable due to strong molecular interactions with polar function groups on polymer chains, (ii) freezable bound water, which exhibits a crystallization point lower than 0°C and (iii) free water, which crystallizes at around 0 °C (Ping et al., 2001, p. 8461; Faroongsarng & Sukonrat, 2008, p.153). Both non-freezable and freezable water are categorized as bound water.

Compared to the interaction of paper and liquid water, the interaction of paper and hydrogels is somehow distinct: When gels directly touch a paper substrate, the water in gels is, on the one hand, indrawn into pores of paper by the forces of adhesion applied by the paper surface to adhere water molecules (as long as the paper substrate is not strongly sized), and on the other hand, hold on to the gels by opposite forces of intermolecular or capillary forces inside the gels. Meanwhile, water vapor can travel abidingly into the paper by gas diffusion, surface diffusion and bulk-solid diffusion. The water content in paper increases from ca. 8% to 24% with the accumulation of monomolecular, multimolecular and capillary water in cellulose (see Fig. 4.10 and 4.11). Further introduction of water may cause irreversible damages similar to the reaction of paper to bulk water. Therefore, the rate of water introduction into paper substrate is vitally related to intermolecular or capillary forces inside the gels, which also reflects the mobility of both the bound water and the free water absorbed in gels. These forces are strongly affected by the gel properties, such as the structure and concentration of the gels, the working temperature, as well as other applied forces like gravity of the gels or external pressure during conservation treatment.

When a barrier paper is presented between gels and the paper substrate, the water in gels is firstly absorbed by the barrier paper and raises its water content with the accumulation of monomolecular, multimolecular and capillary water. As long as the barrier paper is not completely saturated with water, the paper substrate has only contact with the multimolecular and a small amount of capillary water in the barrier paper instead of directly to the free water in gels. The wetting through liquid water on the paper substrate and the penetration of liquid water into pores therefore hardly occur, the humidification of paper substrate is achieved mostly by gas diffusion, surface diffusion and bulk-solid diffusion of water vapor. Once the barrier paper gets wetted, the contact between paper substrate and liquid water is still not avoidable.

This chapter is going to discuss three selected hydrogels – methyl hydroxyethyl cellulose (Tylose® MH), agarose and gellan gum, which are commonly used in paper conservation. In each section, the properties of the gel, its preparation method and construction of the humidification sandwich are presented. The performance and working properties of each material as a localized humidification agent will be discussed in Chapter 5.2.3.

4.2.3.1 Methyl Hydroxyethyl Cellulose (Tylose® MH)

Cellulose ethers, such as methylcellulose (MC), carboxyl methyl cellulose (CMC) or methyl hydroxyethyl cellulose (MHEC, also referred to as HEMC), have already been used in paper conservation since the second half of 20th century. They are derived from cellulose, but they tend to have a lower degree of polymerization than cellulose (Feller & Wilt, 1990, pp. 23-24). In the field of paper conservation, besides being used as sizing agent and as adhesive for backing or mending, cellulose ethers are also commonly used as poultice materials to soften adhesives through paper due to their high water content as well as their water retention power (Baker, 1982; Baker, 1984, p. 55).

The MHEC products from Tylose® is a semiflexible linear-chain polysaccharide, under the product name of Tylose® MH. The difference to MC is that MHEC contains a small amount of hydroxyethyl substitution (Henry et al., 1989, p. 32-33, Fig. 4.13). Tylose® MH products are water soluble non-ionic polymers with standard etherification, which is available in wide selection of mean viscosity ranging from 50 mPa•s to 60000 mPa•s [2]. The MHEC product employed in this study is Tylose® MH 30000 YP4, which, according to supplier information, is white powder and exhibits a degree of substitution relative to methylation (DS value) of 1.70, and a molar degree of substitution relative to hydroxyethylation (MS value) of 0.15. Tylose® MH 30000 YP4 is delayed soluble in cold water, and its viscosity value is 20000 - 27000 mPa·s, which increases with the growth of concentration.

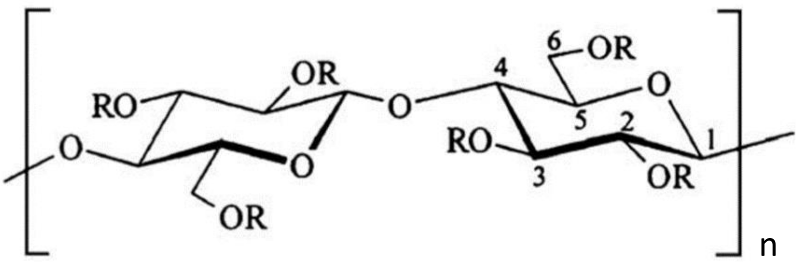


Fig. 4.13: Chemical structure of methyl hydroxyethyl cellulose, R = H, CH_3, $(CH_2CH_2O)_nH$. (Source: Pourchez et al., 2006, p. 289).

[2] The viscosity level is based on Hoeppler: 2% solution of the commercial product with 5% moisture content, 20ºC, 20ºdH (German hardness).
Source:https://www.setylose.com/en/products/methyl_cellulose/tylose_mh/index.vist/modul,detail,51/index.vist

Under room temperature, MHEC can only be dissolved in cold water and swell to form a hydrogel with flow properties but does not form a gel with a stable structure, which happens only when the temperature is beyond its thermal gel point (Greminger and Krumel 1980, pp. 7-8). When MHEC is dissolved in cold water, hydrophilic groups contained by this linear-chain polysaccharide increase osmotic pressure in the gel that leads to swelling (Kabir et al. 2018, p. 157). The swelling process is not infinite and the degree of swelling can be elucidated by Flory-Rehner theory – the equilibrium swelling theory – using Gibbs free energy as presented in equation 4.1 (Koetting et al. 2015, p. 2):

$$\Delta G_{total} = \Delta G_{mixing} + \Delta G_{elastic} \tag{4.1}$$

ΔG_{total} is the total free energy of the polymer chains, while ΔG_{mixing} is the free energy contributions due to enthalpic mixing, which promotes swelling. $\Delta G_{elastic}$ is the free energy contribution due to the elastic forces imposed by the crosslinked hydrogel networks, which promotes contraction. The equilibrium of swelling is attained when there is no driving force for swelling, namely $\Delta G_{total} = \Delta G_{mixing} + \Delta G_{elastic} = 0$. Under this circumstance, MHEC is able to retain a three-dimensional structure without completely dissolved in the water, but the chains possess a certain degree of lubricity since the swelled polymer molecules are generally held by hydrogen bonding, so the network is unstably structured and able to flow. As the temperature rises, the hydrogen bonding between water molecules weakens and the interaction between chains dominates, which eventually results in the formation of a gel with a stable structure (Greminger & Krumel, 1980, p. 8). This thermal gelation process is reversible upon cooling. The thermal gel point of MHEC is about 70°C, which is higher than MC whose thermal gel point is about 55 °C due to the small amount of hydroxyethyl substitution of MHEC (Greminger & Krumel, 1980, p. 3).

In the field of conservation, the swelling property of MHEC in cold water, through which the intermolecular forces between water and the polymer chains is established, is commonly utilized to achieve a water retention power. Since water appears as a plasticizer in the gel network, by adjusting the network density – the viscosity of the solvent, a MHEC gel with a desired water retention power can be attained. Based on the previous experiments, 10 wt% Tylose® MH 30000 YP4 has been proved to be a decent humidification material, which is prepared through the following process:

- 450ml deionized water is added to 50g Tylose® MH 30000 YP4 powder (Fig. 4.14 a).
- Due to the delayed solubility of Tylose® MH 30000 YP4, the powder is firstly dispersed in water (Fig. 4.14 b), it then swells slowly (Fig. 4.14 c) until the equilibrium is reached. After ca. 24 hours, it forms a pseudoplastic gel with high viscosity (Fig. 4.14 d).

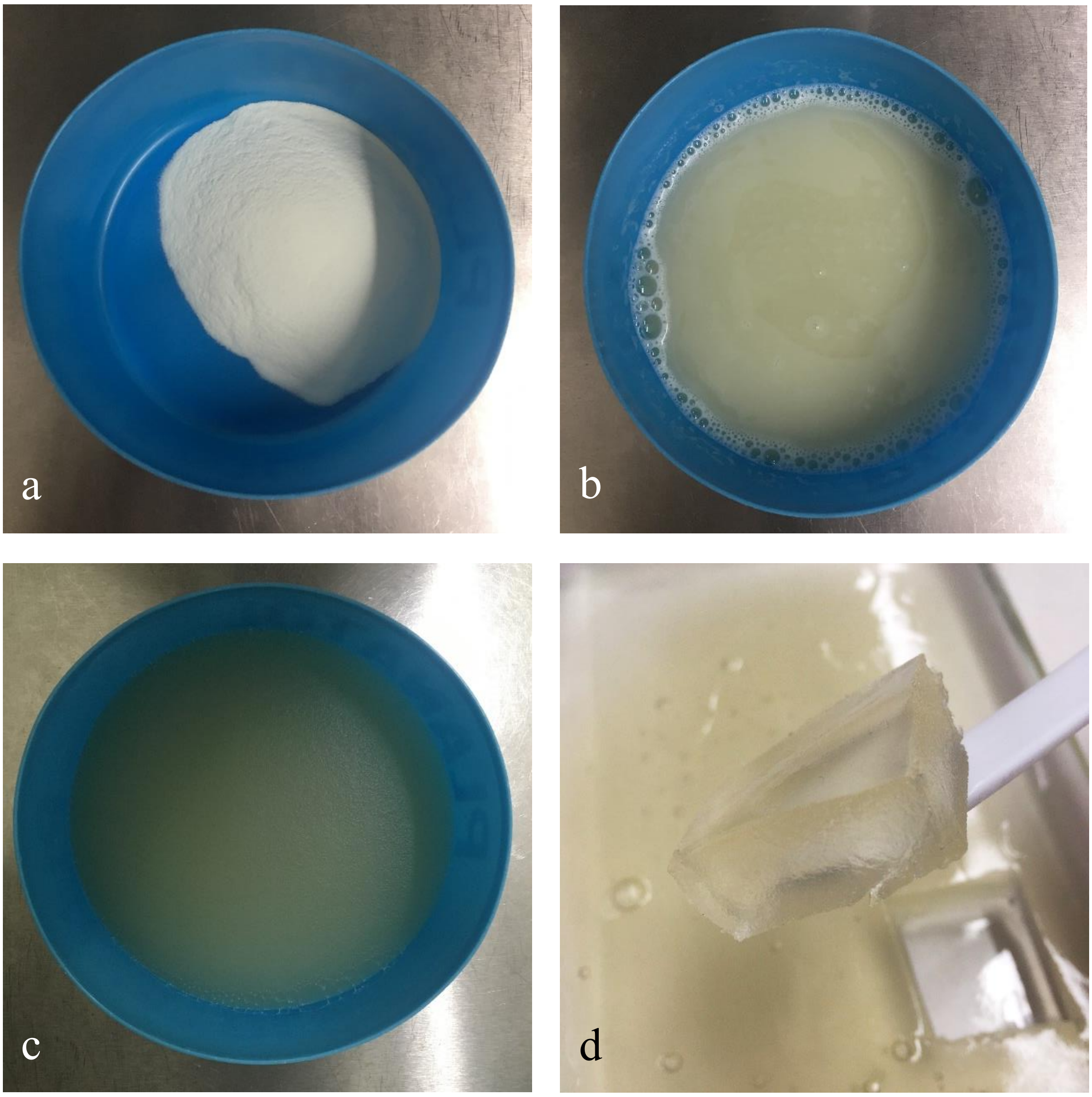


Fig. 4.14: Preparing the 10 wt% Tylose® MH 30000 gel. (a) Dry powder of Tylose® MH 30000. (b) Tylose® MH 30000 powder in water (10 wt%) after thoroughly dispersed. (c) 10 wt% Tylose® MH 30000 during swelling. (d) The equilibrium of swelling is attained and a pseudoplastic gel with a high viscosity is formed.

For a localized removal of mending papers, the humidification sandwiches are constructed as:

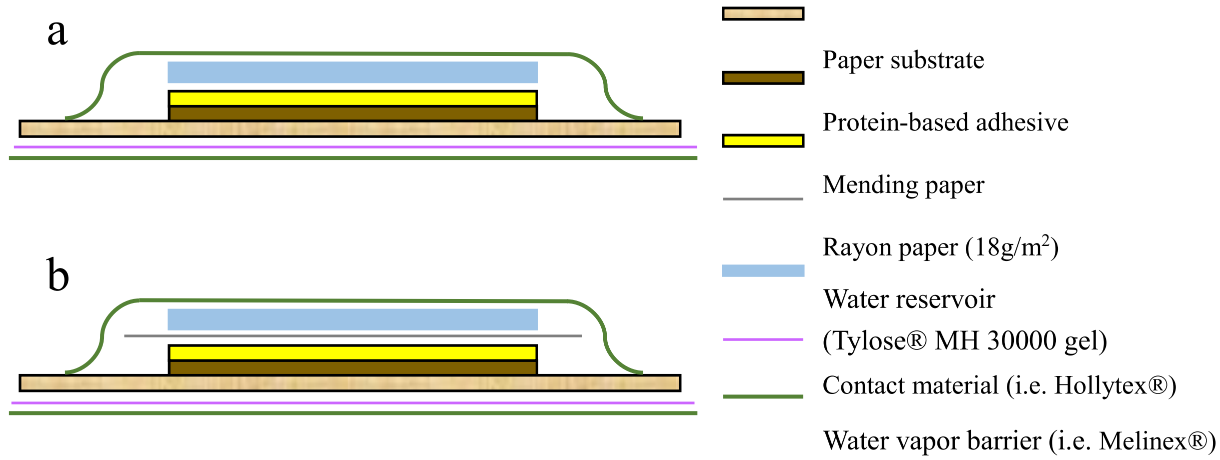


Fig. 4.15: Schematic diagrams of humidification sandwiches using (a) Tylose® MH 30000 gel and (b) Tylose® MH 30000 gel in combination with a sheet of Rayon paper for removing mending papers.

Since the 10 wt% Tylose® MH 30000 gel is pseudoplastic and owns high viscosity, it can be cut into a similar shape to the mend, but neither the shape nor the thickness of the gel stays still. The gel tends to flow due to external pressure or its self-gravity. The shaped gel can be placed directly on the mending paper (Fig. 4.15 a). The gel can also be applied together with a barrier paper, which is considered to minimize residue left on the paper after a conservation treatment. For the barrier paper applied in this study, the Rayon paper with a weight of $18g/m^2$ is selected. Rayon paper is made from regenerated cellulose fiber – a semisynthetic fiber, which can balance the stability of a synthetic fiber and the water absorption ability of a natural fiber. The gel can also be placed firstly on a sheet of Rayon paper, which will be humidified by the gel and then stretches, then placed together with the Rayon paper on the mending paper, making sure that no crease occurs on the Rayon paper (Fig. 4.15 b). Two Polyester films are placed on top and bottom of the humidification sandwich to keep the moisture inside.

4.2.3.2 Agarose

The literatures of paper conservation from the past decade reveal growing interest in using agarose gel as a conservation material for local treatment such as targeted cleaning and adhesive removal. It has been evaluated as a good alternative to cellulose ether poultices as a humidification agent for local treatment of removing adhesives on paper objects (Warda et al., 2007, p. 264).

Agarose is one of the components of agar (also known as agar-agar), which is a linear polysaccharide that accumulates in the cell walls of *Agarophyte algae*. The rest fractions were generally named agaropectin (Armisén & Galatas, 2000, p. 22). Agarose is an alternating copolymer with repeated unit of 1,3-linked β-D-galactopyranose and 1,4-linked 3,6-anhydroα-L-galactopyranose (Araki, 1956, p. 543, Fig. 4.16), which gives the agar its gelling power. The molecular weight of agarose is beyond 100,000 Daltons and often surpasses 150,000 Daltons; the sulfate content is normally under 0.15%. As agaropectin, the non-gelling polysaccharide, consists of lower molecular weight (usually below 20,000 Daltons) and higher content of sulfates (5%-8%) (Armisén & Galatas, 2000, pp. 27-28).

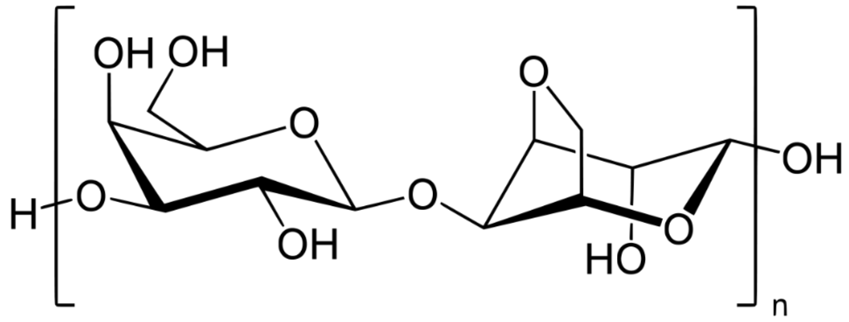


Fig. 4.16. Chemical structure of agarose (Source: Samiey & Ashoori, 2012, p. 2)

The mechanism of forming an agarose gel is significantly different from that of the swelling of a cellulose ether gel: Unlike the relatively random colloidal polymer chains surrounded by water molecules in the cellulose ether gel, the agarose gel contains a 3-fold double helix which is stabilized only by van der Waals forces. No hydrogen bond presents in the double helix. To achieve an agarose gel, agarose dry powder is dissolved in boiling water, then poured into a mold and cooled. The gelation process is demonstrated in Fig. 4.17. During heating, the agarose randomly coiled molecules can be dissolved in water. Upon cooling, the polymer chains transform to double helices and agglomerate into a three-dimensional macroreticular structure. Due to the formation of three-dimensional aggregation of the double helixes, agarose gel is rigid and slightly turbid. Specifically, it presents a large degree of hysteresis between the melting and gelling temperature: the former is far higher than the latter. To emphasize, the gelling process is not a result of polymerization, which caused by a chemical reaction, but only a simple electrostatic attraction. The gel is so-called “physical gel” which is reversible: It can melt by heating over its melting temperature and gel again while cooling[3] (Rao, 1998, p. 258; Warda et al., 2007, p. 265; Armisén & Galatas, 2000, pp. 28-31; Dai & Matsukawa, 2013, p. 38).

After gelation, unlike cellulose ether gel which is theoretically a non-Newtonian fluid that owns a shear-thinning property, agarose gel is rigid and has a spongy structure and can hold a great amount of water in its interior network, which can shift freely through the mesh capillaries. The water can then be ejected from the gel due to its syneresis capacity. Once the undried synergized gel is immersed in water, it can reverse to its previous form (Armisén &

[3] This reversible sol-to-gel and gel-to-sol transformations can be repeated indefinitely without the presence of aggressive substances, through which the agarose molecule could be hydrolyzed and destroyed.

Galatas 2000, p. 31).

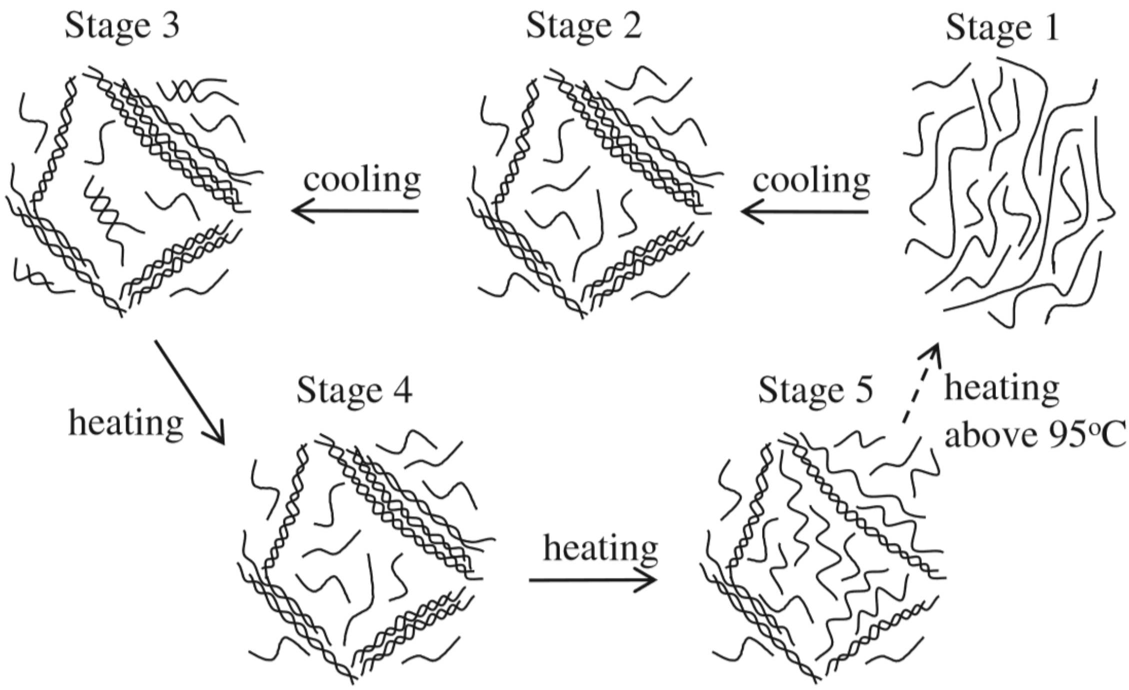


Fig. 4.17: Gelling and melting process of agarose during cooling and reheating (Source: Dai & Matsukawa, 2012, p. 184)

The gel properties are significantly influenced by the agarose sol-concentration. At around 0.3% (w/v), the gelation begins already (Warda et al., 2007, p. 265). As the concentration increases, the viscosity, the gelling temperature of the agarose-sol increases simultaneously; but the pore-size of the spongy structure of the agarose-gel decreases as well as the melting temperature and the stiffness of the gel increases (Mohammed et al., 1998, pp.18-19; Hughes & Sullivan, 2016, pp. 31-32). Besides, as the concentration of agarose increases, the interaction between water molecules and agarose macromolecules, namely the average probability of collision between water molecules and the gel networks also increases due to the accumulating population of double helices and their interconnection. This results in a slight decrease in the mobility of bound water and a significant decline in the mobility of free water in higher concentration gel (Bertasa et al., 2017, pp. 15-16). These properties provide possibilities for conservators to adjust water introduction into paper by preparing agarose gels in different concentrations and thicknesses.

According to previous studies carried out by other conservators, agarose with a gelling temperature (gel prepared at 1.5 wt% concentration) between 34°C and 38°C and a melting temperature (gel prepared at 1.5 wt% concentration) between 90 and 95°C is chosen for this investigation. By far, agarose gel is applied for a wide variety of paper conservation treatments including overall bathing of paper objects, backing and attachment removal, enzyme treatment, local stain reduction etc. (Hughes & Sullivan, 2016, p. 32). Since different treatment demands different properties of the agarose gel, the gel concentration shown in the previous literatures varies from around 1-1.5 wt% (van Dyke, 2004; Warda et al., 2007; Markevicius et al., 2017b) to around 5 wt% (Hughes & Sullivan, 2016; Barbisan & Dupont, 2017; Sullivan et al., 2017), while the thickness of prepared gel from 2mm to 1cm. As gel with a higher concentration and a slighter thickness are generally considered to provide a better control of the rate of water introduction into paper during the treatment, preliminary experiments of agarose gels with different concentrations and thicknesses have been carried out.

The result of the preliminary experiments showed that 2mm gels presented good performances in localized treatment, while thicker gels were too stiff to adjust itself in accordance with paper surface, and they also raised the risk of tideline formation at the same time. As already discussed, besides the concentration and the thickness (gravity) of gels, the working temperature and the external applied pressure during the treatment also have a direct impact on the speed of water introduction. Therefore, the agarose gels applied for the further experiments coupled with different temperature and different working patterns are prepared in 2 wt%, 3 wt%, 4 wt%, 5 wt% and 6 wt% through the following process:

- 94-98 ml water (respectively for 6 wt%, 5 wt%, 4 wt%, 3 wt% and 2 wt% agarose gels) is preheated with a microwave to over 90°C.
- The water included a magnetic stir-bar is placed on a hot plate heated over 90°C. 2-6g agarose (respectively for 2 wt%, 3 wt%, 4 wt%, 5 wt% and 6 wt% agarose gels) is dissolved in the water.
- The mixture is stirred until a clear solution appears (Fig. 4.18 a, b). The stirring takes about 30-90 minutes depending on the concentration.
- The solution is poured into a plastic or glass container and cooled to room temperature. Make sure the layer's thickness is 2mm. For this investigation, glass plates with spacers (thickness: 2mm) which normally utilized for electrophoresis are applied for gel casting (Fig. 4.18 c). 2 wt% and 3 wt% agarose can be dropped vertically between the two glass plates and cooled to room temperature (Fig. 4.18 d).
- However, the viscosity and the gelling temperature of agarose solution as of 4 wt% is too high to cast a continuous gel layer through a vertically pouring between the two glass plates. A better method for casting 2mm agarose with high concentration is laying one glass plate assembled with two spacers, pouring the agarose solution on the plate when it is still at high temperature (Fig. 4.18 e), and then placing another glass plate onto the first glass plate. The upper glass plate should be hold initially lopsided and laid onto the nether plate from one glass edge (Fig. 4.18 f), then slowly placed down (Fig. 4.18 g). Two glass plates are pressed together, and the agarose solution is squeezed in between to form a 2mm gel sheet. This method can effectively avoid the formation of air bubbles in the gel. After cooling to room temperature, the previous clear solution becomes a continuous turbid gel with a uniform thickness (Fig. 4.18 h, i).

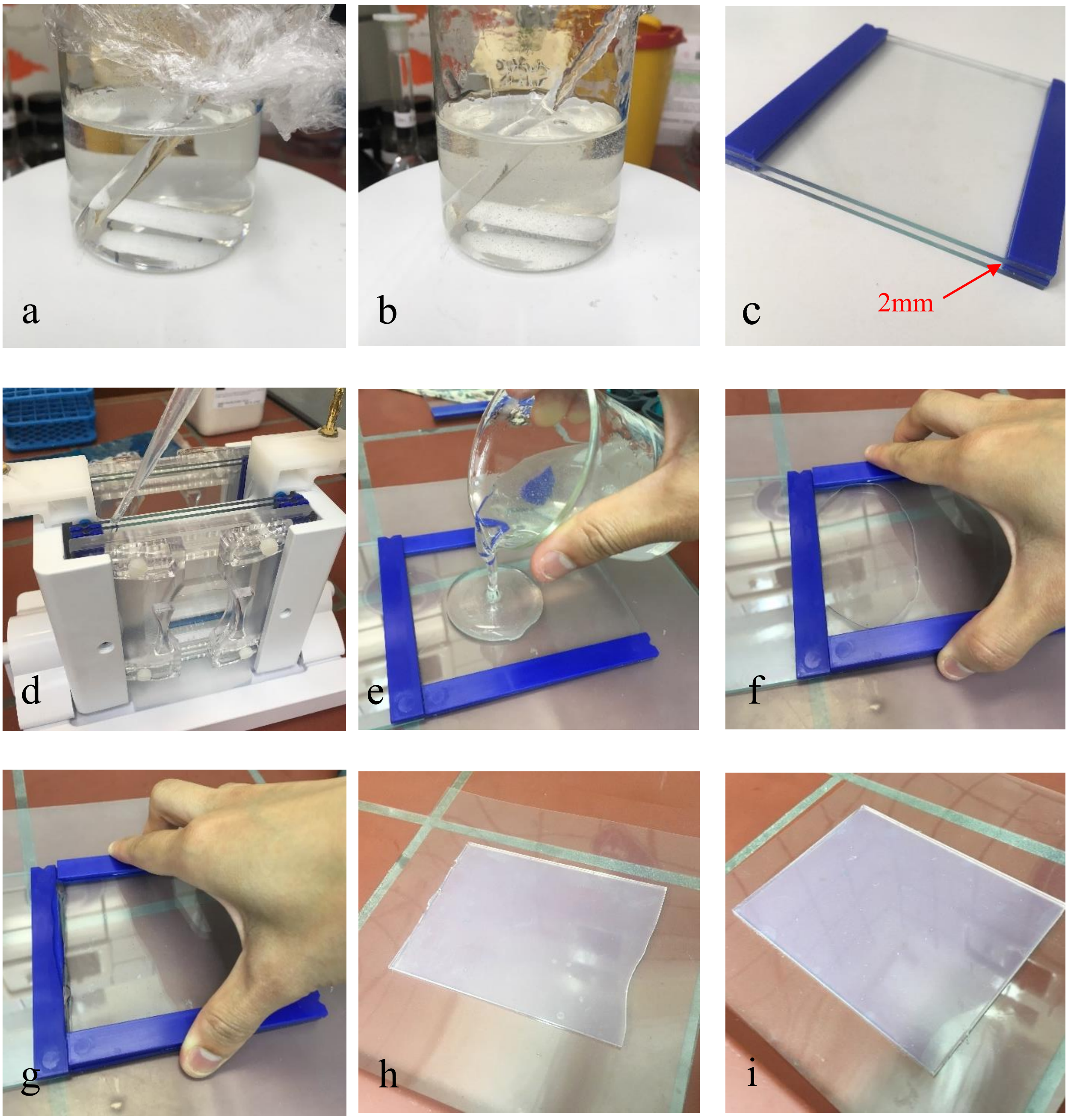


Fig. 4.18: Preparing the agarose gels. (a) Clear solution of 2 wt% agarose after heating and stirring. (b) Clear solution of 6 wt% agarose after heating and stirring. (c) Glass plates with two 2mm thick spacers. (d) Pouring the 2 wt% agarose solution vertically between the two glass plates. (e) Pouring the 6 wt% agarose solution onto the glass plate as it is still at high temperature. (f) Holding the upper glass plate initially lopsided and placing it onto the nether plate from one glass edge. (g) Slowly placing the whole upper glass down and pressing. (h) After cooling and removing from the glass plates, a turbid agarose gel (2 wt%) appears. (i) After cooling and removing from the glass plates, a turbid agarose gel (6 wt%) appears.

For a localized removal of mending papers, the humidification sandwiches are constructed as:

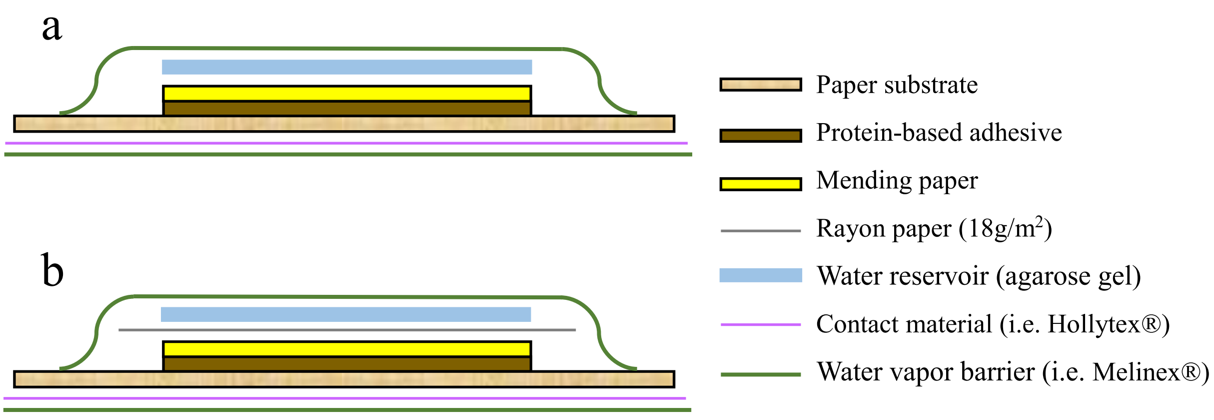


Fig. 4.19: Schematic diagrams of humidification sandwiches using (a) a 2mm layer of agarose gel and (b) a 2mm layer of agarose gel in combination with a sheet of Rayon paper for removing mending papers.

Since the agarose gel is rigid and translucent, it can be cut into the same shape as the mend: A template of the mend can be firstly created using a polyester film (i.e. Melinex®) and a permanent marker. The 2mm gel is placed on top of the template and a scalpel is used to cut the gel into the shape. The shaped gel sheet should then blot up excess moisture gathered on the gel's surface, and then it can be placed directly on the mending paper (Fig. 4.19 a). The gel can also be placed firstly on a sheet of Rayon paper, which will be humidified by the gel and then stretches, then placed together with the Rayon paper on the mending paper, making sure that no crease occurs on the Rayon paper (Fig. 4.19 b). Two Polyester films are placed on top and bottom of the humidification sandwich to keep the moisture inside.

4.2.3.3 Gellan gum

Another conservation material applied for cleaning treatments or adhesive removal is the rigid hydrogel of gellan gum. This conservation process is developed in ICPAL Laboratory for the Conservation of Library Materials in Rome since 2003 (Iannuccelli & Sotgiu, 2010, p. 25). Gellan gum is a high-molecular-weight polysaccharide secreted by the microorganism *Sphingomonas elodea* and it functions as a structuring and gelling agent in food and biomedicine industry (Botti et al., 2011, p. 1; Sworn, 2000, p. 117). The primary structure of gellan gum is a linear tetrasaccharide based on repeating β-D-Glucose, α-L-Rhamnose, and β-D Glucuronic acid units. The properties of gels vary depending on acyl contents. Low acyl (LA) gellan gum (Fig. 4.20), which the acyl groups are completely removed, is applied commonly in paper conservation due to its formation of rigid, non-elastic and brittle hydrogels (Botti et al., 2011, p. 1; CP Kelco, 2007, p. 4).

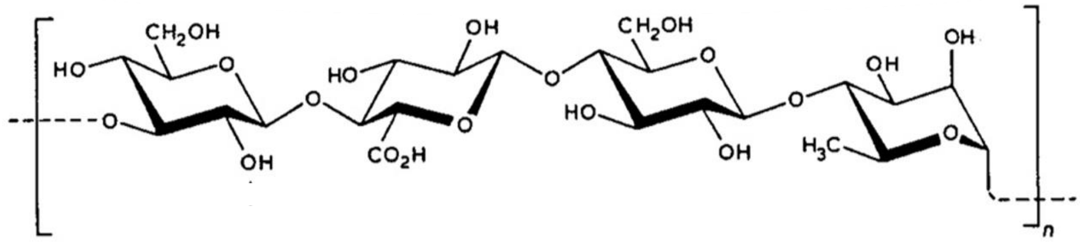


Fig. 4.20: Chemical structure of deacetylated gellan gum (Source: Morris et al., 2012, p. 375)

The formation of gellan gel, to a certain extent, differs from the formation of agarose gel, which takes generally three steps – dispersion, hydration and gelation. During dispersion, it is to ensure that the gellan gum particles are fully dispersed in the solvent and do not clump together, otherwise they can end up in incomplete hydration and gelation. Gellan gum is insoluble in cold water, and nevertheless, it tends to swell when low content of cation presents. By heating to hydration temperature[4] of LA gellan gum, gellan molecules present as disordered coils in aqueous solution. Similar to agarose, the gelation of gellan occurs during the cooling process, as the molecules undergo a disorder-order transition and form ordered double helices. Differs from agarose gel, the conformation of 3-fold double helices in a LA gellan gel is followed by associations between the helices through weak interactions such as intra- and inter-chain hydrogen bonds as well as Van der Waals forces in the absence of cations (Fig. 4.20). However, when gel promoting cations (especially Ca^{2+}) present, the aggregation of the gellan double helices can be promoted via direct carboxylate…calcium…carboxylate interactions and therefore a three-dimensional network is formed (Fig. 4.21). During the practice, a salt such as calcium acetate $Ca(CH_3COOH)_2$ can be added to the deionized water in order to obtain a hard and brittle gel. One particular property of the gellan sol-gel transition process is the so-called “snap set” – the transition sets instantaneously once the gelling temperature has been reached, which is normally in the range of 30 - 50ºC. Similar to agarose gel, LA gellan gel demonstrates also a significant thermal hysteresis between the melting and gelling temperature: the gels melt at a higher temperature than that at which they set. However, unlike agarose gel, under most circumstances LA gellan gel is not thermo-reversible below 100°C. (Rao, 1998, pp. 268-271; Sworn, 2000, pp. 118-122; CP Kelco, 2007, pp. 5-6; Iannuccelli & Sotgiu, 2010, p. 31)

After gelation, gellan gel also has a spongy structure and can hold a great amount of water in its interior network. The water can shift freely through the mesh capillaries.

[4] The hydration temperature of LA gellan gum, ranging from room temperature to boiling point, depends on the type and concentration of ions in solution.

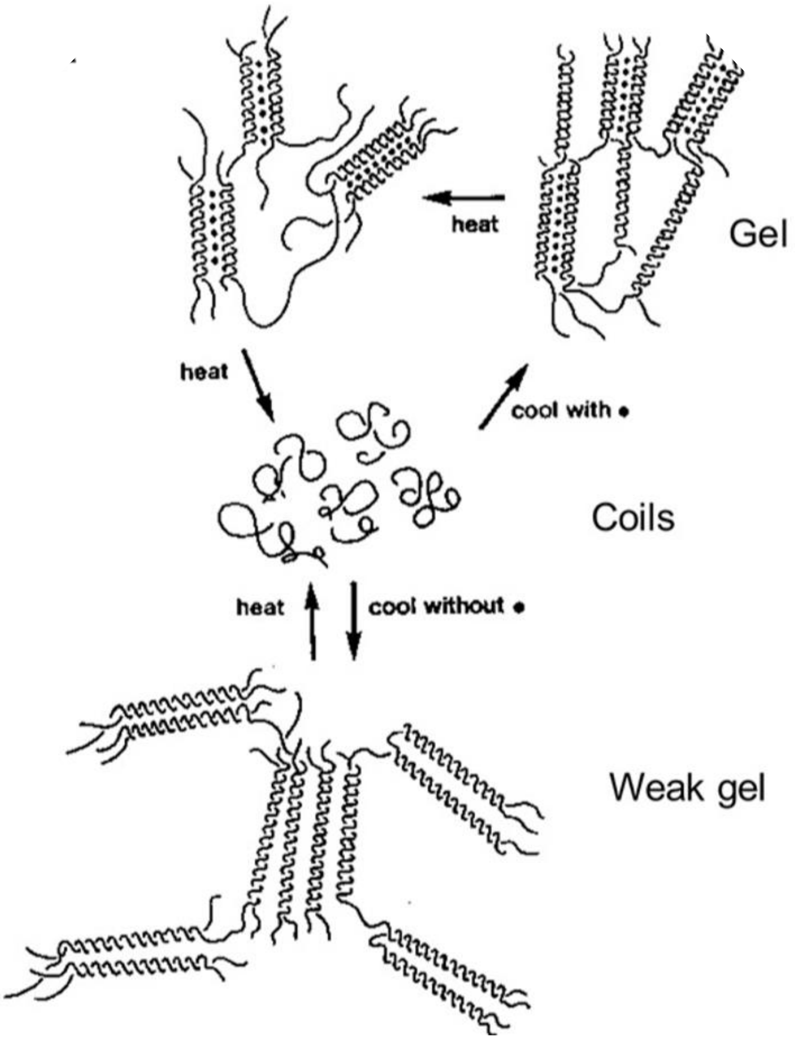


Fig. 4.21: Gelling process of LA gellan gum, filled circles denote cations that promote aggregation of gellan double helices. The dots "·" represent promoting cations. (Source: Morris et al., 2012, p. 393)

Thanks to the presence of Ca^{2+} at only around 0.05% (w/v), the gellan-sol is capable to form a self-supporting gel (Sworn, 2000, p. 122). Similar to agarose gel, as the concentration increases, the viscosity and the gelling temperature of sol as well as the stiffness of gel increase (Tang et al., 1997, p. 279). However, the properties of LA gellan gel are not only influenced by the gellan sol-concentration, but are also significantly dependent on the cation concentration in the sol. With added calcium or sodium ions, the gelling temperature increases, while the gel strength enhances until a maximum is reached but then decreases with further addition of ions because the gel texture becomes more brittle (Tang et al., 1997, p. 279; CP Kelco, 2007, p. 8). The water holding capacity and the rate of water diffusion of gellan gel are also affected by the gel concentration and the cation concentration: Generally speaking, the mobility of bound water decreases slightly and the mobility of free water decreases significantly in higher concentration gel.

Compared to agarose gel, gellan gel is more transparent but appears to be slightly yellow. According to the earlier researches from conservators, Kelcogel LA Gellan Gum from CP Kelco U.S., Inc. is widely applied, which is therefore also selected for this study. Similar to the application of agarose gel, the concentration of gellan gel varies from around 2 wt% (Iannuccelli & Sotgiu, 2010; Botti et al., 2011; Mazzuca et al., 2014) to around 5 wt% (Hughes & Sullivan, 2016; Sullivan et al., 2017), while the thickness of prepared gel from 2mm to 1cm. After the preliminary experiments have been carried out, it could be determined that 2mm gellan gels presented good performances for a localized treatment. The selected cation-resource and its concentration is determined as 0.4g/L calcium acetate. The selected gellan gels applied for the further experiments coupled with different temperature and different working patterns are prepared in 2 wt%, 3 wt%, 4 wt% and 5 wt%, whereas the preliminary experiment has shown that gellan gel with a concentration higher than 5 wt% is almost impossible to be casted uniformly into a continuous 2mm gel sheet due to its high viscosity, high gelling temperature and in particular the “snap set” property. The gels are prepared through the following process:

- 0.4 g/l calcium acetate is dissolved into 95-98 ml water (respectively for 5 wt%, 4 wt%, 3 wt% and 2 wt% gellan gels). 2-5g gellan gum powder (respectively for 2 wt%, 3 wt%, 4 wt% and 5 wt% gellan gels) is added into the water.
- Stir the water until the gum powder is fully dispersed in the water without clumping together (Fig. 4.22 a, b).
- For 2-3 wt% gellan gel, the dispersion is then heated in a microwave oven at 800 W power until it turns into a transparent solution (Fig. 4.22 c). As for 4-5 wt% gellan gel, the dispersion is heated in a microwave oven at 800 W power to a solution that contains massive small air bubbles, which cannot escape from the solution during the heating in the microwave due to the high viscosity of the gellan sol. The solution should then be added with a magnetic stir-bar, placed on a hot plate heated over 90°C and stirred until the air bubbles disappear as much as possible (Fig. 4.22 d). The final solution of 5 wt% gellan is not completely clear but turbid and yellow.
- The solution is poured into a plastic or glass container and cooled to room temperature. Make sure the layer’s thickness is 2mm. For this investigation, glass plates with spacers are applied for gellan gel casting (Fig. 4.18 c). Unlike the casting of agarose gel, only 2 wt% gellan gel can by casted by pouring vertically through a small funnel between the two glass plates to form a continuous gel sheet. Other gels with higher concentration, however, cannot form a continuous gel sheet through a vertical casting due to the “snap-set” property: The transition from sol to gel sets instantaneously once the gellan sol is in contact with the cold glass plates. Therefore, the casting of 2mm gellan gel in concentration of 3-5 wt% should be obtained by laying one glass plate assembled with two spacers, pouring the gellan solution on the plate when it is still at high temperature (Fig. 4.18 e), placing another glass plate onto the first glass plate. Two glass plates are

then pressed together, and the gellan solution is squeezed in between. This process should be conducted as quickly as possible to prevent the formation of an “interlayer” due to the “snap-set” effect. After cooling to room temperature, the previous solution becomes a continuous and relative transparent gel with a uniform thickness (Fig. 4.22 e, f).

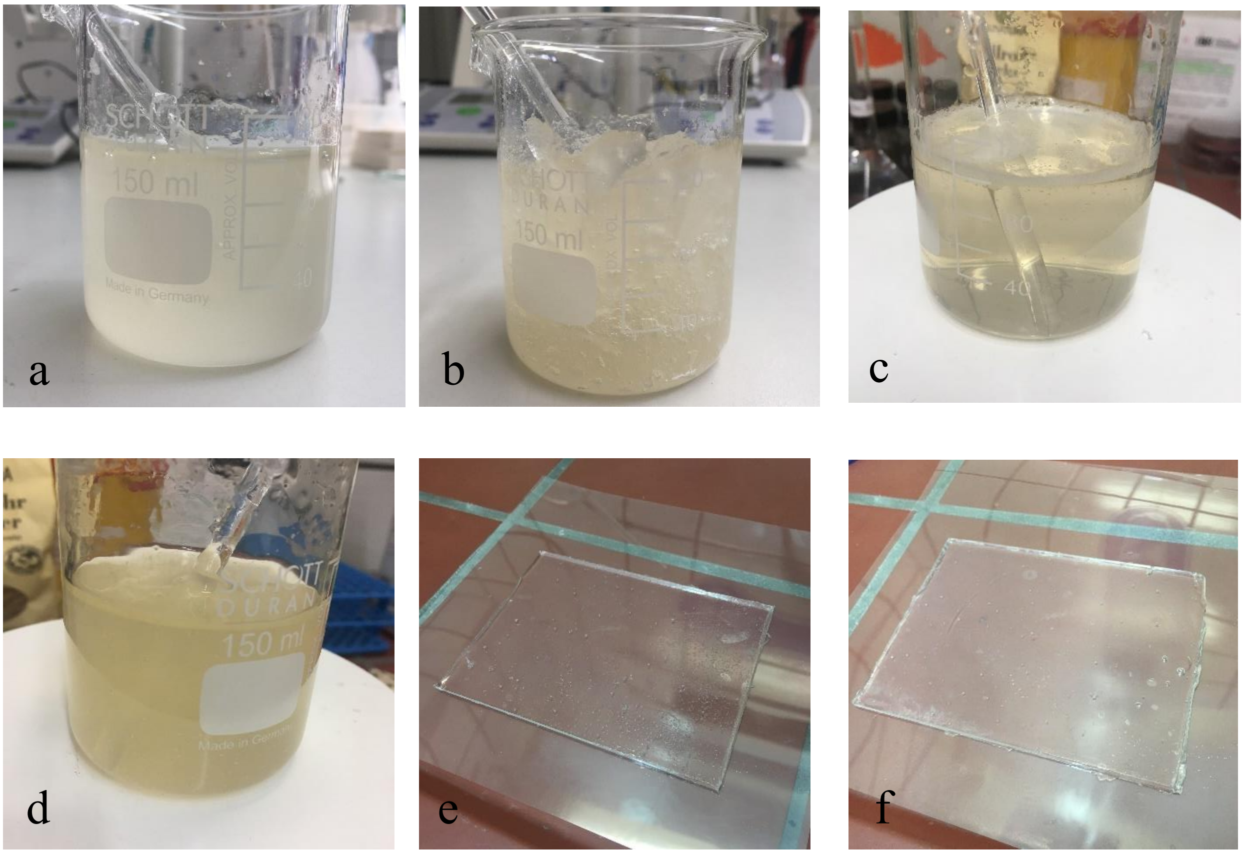


Fig. 4.22: Preparing the gellan gels. (a) Dispersion of gellan powder in water (3 wt%) after swelling. (b) Dispersion of gellan powder in water (5 wt%) after swelling. (c) Clear solution of 3 wt% gellan after heating. (d) Turbid solution of 5 wt% gellan sol after heating and stirring. (e) After cooling and removing from the glass plates, a translucent gellan gel (3 wt%) appears. (f) After cooling and removing from the glass plates, a translucent gellan gel (5 wt%) appears.

For a localized removal of mending papers, the humidification sandwiches are constructed as:

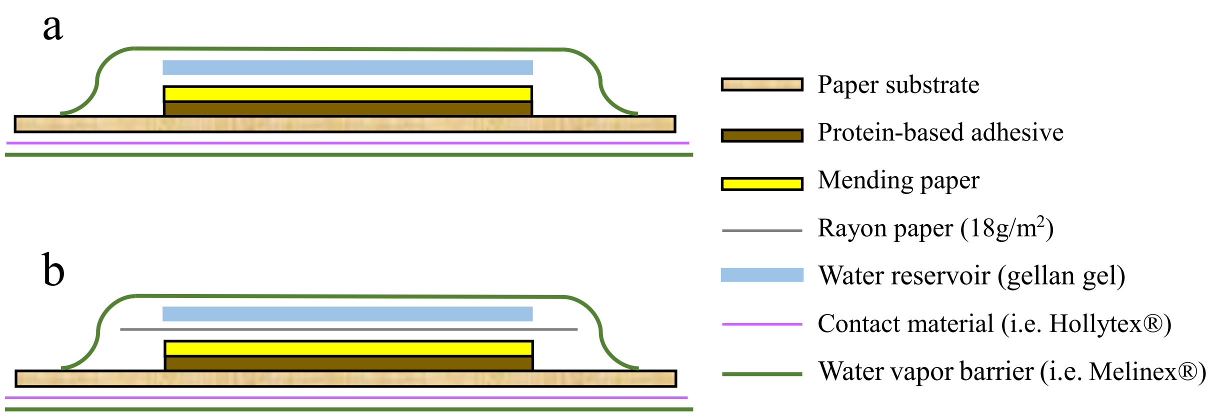


Fig. 4.23: Schematic diagrams of humidification sandwiches using (a) a 2mm layer of gellan gel and (b) a 2mm layer of gellan gel in combination with a sheet of Rayon paper for removing mending papers.

Similar to the application of agarose gel, the gellan gel can be cut into the same shape as the mend due to its translucency and rigidity. The shaped gel sheet should then blot up excess moisture gathered on the gel's surface, then it can be placed directly on the mending paper (Fig. 4.23 a) or in combination with a Rayon paper (Fig. 4.23 b). Two Polyester films are placed on top and bottom of the humidification sandwich to keep the moisture inside.

4.3 Coupling Humidification Sandwiches and Heat Transfer

The first part of this chapter (Chapter 4.3.1) will discuss the feasibility of combining moisture and heat transfer through coupling the humidification sandwiches, which are described in Chapter 4.2, with the IMAT mat through several working patterns. After the optimal working pattern is selected, the final arrangement of the humidification sandwiches with heat transfer, which will be applied in the main investigation, will be presented in the second part of the chapter (Chapter 4.3.2).

4.3.1 Working Patterns of Combining Heat Transfer and Moisture Transfer

Owing to the numerous magnificent properties owned by the mat, various arrangements of coupling an object with a humidification sandwich and the IMAT heater can be implemented. According to the previous studies on the IMAT heater in the field of painting, graphic and textile conservation, the heating mat is possible to be placed on the top of an art work (Markevicius et al., 2014, p. 12), or under an art work (Meyer et al., 2013, p. 638) as well as applied on both side of an art work (Markevicius et al., 2017b, p. 70) in order to meet different demands of specific applications in conservation. Thus, preliminary experiments on selecting an optimal working pattern combining moisture transfer and heat transfer for removing old repairs in bound manuscripts and rare prints were carried out on mock-ups (Fig. 4.24). The schematic diagrams for each combination of the humidification sandwich, the IMAT heater and the mock-up are presented in Fig. 4.25 – Fig. 4.27.

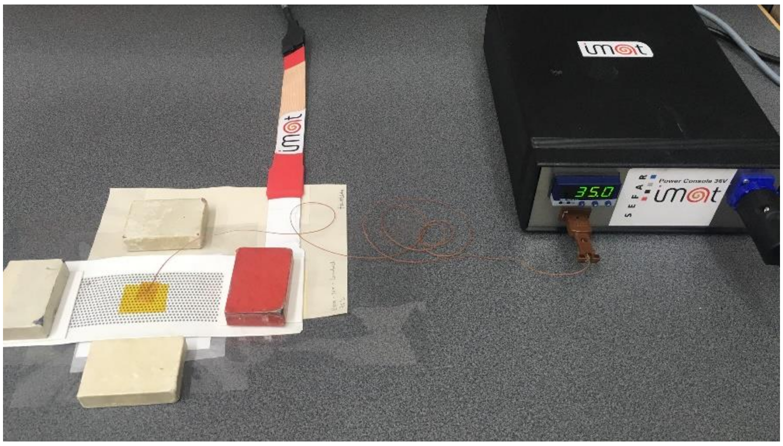


Fig. 4.24: Preliminary experiments on selecting an optimal working pattern combining moisture transfer and heat transfer, tested on mock-ups.

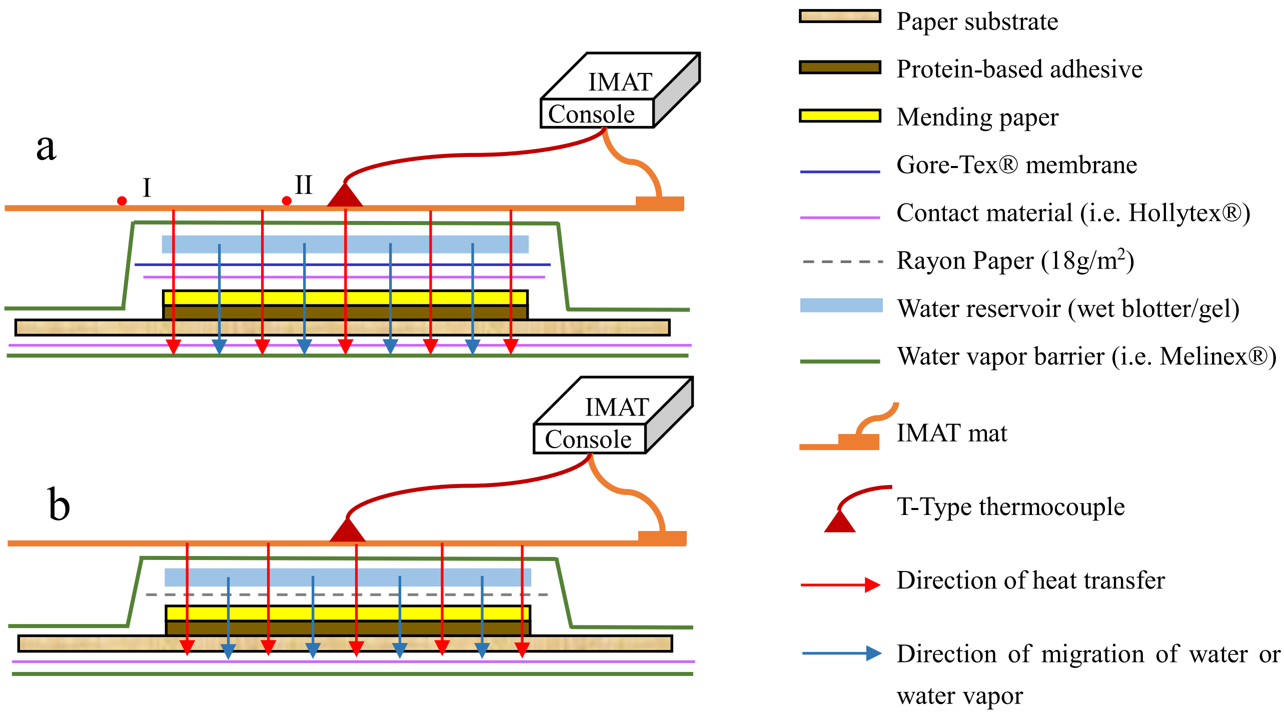


Fig. 4.25: Schematic diagrams of working pattern A: IMAT mat in combination with a Gore-Tex sandwich (a) or a gel sandwich (b).

When the samples are treated by working pattern A, water reservoirs are placed on the sample and the mend faces up. Two polyester films are placed on top and bottom of the humidification sandwich. The IMAT mat is placed on top. In this case, thermal energy transfers from the mat though the water reservoirs and heats the water inside. The warm water or the warm water vapor then travels into the mending paper and adhesive.

Since the introduction of heat and moisture into mending paper and adhesive is carried out through a localized treatment, not the whole area covered by the mat has contact with the water reservoirs (the mat is bigger than the treated area). As discussed in Chapter 3.3, one should notice that the different thermal responses of different materials result in a disparity of temperature distribution on the mat surface, for instance the two red spots shown in Fig. 4.25: The temperature of spot I is clearly higher than the temperature of spot II before the water reservoirs reaches the desired temperature. Therefore, the thermal couple should be fixed by the polyimide tape to the mat, on top of the water reservoirs, making sure that the humidification sandwich and the mend belong to the *system*, but not to the *surroundings* during this heat transfer process.

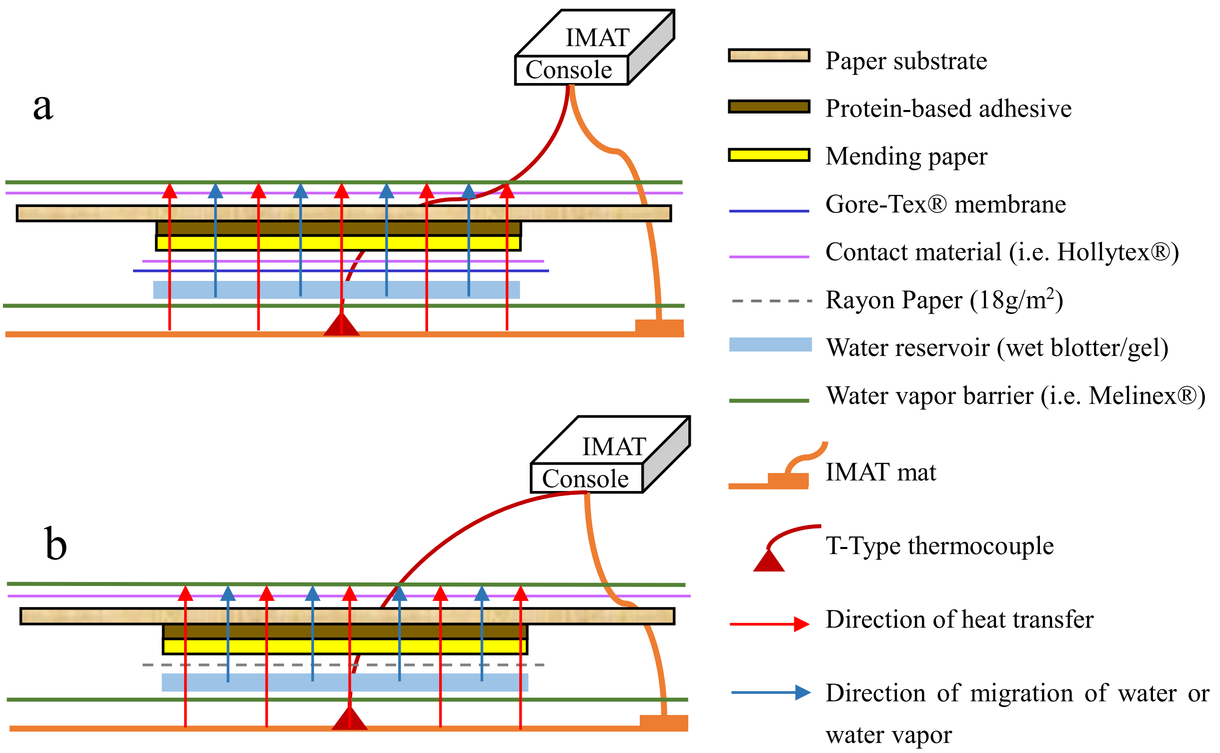


Fig. 4.26: Schematic diagrams of working pattern B: IMAT mat in combination with a Gore-Tex sandwich (a) or a gel sandwich (b).

When the samples are treated through working pattern B, water reservoirs are placed under the sample and the mends faces down. Two polyester films are placed on top and bottom of the humidification sandwich. IMAT mat is placed on the bottom. In this case, thermal energy also transfers from the mat though the water reservoirs and heats the water inside, but from bottom to top. The warm water or water vapor then travels into the mending paper and adhesive. In this case, the thermal couple should be taped underneath the water reservoirs, making sure that the humidification sandwich and the mend belong to the *system*.

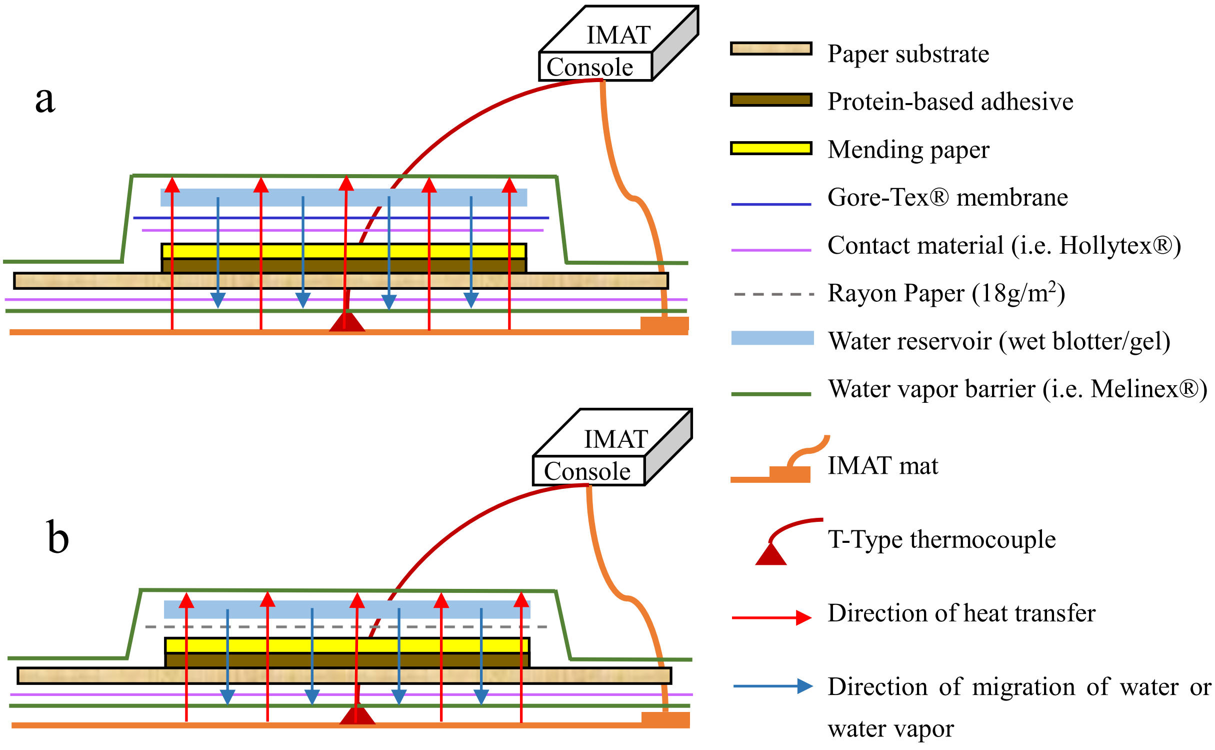


Fig. 4.27: Schematic diagrams of working pattern C: IMAT mat in combination with a Gore-Tex sandwich (a) or a gel sandwich (b).

When the samples are treated through working pattern C, water reservoirs are placed on the sample and the mend faces up. Two Polyester films are placed on top and bottom of the humidification sandwich. IMAT mat is placed on the bottom. In this case, heat transfers directly from the mat to the sample paper and adhesive, whereas the cold water in the water reservoirs travels into the mending paper and adhesive. Under this circumstance, the top of the adhesive layer has contact with moisture which is not heated, whereas the bottom of the adhesive layer is dry but warmed through IMAT mat. The thermal couple is taped underneath the mending paper, making sure that the humidification sandwich and the mend belong to the *system*, but not to the *surroundings* during this heat transfer process.

After the preliminary experiments, the performances of each working pattern were evaluated. Although the working pattern C seemed to be the most practical and accessible procedure during a localized treatment, it brought about an unsatisfied result: the mending papers could not be enough humidified and the adhesives could not swell sufficiently. This phenomenon could possibly be explained by: for a given relative humidity, the density of moist air decreases with increasing temperature (Boukhriss et al., 2013, p. 1292). Thus, heat coming from the bottom provided by the mat, to a certain extent, "prevents" the moisture coming from the top since moist air with higher temperature tends to go up rather than go down, which results in an unfulfilled humidification.

In comparison, working pattern A and B presented much better results, as the water reservoirs were heated through the mat so the mend was, as a matter of fact, humidified with warm water or warm water vapor. As discussed in the previous chapter, moisture is introduced by Gore-Tex sandwich into objects through diffusion of water vapor. During the humidification, samples absorbed the warm water vapor in the Gore-Tex sandwich until the new EMC conforms to the RH value inside the sandwich was established, which was generally accelerated through the thermal energy input. Therefore, it showed almost no difference between working pattern A and B when Gore-Tex sandwich was applied.

As for hydrogels, the introduction of moisture into objects is realized through a combination of gas diffusion, surface diffusion and bulk-solid diffusion of water vapor and slow capillary flow of water. All these mechanisms will occur when the mending paper has good contact with the gels, no matter the gel is applied from above the samples (working patter A) or beneath the samples (working pattern B, but against gravity). However, when the contact is not guaranteed and some air pockets exist between the gel and the mending paper, the humidification will not be even: The spots where air pockets sit are only be humidified through gas diffusion of water vapor. In the case of localized treatment, the gel can conform better to the surface texture of the mending paper to ensure a good contact if it is placed onto the sample than underneath the sample, mainly because the gel is either pseudoplastic (i.e. Tylose® gel) or rigid but flexible (i.e. agarose or gellan gel with a slight thickness) and contain a certain degree of weight. Besides, it is also easier to arrange the position of the gel if it is placed on the mending papers.

After several preliminary experiments, working pattern A is evaluated as a proper option for detaching a mending paper, by which all four humidification sandwiches can be applied. Working pattern B is nevertheless more suitable for i.e. detaching an old backing from a sensitive paper substrate, where a visual monitoring of the treatment process is demanded. In this study, therefore, working pattern A is eventually selected for the main investigation.

4.3.2 Arrangement of the Humidification Sandwiches with the IMAT Heater

Although the working pattern A is evaluated to own the highest feasibility and efficacy during a localized removal of old mending, the sandwich arrangement shown in Fig. 4.25 is not complete. During the preliminary experiment, two factors significantly related to the temperature change and heat transfer were noticed:

1) The relationship between saturated vapor pressure of water in air and temperature

Water vapor always presents in air in thermodynamic equilibrium with its condensed state. The pressure exerted by the amount of water which exists above the surface of its condensed phases is termed water vapor pressure (Banik & Brückle, 2018, p. 305). When the escaping and returning water molecules between the gas phase and the condensed phases reach a thermodynamic equilibrium, the water vapor pressure is saturated. The saturated water vapor pressure is a function of temperature only, which increases with a raised temperature, and is irrelevant to the presence of other gases. In other words, the absolute humidity (AH) – the water content of air – increases with a raised temperature at a given RH value. Once the pressure is beyond the saturated vapor pressure, the water vapor will condense.

It is determined that the relationship between saturated vapor pressure of water and temperature plays a vital role in the humidification sandwich when heat is extra applied: In Fig. 4.28, the temperature at the orange dot is higher than the temperature at the green dot, because heat loss occurs on the one hand through the mending paper, the adhesive layer and the paper substrate, and on the other hand through the support of the sandwich (i.e. working table or text block). Therefore, once the water vapor pressure at the orange dot approaches to the saturated state, the water vapor pressure at the green dot becomes oversaturated. Water vapor will partly condense at the surface of the polyester film since the absolute humidity decreases at a same RH value with a lower temperature. The paper substrate has, as a result, yet direct contact with liquid water (condensation water), which will lead to the formation of tideline on paper substrate (Fig. 4.29). After tested with several papers and boards, an archival board with a thickness of 0.35 mm is recommended to be placed between the paper substrate and the polyester film.

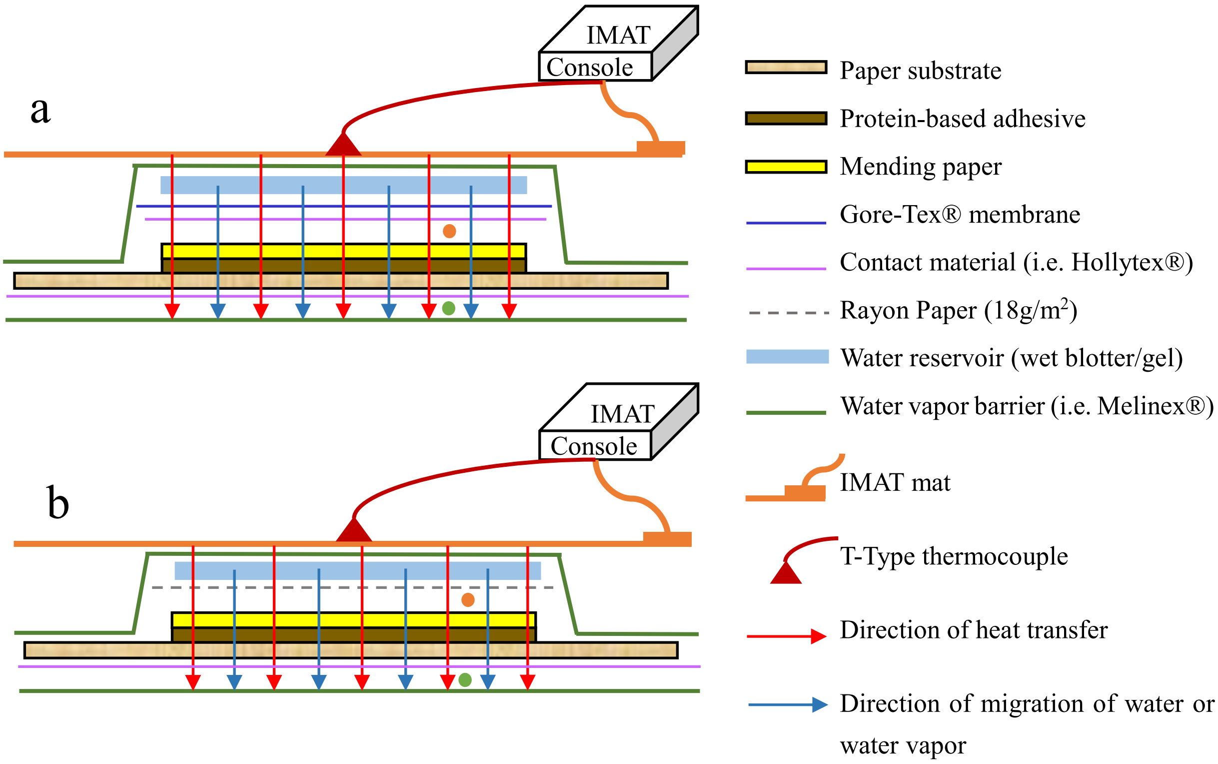


Fig. 4.28: Schematic diagrams of working pattern A: IMAT mat in combination with a Gore-Tex sandwich (a) or a gel sandwich (b).

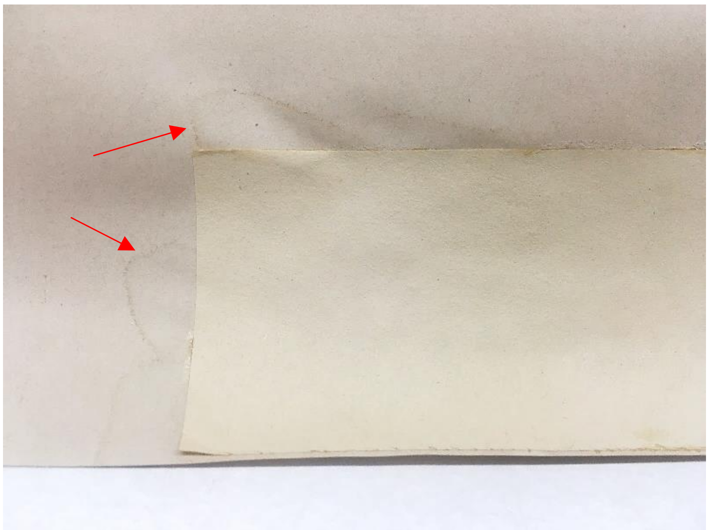


Fig. 4.29: Formation of tideline on the paper substrate of a mock-up due to the direct contact with condensation water.

2) Heat loss due to the surroundings condition

As mentioned in Chapter 3.2, heat loss can possibly occur if the thermal energy is not completely held inside the system – the mat and the humidification sandwich – but transfers further into the surroundings such as the air, the working table under the sandwich or the text block when the treatment is carried out *in situ*. Therefore, to achieve an optimal heat transfer condition, heat isolation sheets applied to the both side of the sandwich is recommended.

The complete humidification is shown in Fig. 4.30.

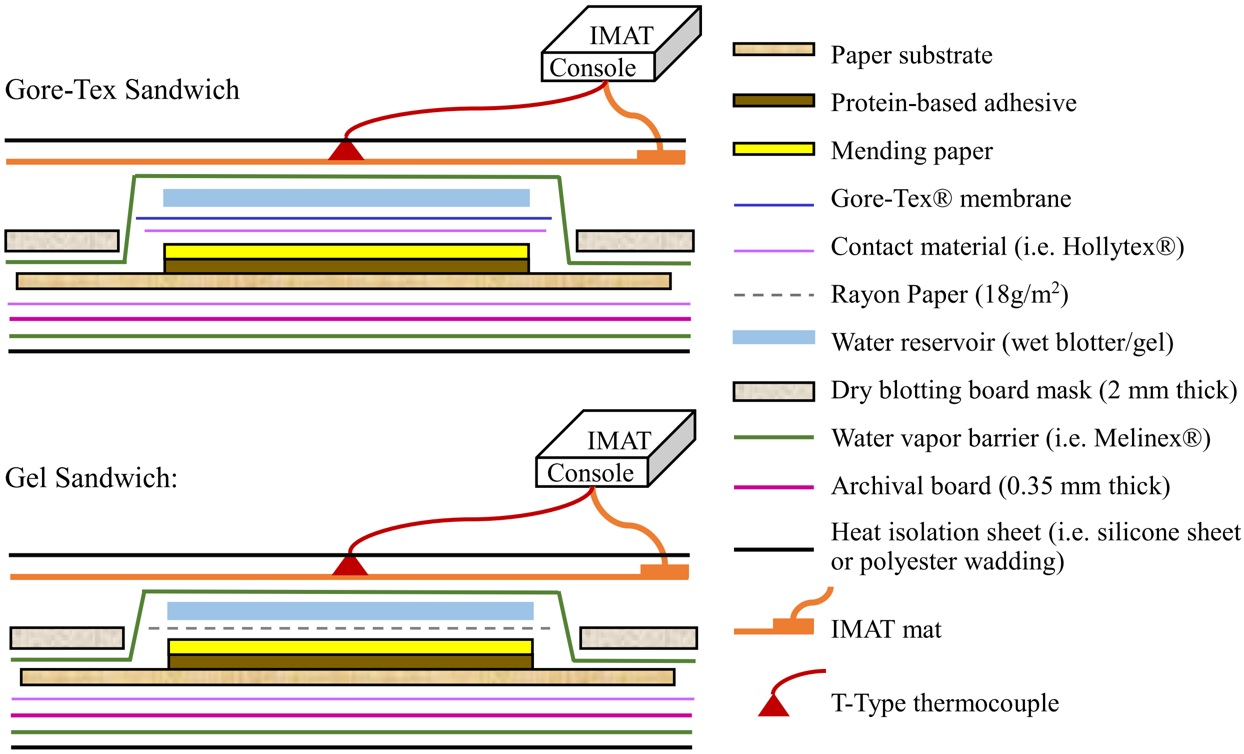


Fig. 4.30: Schematic diagrams of the complete humidification sandwich with heat transfer.

- Function of the archival board: preventing the paper substrate from having direct contact with the condensation water.

- Function of the heat isolation sheets: Two thin silicone sheets or polyester wadding placed on and under the sandwich can help to minimize the heat loss through the environment, which is yet not always required especially when the accessibility to the working area is limited.

- Function of the dry blotting board mask: During a heat transfer process, some parts of the mat have no contact with the humidification sandwich. These parts can be overheated since the heat capacity of the water reservoir is much higher than that of the air or of the paper substrate. A mask of the humidification sandwich made from a dry blotting board can absorb a considerable amount of thermal energy provided by the mat, which not only prevents some area of the paper substrate from being overheated, but also protects the mat from being partly overheated beyond its limitation.

5 Evaluation of Each Treatment Variation

After the preliminary experiment, it can be determined that the general principle of coupling humidification sandwich with the IMAT heater is to humidify the mends with warm water or warm water vapor through different mechanisms. However, this statement raises further questions: How exactly does an input of thermal energy interact on each humidification sandwich? How exactly does this new method of combining moisture with heat transfer influence the conservation treatment? With these issues in mind, the main investigation series are designed with the following aims:

1) Verifying the working properties of the three IMAT prototypes – characteristics of each IMAT prototype and their heating performance.
2) Characterizing the thermal performance of each humidification sandwich coupled with heat transfer.
3) Evaluating the working properties of each treatment correlated with different humidification sandwiches and treating temperatures – performance of moisture introduction during an input of thermal energy as well as the feasibility and efficacy of temperature-related optimization on the detachment of old mending paper.

All the experiments were carried out on mock-ups or other samples.

5.1 Materials and Methods

1. Mock-up Preparation

As written in Chapter 4.1, two papers chosen as the paper substrates of the mock-ups were Anton Glaser Nr. 2062 and the old wood pulp paper with a printed map. Two papers selected as mending paper were Anton Glaser Nr. 2061 and the old typing paper. Hide glue and bone glue were chosen as adhesives. Mending papers were cut into 4.5 cm * 15 cm stripes and glued with 30% hide glue or 30% bone glue to the long sides of substrate papers, which were cut into 15 cm * 25 cm pieces (Fig. 5.1). Each combination of substrate and adhesive – rag paper with hide glue, wood pulp paper with hide glue, rag paper with bone glue, wood pulp paper with bone glue – was prepared with 50 samples. The total 200 samples were dried between dry blotters for 5 days.

The mock-ups were aged for two weeks in an environmental aging chamber under the condition of 65 °C as well as a cycling humidity of 35% and 80% which was changed every 3 hours. Fig. 5.2 shows the samples after the artificial accelerated aging.

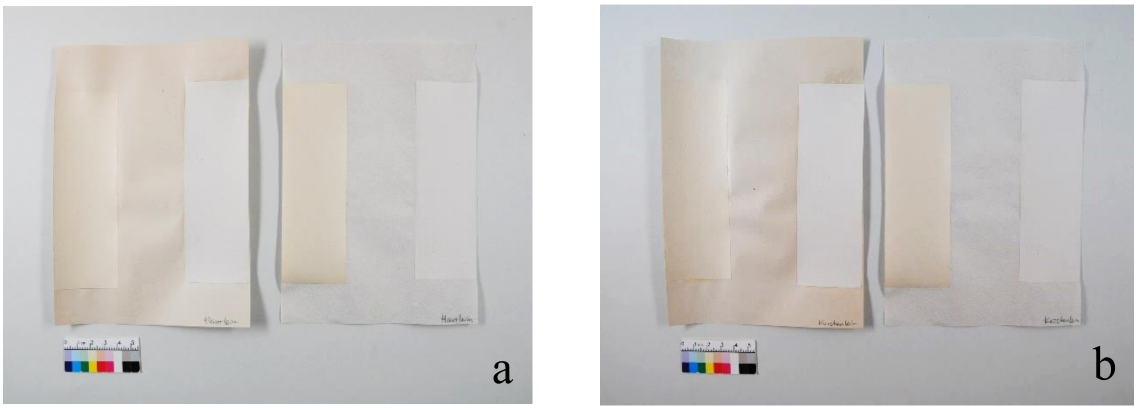


Fig. 5.1: Mock-ups before aging. (a) Rag paper as substrate (left) and wood pulp paper as substrate (right), mending papers made of typing paper (left stripes) and thick rag paper (right stripes), glued with hide glue. (b) Rag paper as substrate (left) and wood pulp paper as substrate (right), mending papers made of typing paper (left stripes) and thick rag paper (right stripes), glued with bone glue.

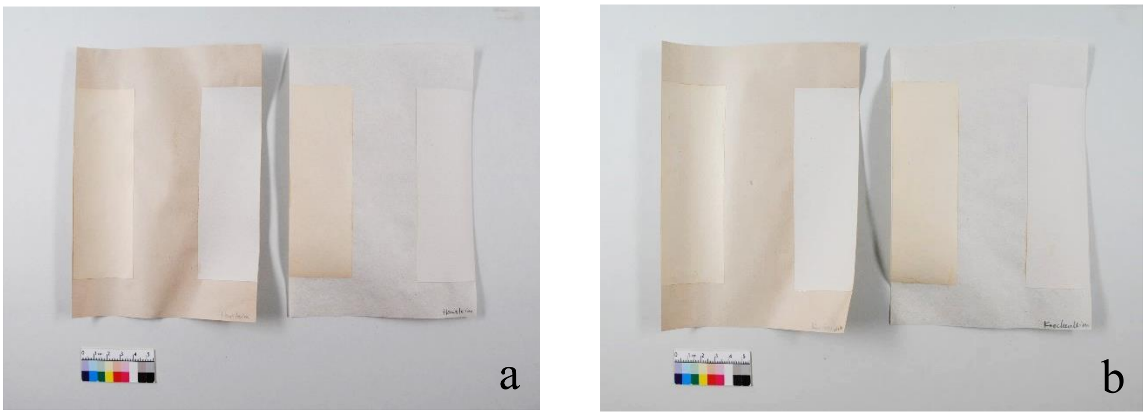


Fig. 5.2: Mock-ups after aging. (a) Rag paper as substrate (left) and wood pulp paper as substrate (right), mending papers made of typing paper (left stripes) and thick rag paper (right stripes), glued with hide glue. (b) Rag paper as substrate (left) and wood pulp paper as substrate (right), mending papers made of typing paper (left stripes) and thick rag paper (right stripes), glued with bone glue.

2. Gel Preparation

Tylose® MH 30000 gel, agarose gel and gellan gel were prepared in 10 wt%, 2-6 wt% and 2-5 wt% concentration respectively. Agarose gel and gellan gel were casted in 2mm sheets. The preparation followed the procedures described in Chapter 3.2.2 – 3.2.4.

3. Temperature Monitoring

Temperature monitoring for the heat distribution of the IMAT prototypes, the thermal response and the heat loss of the humidification sandwiches were conducted by OMEGA handheld data logger thermometer OM-EL-ENVIROPAD-TC and thermographic camera FLIR SC660. The OMEGA data logger thermometer records temperature readings via the attached thermocouple probe, for which a T-type thermocouple was applied. The thermometer was set to data logging mode and it could take temperature readings for the desired time interval. All readings could be presented on a temperature vs time graph. Thermographic camera FLIR SC660 was applied to detect the heat distribution of the IMAT prototypes and the humidification sandwiches during heating.

4. Moisture Detection

The performance of moisture in Gore-Tex sandwich and gel sandwich was determined by the Watesmo test paper. This test paper allows the qualitative detection of water not only in the liquid and but also in the vapor phase. Through an irreversible color reaction from light blue to dark blue, the presence of water and water vapor can be easily detected.

For the determination of water in liquid phase, the test paper develops dark blue spot on contact with liquid water. For the determination of water in vapor phase, dipping the paper into absolutely anhydrous isopropanol before the detection is often required to ensure a high sensitivity since the paper does not react with atmospheric moisture. However, under an extremely high RH condition, the sensitivity of the test paper without pretreatment with isopropanol is also satisfactory. The intensity of the blue color reflects the amount of absorbed water vapor.

5. Visible and Ultraviolet Light Photography

Mock-ups treated with different humidification sandwiches under different temperature conditions and samples in tideline determination test were photographed before and after the treatments under visible and ultraviolet light. Visible photography was conducted by a Nikon D700 with Nikon AF-S Nikkor 16-85mm zoom lens. For ultraviolet photography, Herolab UV hand lamp with 256 nm and 365 nm wave length were used.

6. Digital Microscopy and Scanning Electron Microscopy

Digital microscopy was performed by Hirox 3D digital microscope RH 2000 with MXB-2016Z high-performance zoom lens. The three IMAT prototypes were non-destructively characterized by the means of this 3D microscope. Mock-ups after treatments were also microscopically captured. Scanning electron microscopy was conducted by Phenom ProX desktop scanning electron microscope. The morphology of the fiber of the mock-up paper substrates before and after treatments were examined.

5.2 Results and Discussion

5.2.1 Working Properties of the IMAT Prototypes

1. Characteristics of each prototype

The three IMAT prototypes were examined by 3D digital microscope and the results are shown in Fig. 5.3 – 5.5.

The middle-sized, meshed IMAT prototype (Fig. 5.3) showed a microscopic lattice structure with each mesh size of circa 0.5 mm x 0.5 mm, which allowed air and water vapor to travel through. Each CNTs wire with a thickness of 0.1 – 0.2 mm was coated with an insulator layer. The insulation coating of this prototype was not ideal that some spots of the lattices were already exposed to the air (see red arrow in Fig. 5.3 c). Additionally, parts of the main wires also lacked an intact insulator layer (see red arrow in Fig. 5.3 d).

The large IMAT prototype (Fig. 5.4) showed a similar microscopic lattice structure with a similar mesh size to the first prototype, whereas the wires were completely imbedded in a silicone layer without another insulator coating. The silicone layer was intact, which promised a good insulation property, a certain degree of transparency as well as a certain degree of resistance and resilience to physical stress factors related to frequent use of the mat. Yet it also eliminated the ability of air and water vapor permeance. In addition, a defection of one of the main wires was found (see red arrow in Fig. 5.4 c)

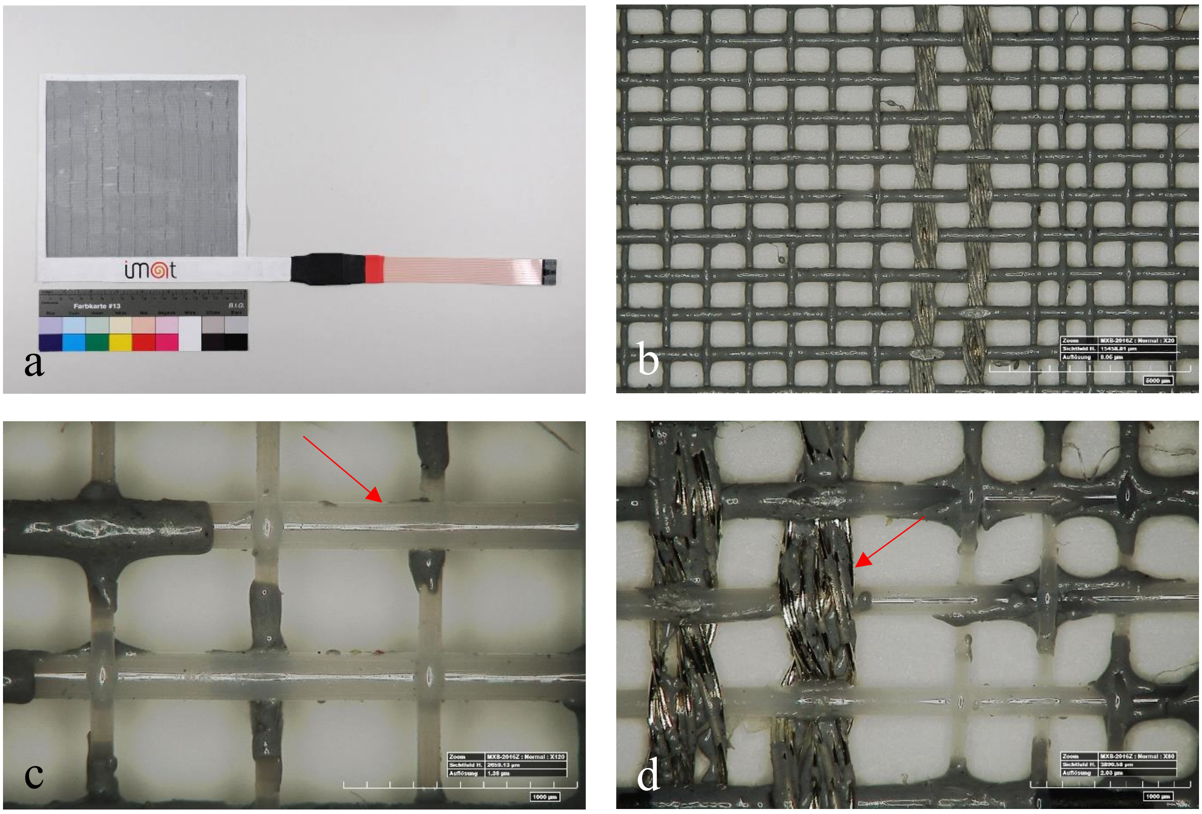


Fig. 5.3: Overview (a) and microscope images (b, c, d) of the middle-sized, meshed mat.

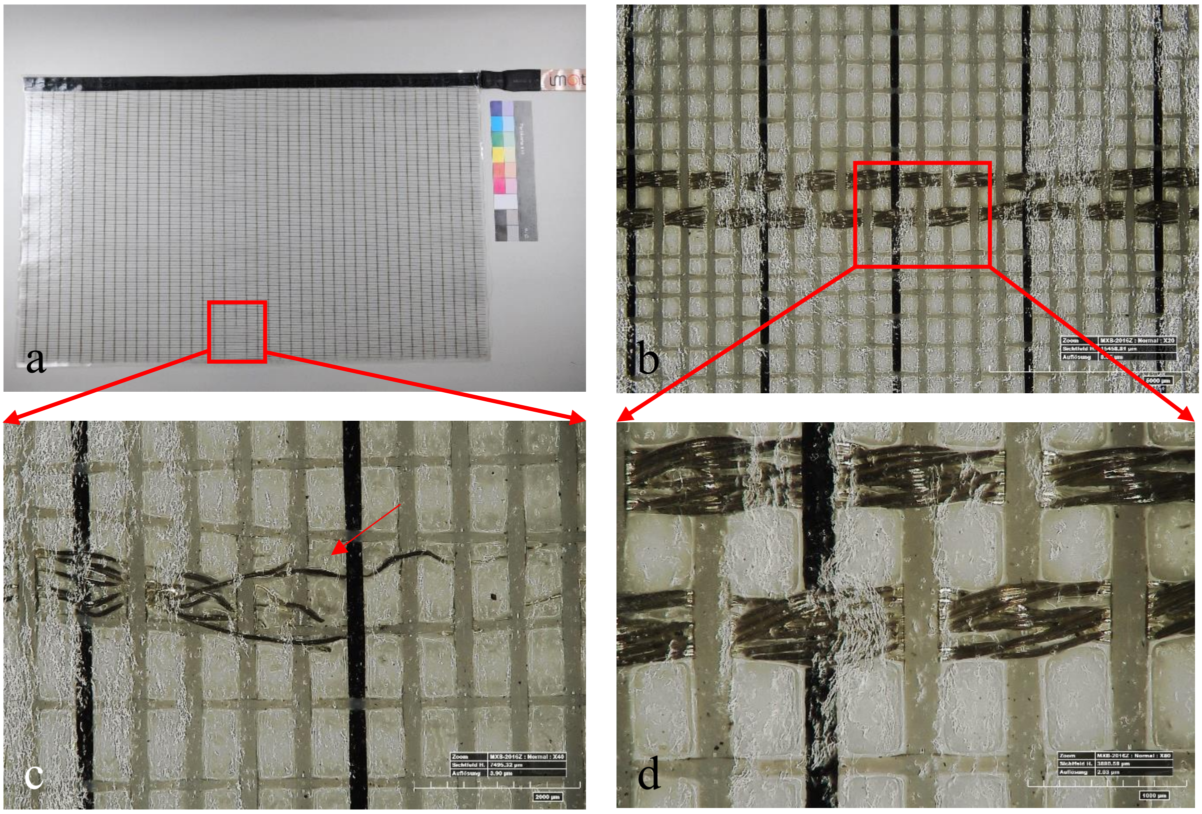


Fig. 5.4: Overview (a) and microscope images (b, c, d) of the large mat.

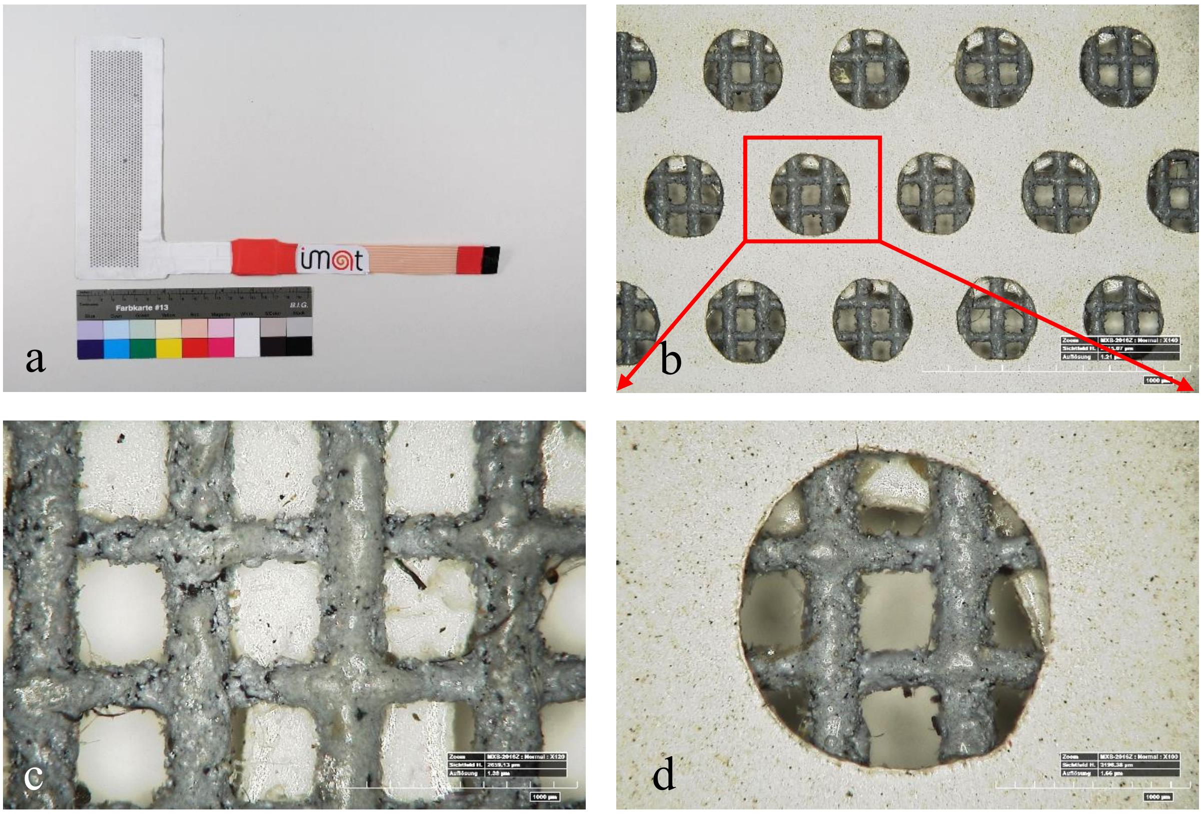


Fig. 5.5: Overview (a) and microscope images (b, c, d) of the small mat.

Finally, the small IMAT prototype (Fig. 5.5) also obtained a lattice structure with each mesh size of circa 0.4 mm x 0.4 mm, which allowed air and water vapor to travel through. Compared to the first prototype, the CNTs wires of this mat, whose thickness is 0.2 – 0.25 mm, possessed a thicker but more intact insulator coating. The whole mesh was then covered both sided with a polyurethane layer with small holes on it. The polyurethane layer maintained the breathability of the mat and provided an extra protection from mechanical damages. Yet it also concealed the transparency of the mat.

2. Heat distribution of each prototype

The thermographic images of the three IMAT prototypes during heating in air are shown in Fig 5.6 – 5.8.

The middle-sized, meshed IMAT prototype (Fig. 5.6) showed a generally uniform heat distribution during the whole heating process as the target temperature could be reached within seconds, which could meet the expectations of an optimal heating performance. However, the rightmost part of the mat was partially defective and the margins of the mat covered by a white polyester layer were also not heated.

In comparison, the large IMAT prototype (Fig. 5.7) showed a rather uneven heat distribution at the beginning of the heating process and a bit slower heat response than a smaller mat (Fig 5.7 c). Nevertheless, the target temperature could still be reached within a minute and after circa 80 seconds, the heat distribution was regulated to become uniform (Fig 5.7 d). The “lattice-structure” of the mat could be remarkably noticed during the heating process, while some errors occurred on the middle part of the mat and some lattices that those areas could not be heated successfully to the target temperature. Additionally, the edges of the mat could not be ideally heated either.

Finally, the small IMAT prototype (Fig. 5.8) presented an unsatisfactory heating performance: Although the target temperature could be approached within seconds, the heat distribution of the mat during the whole heating process was uneven. The lower part of the mat shown in Fig. 5.8 c and Fig. 5.8 d was always partially overheated up to 20 °C beyond the target temperature. Additionally, in contrast to the other two mats, this mat could fairly be heated up till the edges.

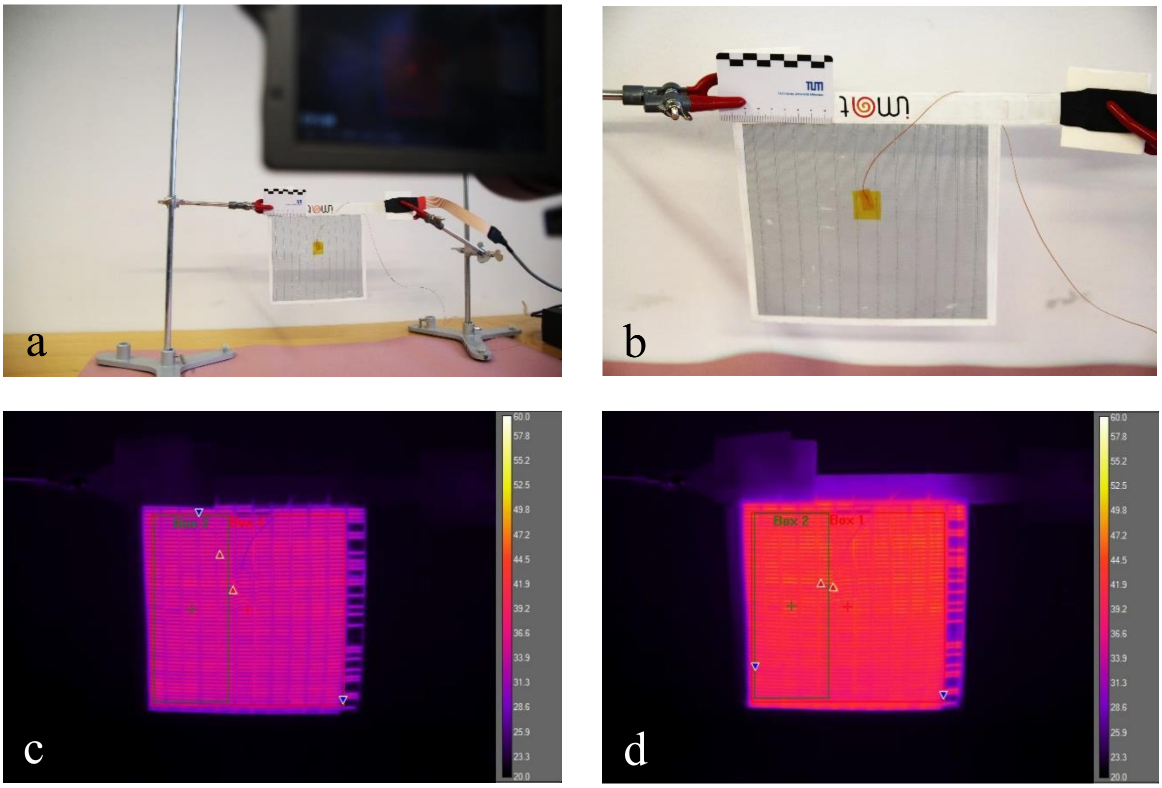


Fig. 5.6: Thermographic experimental setup (a, b) and thermographic images obtained for the middle-size, meshed, translucent and breathable IMAT prototype after 5s (c) and 20s (d) when it was hanged in air and set at 45°C. Temperature scale of the thermographic images: 20°C – 60°C.

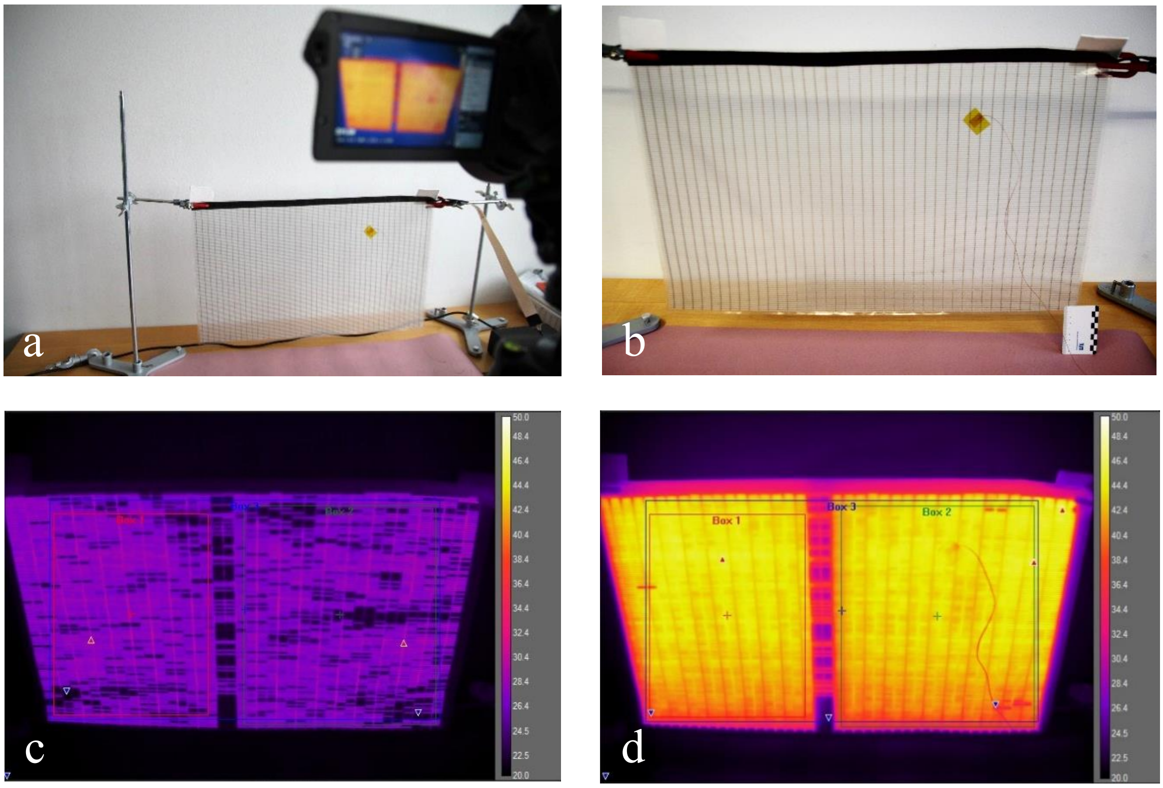


Fig. 5.7: Thermographic experimental setup (a, b) and thermographic images obtained for the large, translucent but not breathable IMAT prototype after 5s (c) and 80s (d) when it was hanged in air and set at 45°C. Temperature scale of the thermographic images: 20°C – 50°C.

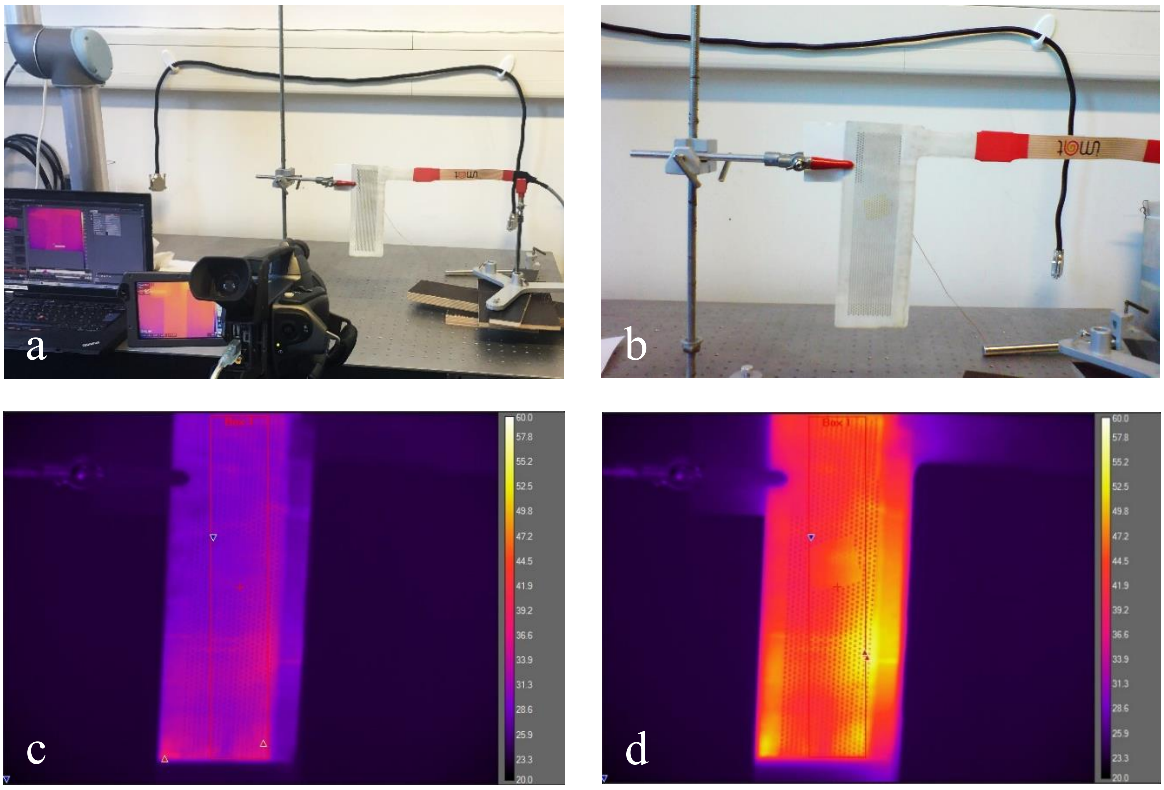


Fig. 5.8: Thermographic experimental setup (a, b) and thermographic images obtained for the small, breathable but not translucent IMAT prototype after 5s (c) and 20s (d) when it was hanged in air and set at 45°C. Temperature scale of the thermographic images: 20°C – 60°C.

3. Discussion of the results

The middle-sized, meshed prototype and the small prototype were air and water vapor permeable, while the meshed prototype and the large prototype were translucent. The meshed and breathable mat showed the most satisfactory heating performance. However, the heating performance of the other two prototypes were less gratifying: The large and transparent mat showed several defections, among which the defection of the middle part could be possibly traced back to a manufactural error on the main wire (Fig. 5.4), while the defection on other lattices might be caused by frequent use or maybe some other manufactural errors. The small, breathable but not transparent mat showed partial overheated spot. This could be traced back to some interior damages possibly resulted by incautious handling, since this mat were already tried and tested by several conservators for different applications before it is applied in this project. Additionally, the meshed prototype had an insulation problem: Direct contact with water or metal tools applied in the treatment as well as any other highly conductive materials would cause a short circuit, which could result in deterioration of the mat or even damages on the treated object and injuries to the operating personnel.

Nevertheless, these prototypes are not final products but rather a demonstration of the working principles. The results above are partly acceptable as the prototypes were not designed and produced with high resilience from the beginning.

5.2.2 Thermal Performance of Humidification Sandwiches Coupled with Heat Transfer

In this section, thermal response of different water reservoirs and heat loss inside each humidification sandwich were determined by monitoring the temperature trend of water or water vapor. In addition, temperature distribution of each water reservoir during heating was detected by thermographic camera. The meshed, breathable and translucent IMAT prototype with a uniform heat distribution was applied for this experiment.

1. Water vapor in a Gore-Tex sandwich

Since humidification by a Gore-Tex sandwich is achieved by exposing an object to an elevated RH condition, the temperature of water vapor inside the sandwich is therefore one of the key parameters of the humidification treatment. The temperature trend of water vapor inside a Gore-Tex sandwich during an input of thermal energy was detected. The T-type thermocouple of the data logger thermometer was placed inside the sandwich (Fig. 5.9).

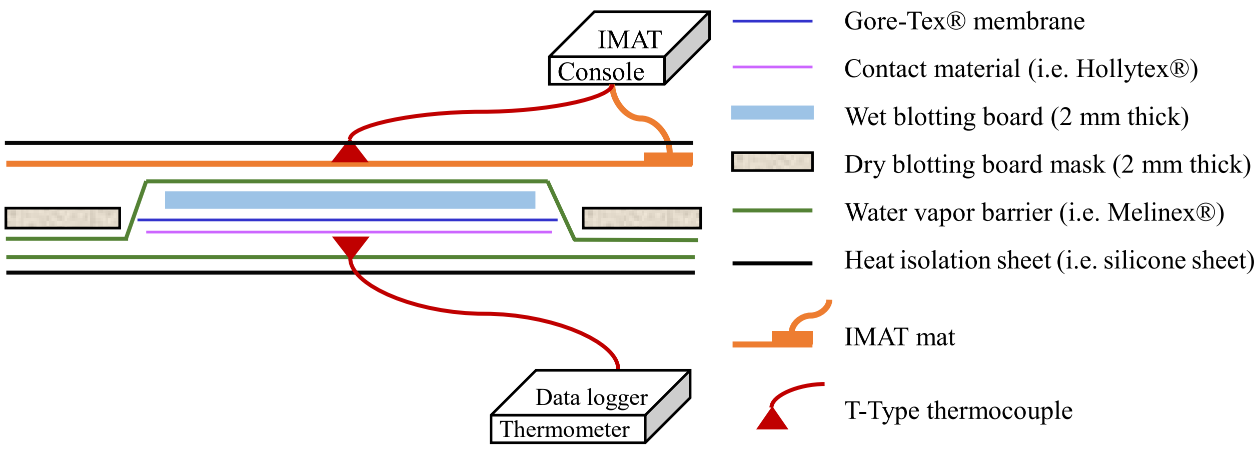


Fig. 5.9: Schematic diagram of the temperature monitoring of the water vapor inside a Gore-Tex sandwich.

As the temperature trends shown in Fig. 5.10, the target temperature set by the IMAT console was 45 °C, but the temperature of water vapor inside both Gore-Tex sandwiches could not reach 45 °C. In this experiment, heat loss was around 3°C. When the blotter was firstly immersed in a cold water bath before placed on the Gore-Tex® membrane, temperature of water vapor inside the sandwich began at a low degree and rose up rapidly during the first few minutes. This increase then slowed down, and the temperature reached 42 °C ± 1 °C within 6.5 minutes. When the blotter was immersed in a warm water bath before placed on the Gore-Tex® membrane, temperature of water vapor inside the sandwich began at a higher degree, then raised up mildly to 42 °C ± 1 °C within 4.5 minutes.

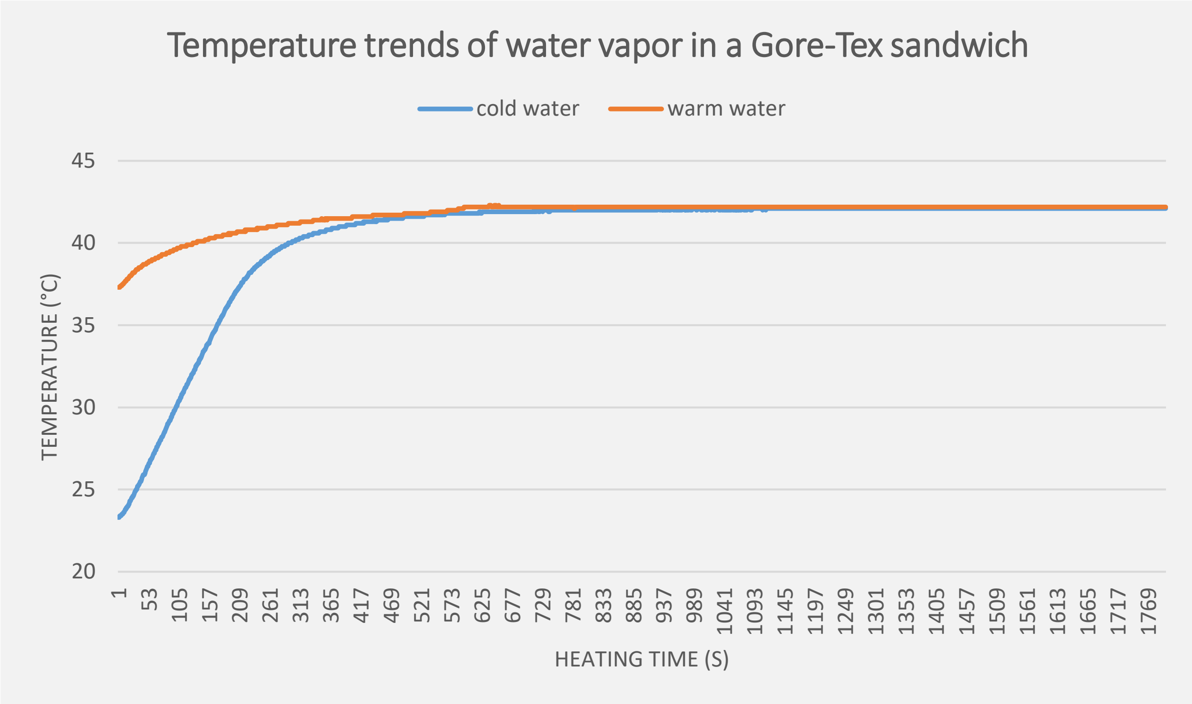


Fig. 5.10: Temperature trends of water vapor inside a Gore-Tex sandwich during a 30 minutes thermal energy input through an IMAT mat. The IMAT mat was set at 45 °C. The two curves present respectively the sandwiches whose blotter was immersed in a warm water bath (orange) and a cold water bath (blue) before placed on the Gore-Tex® membrane.

The temperature distribution of a wet blotting board after circa 2 minutes of heating is shown in Fig. 5.11. Although the temperature of the whole blotter was not completely identical, the difference was not dramatic.

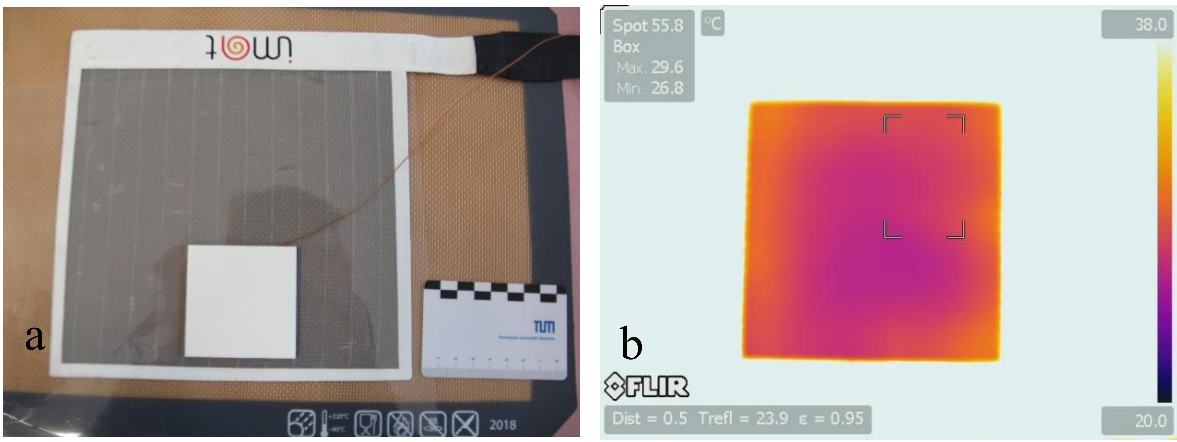


Fig. 5.11: Thermographic experimental setup (a) and thermographic image obtained for a wet blotter heated after circa 2 min (b). Temperature scale of the thermographic image: 20°C – 38°C.

2. Water in different hydrogels

Since humidification by a gel-sandwich is achieved by the contact with a water reservoir that has a strong power of water retention, the temperature of water at the bottom side of the gel is therefore one of the key parameters of the humidification treatment. The temperature trend of the bottom side of each gel during an input of thermal energy was detected. The T-type thermocouple of the data logger thermometer adhered to the bottom side of each gel (Fig. 5.12).

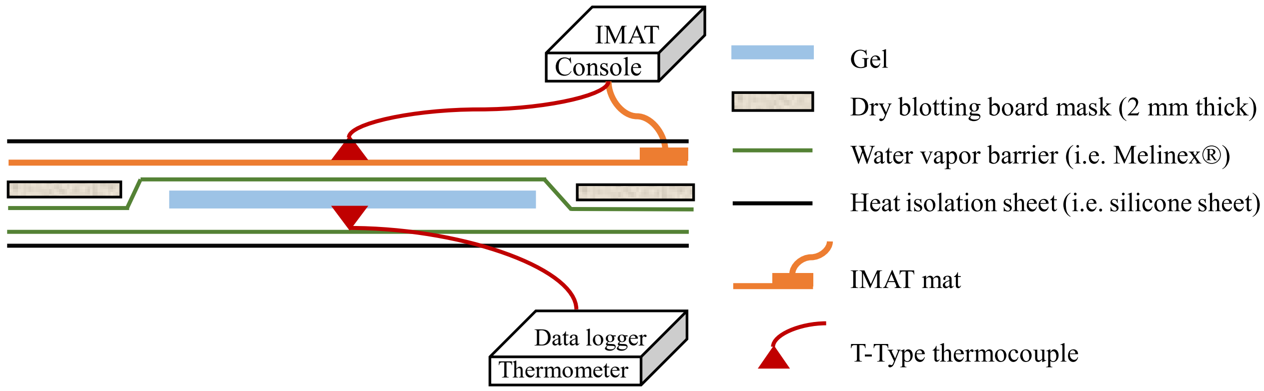


Fig. 5.12: Schematic diagram of the temperature monitoring of the bottom side of each gel.

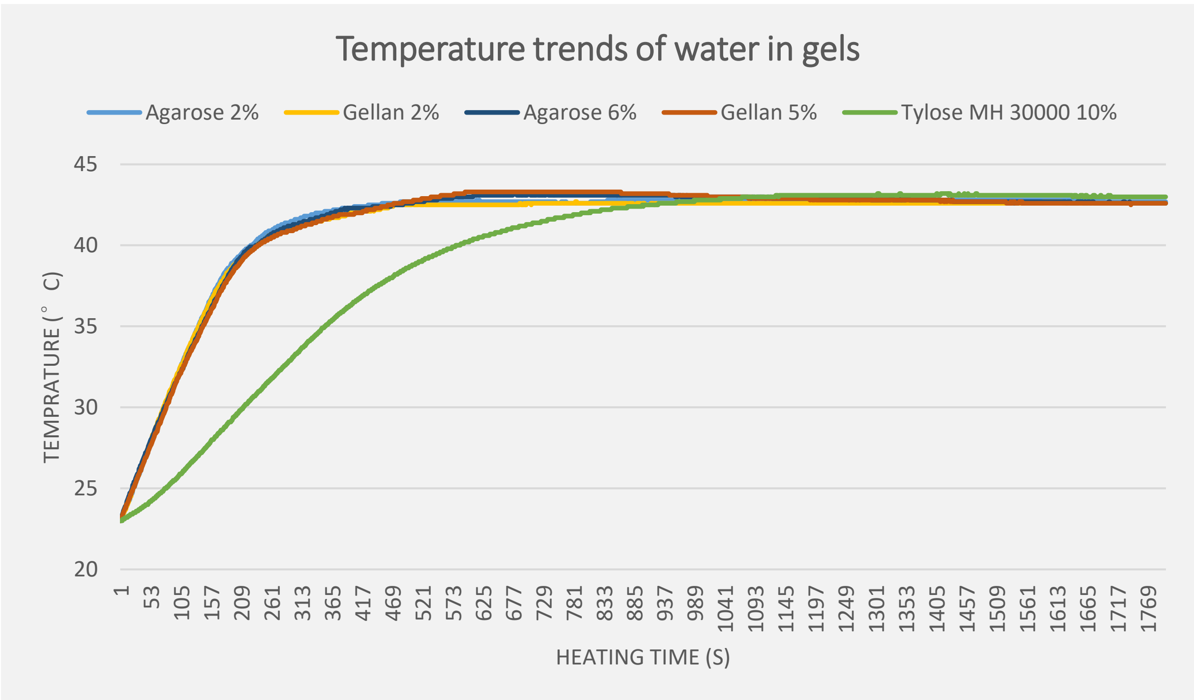


Fig. 5.13: Temperature trends of the bottom side of different gels during a 30 minutes thermal energy input through an IMAT mat. The IMAT mat was set at 45 °C, while the “start temperature” of each gel was 23 °C. Five curves present respectively a 2mm thick layer of agarose gel in 2 wt% concentration (blue), a 2mm thick layer of gellan gel in 2 wt% concentration (yellow), a 2mm thick layer of agarose gel in 6 wt% concentration (dark blue), a 2mm thick layer of gellan gel in 5 wt% concentration (orange), and a 3-5mm thick layer of Tylose® MH 30000 in 10 wt% concentration (green).

As the temperature trends shown in Fig. 5.13, the target temperature was set by the IMAT console at 45 °C, but the temperature of the bottom side of each gel could not reach 45 °C. In this experiment, heat loss of each gel-sandwich was 2 °C – 2.5 °C.

The temperature changes of the agarose gels and gellan gels presented similar trends: it began at 23 °C and rose up rapidly during the first few minutes. This increase then became tardy, as the temperature reached 42.7 °C ± 1 °C within circa 5-6 minutes. However, the rise of temperature of the Tylose® MH 30000 gel was obviously much milder. It took the Tylose® MH 30000 gel around 12.5 minutes to reach 42.7 °C ± 1 °C.

The temperature distributions of agarose gel in 2 wt% concentration and of Tylose® gel in 10 wt% concentration after circa 2 minutes of heating are shown in Fig. 5.14. The temperature of agarose gel was obviously much more uniform than that of Tylose® gel, the former obtained only a slight unevenness similar to the wet blotter. Nevertheless, the temperature of the edges of Tylose® gel was clearly high than the temperature of the center.

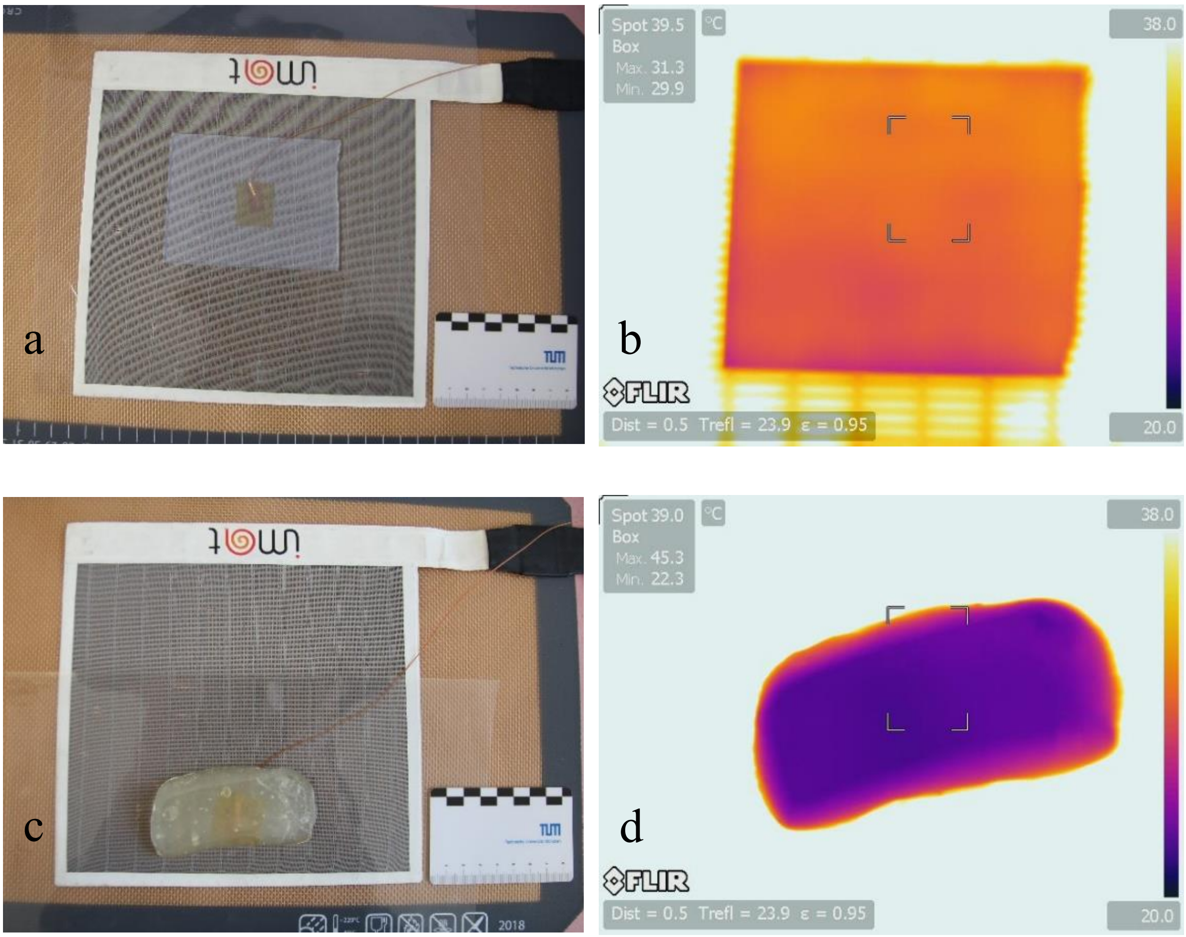


Fig. 5.14: Thermographic experimental setup for agarose gel in 2% concentration (a) and for Tylose® gel in 10% concentration (c) as well as thermographic images obtained for the agarose gel heated after circa 2 min (b) and or for the Tylose® gel after circa 2 min (d). Temperature scale of the thermographic images: 20°C – 38°C.

3. Discussion of the results

Heat loss occurred in each humidification sandwich, the rate of heat transfer was lower than 100% due to the non-ideal thermal conductivity of materials in the sandwich, for example, the blotter, the water inside the blotter, the gel, the polyester film, the Gore-Tex® membrane and the Holytex fleece. Heat loss caused by the surroundings could also affect the input of thermal energy inside the sandwich, which was yet already minimized by the silicone sheets.

The thermal response was significantly dependent on the initial thermal energy of the system, the thermal properties and the thickness of the materials inside each humidification sandwich. In the case of Gore-Tex sandwich, it is recommended that the blotter should be immersed into warm water bath before placing into the sandwich. In the case of gel sandwiches, a 3-5 mm thick Tylose® MH 30000 gel (10 wt%) possessed the slowest thermal response, which could probably be resulted by its thickness and/or its intermolecular forces. Therefore, a preheating procedure of the Tylose® gel is recommended. In comparison, agarose and gellan gel both showed a generally satisfactory thermal response, which was almost unrelated to its concentration. A preheating is not demanded for agarose and gellan gels. However, one should keep in mind that the thermal response of each sandwich is always dependent on the water content of the water reservoir, especially in the case of Gore-Tex sandwich whose water reservoir is a wetted blotter. The thermal response increases with the decreasing water content of the water reservoir as the heat capacity of the system declines. Therefore, the time to reach the thermal equilibrium shown in the results above is not valid for each individual treatment.

The slight unevenness of temperature distributions during the heating process of the wet blotter, agarose gel and gellan gel was mainly due to the contact condition between the mat and the blotter or gels as well as the mobility of the water inside the blotter or gels. This slight unevenness is generally acceptable in a conservation treatment. The stronger unevenness of temperature distributions in the case of Tylose® gel could be explained by the slight fluidity of the gel and a decreasing viscosity due to a raised temperature: tardily, the gel could flow laterally due to its self-gravity and therefore the edges of the gel was thinner than the center, which resulted in a lower heat capacity and a more rapid thermal response. Therefore, unlike a wet blotter, agarose or gellan gel whose heat capacity are more uniformly horizontally distributed, it is hardly possible for Tylose® gel to be evenly heated even though it is coupled with a precise and uniform thermal energy resource. A preheating procedure of the Tylose® gel as well as a regular control of its shape and thickness are recommended in this case, through which the uneven temperature distribution of the gel before it reaches the new thermal equilibrium can be maximally avoided.

After the new thermal equilibrium has been achieved, the temperature of water vapor in a Gore-Tex sandwich or water in gels remained constantly only with a slight fluctuation, which is fairly ideal in a conservation treatment.

5.2.3 Working Properties of Each Treatment Variation

This section is going to evaluate the working properties of each humidification sandwiches under several selected temperature conditions: room temperature (without heating), 35 °C, 40 °C and 45 °C, which are the most commonly applied temperature when dealing with protein-based adhesives. The performance of moisture introduction as well as the feasibility and efficacy for removing old mending papers of each treatment were investigated.

5.2.3.1 Performance of Moisture Introduction

1) Gore-Tex sandwich

12 Gore-Tex sandwiches were prepared, each of them with a piece of Watesmo test paper inside. The sandwiches were treated respectively under room temperature, at 35 °C, at 40 °C and at 45 °C for 10, 30 and 60 minutes. The results are shown in Fig. 5.15.

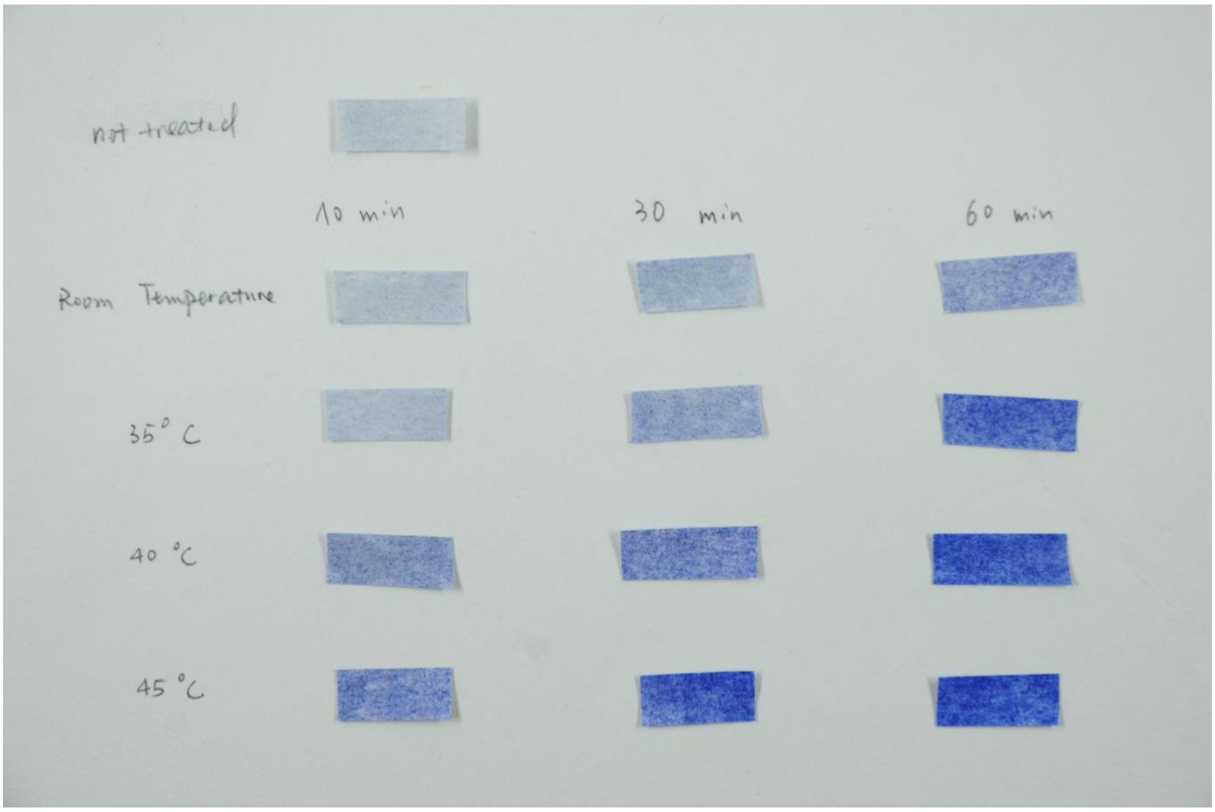


Fig. 5.15: Determination of the performance of moisture introduction in a Gore-Tex sandwich under different temperature condition with different treating time with Watesmos test papers. The intensity of the blue color depends on the amount of absorbed water vapor by the test papers.

Risk of tideline formation was detected by humidifying two blotting papers with a thickness of 0.19 mm (Fig. 5.16) with Gore-Tex sandwiches, respectively under room temperature and at 45°C. With detection through ultraviolet ray with 365 nm wave length, no tideline formation was found after 60 minutes humidification (Fig. 5.7).

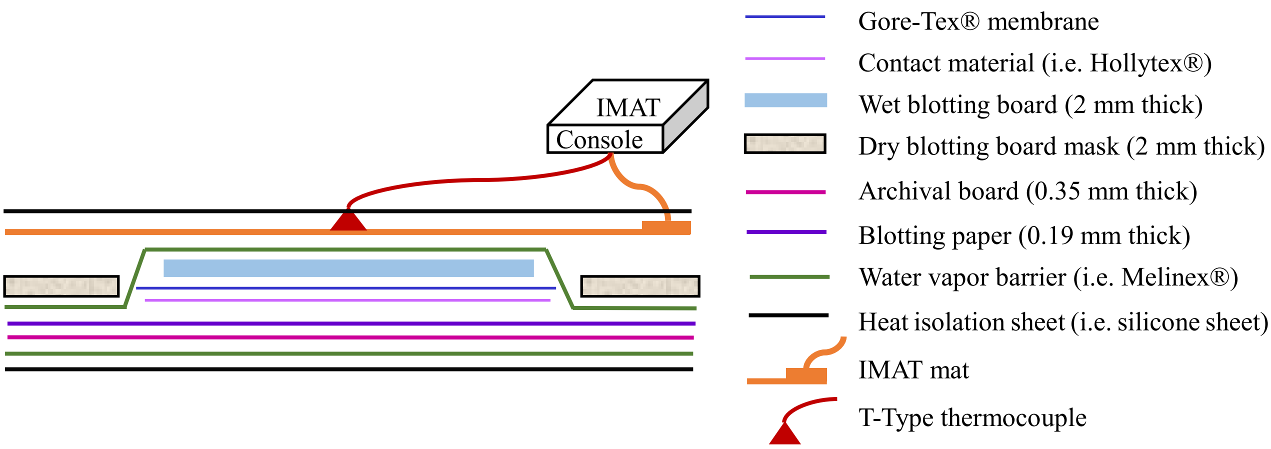


Fig. 5.16: Schematic diagram of the sandwich arrangement in the determination of the tideline formation using a Gore-Tex sandwich.

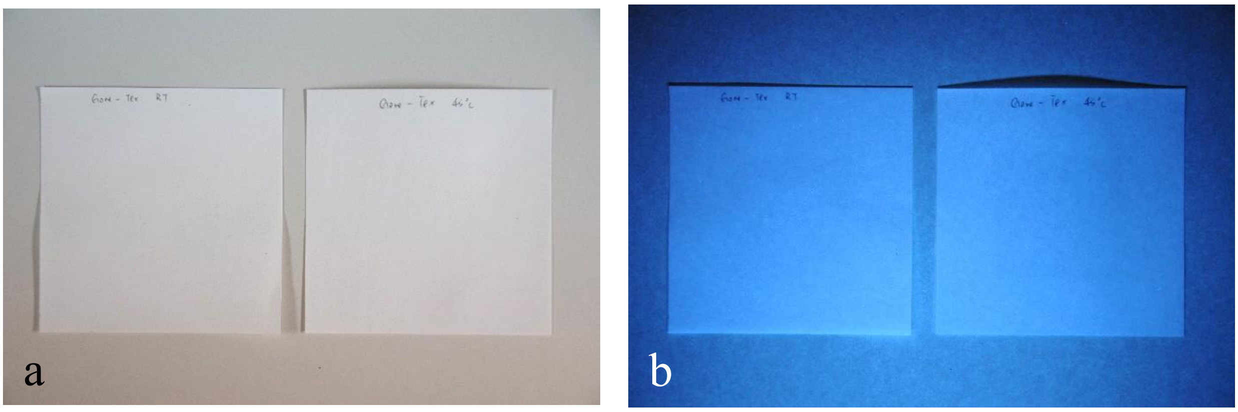


Fig. 5.17: Determination of the tideline formation after 60 minutes treating time with a Gore-Tex sandwich, respectively under room temperature and at 45 °C, with Vis-photography (a) and UV-photography (b).

After the experiments, it could be determined that:

a) With a temperature increase during a humidification process, the required time for a paper to establish a new and higher EMC was accelerated. This could be traced back to the increasing rate of gas diffusion due to enhanced molecular mobility through an input of thermal energy.

b) The risk of tideline formation with a treating temperature not higher than 45 °C and a treating time not longer than 1 hour was extremely low.

   However, further increase of temperature and treating time can significantly raise the amount of water condensated on the surface of the polyester film placed on the bottom of the sandwich. Although the archival board affords a barrier, which is quite sufficient to avoid a direct contact with the condensate water, the moisture content of the board will be continuously enhanced. This can result in a complete penetration of water into the archival board when the humidification is carried out in a long-term period. Therefore, a tideline formation cannot be absolutely avoided when humidifying with a Gore-Tex sandwich.

2) Gel sandwiches

The detection of moisture introduction through different gel sandwiches was much more complicated and difficult to carry out. As discussed in Chapter 4.2.2, the performance of moisture introduction using a hydrogel depends, on the one hand, on the surface properties of the paper, and on the other hand, on the water retention power of the gel. The latter is related to the polymer molecule structure, the intermolecular forces between water and polymer chains, the concentration of the gel, the treating temperature and other applied forces such as its self-gravity and external pressure. Nevertheless, a systematical investigation of all the parameters mentioned above was hardly possible to be completely conducted in this study due to the limitation of time and experimental instrumentations. Therefore, in this section, experiments were only performed to observe some of the parameters, which provided a basic knowledge of this topic and pointed out a direction for further researches in the future.

Several pieces of Tylose® MH 30000 gel were prepared, and a piece of Watesmo test paper was placed under each gel, respectively with and without Rayon paper, treated for 10 and 40 minutes, under room temperature and at 45 °C. A glass plate was placed on the gel to ensure a good contact (Fig. 5.18 a). The results are shown in Fig. 5.18 and summarized as following:

a) Under room temperature: Without the presence of Rayon paper, the color of the test paper changed immediately from light blue to dark blue, which was significantly postponed by the presence of Rayon paper in between during the first 10 minutes. After 40 minutes, the performance of both papers was similar, whereas no sign of direct contact with water or water drops was presented on the tested paper treated with Rayon paper.

b) With a treating temperature of 45 °C: Without the presence of Rayon paper, the color of the test paper also changed immediately from light blue to dark blue. However, part of the test paper, where it was treated with Rayon paper, also changed to dark blue after 10 minutes (see red arrow in Fig 5.18 e). The test paper showed a more obvious sign of a contact with liquid water after 40 minutes (Fig. 5.18 f). Meanwhile, the change of the gel shape after 40 minutes was also more evident (see blue arrow in Fig 5.18 e, f).

Risk of tideline formation of using Tylose® MH 30000 gel in 10 wt% concentration, with and without the presence of Rayon paper, was also detected by humidifying blotting papers with a thickness of 0.19 mm (Fig. 5.19) with Tylose® gel sandwich, respectively under room temperature and at 45°C. With a detection through ultraviolet ray with 365 nm wave length, no tideline formation was found after 40 minutes treating time. Additionally, the presence of Tylose® gel residue was found when there was no Rayon paper applied between the blotting paper and the gel (see red arrows in Fig. 5.20 b).

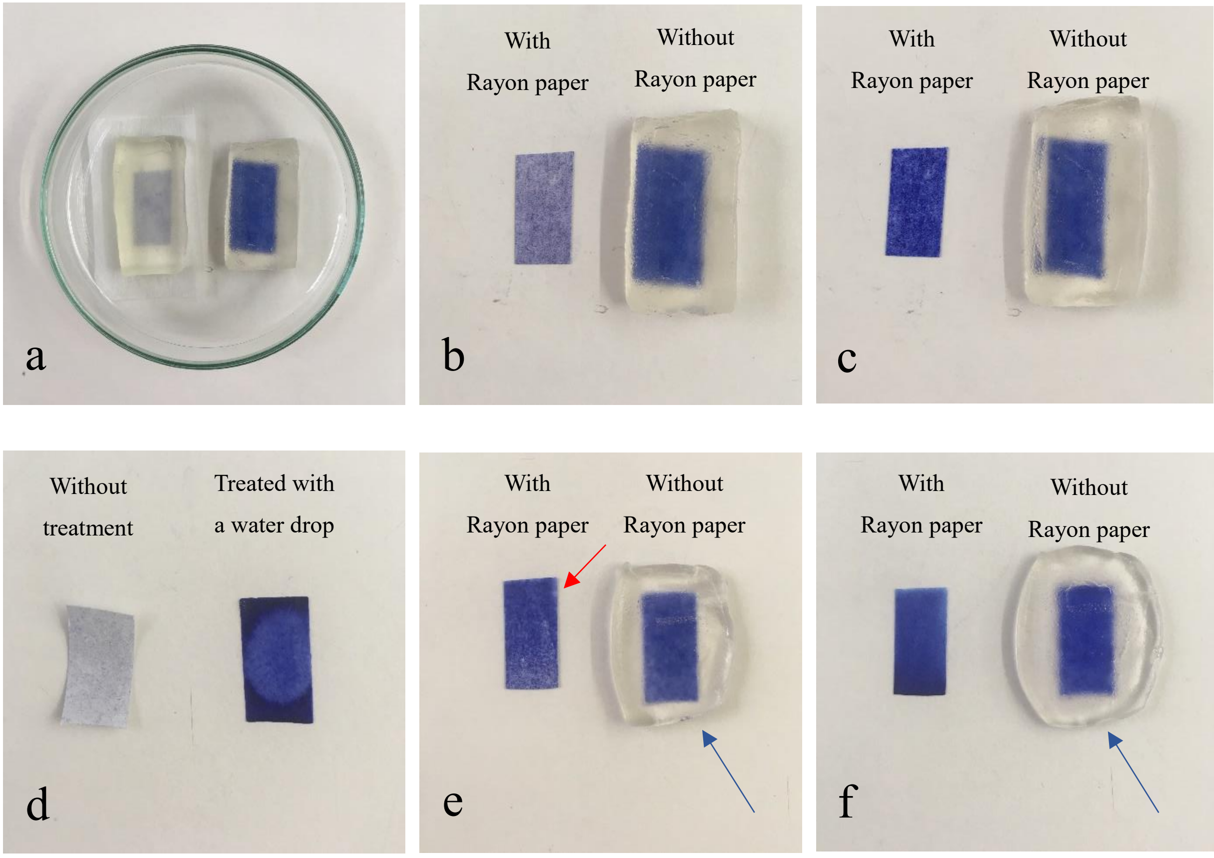


Fig. 5.18: Determination of the performance of moisture introduction through Tylose® MH 30000 gel in 10 wt% concentration (a), respectively under room temperature after 10 min (b), 40 min (c) treating time and at 45 °C after 10 min (e), 40 min (f) with Watesmos test papers. The reaction of the test paper with a water drop presents in (d).

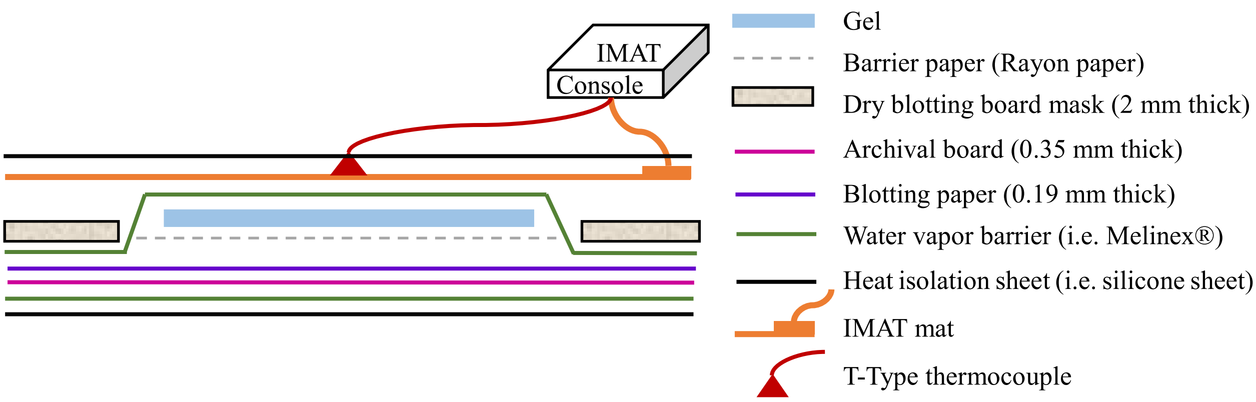


Fig. 5.19: Schematic diagram of the sandwich arrangement in the determination of the tideline formation using gel sandwiches.

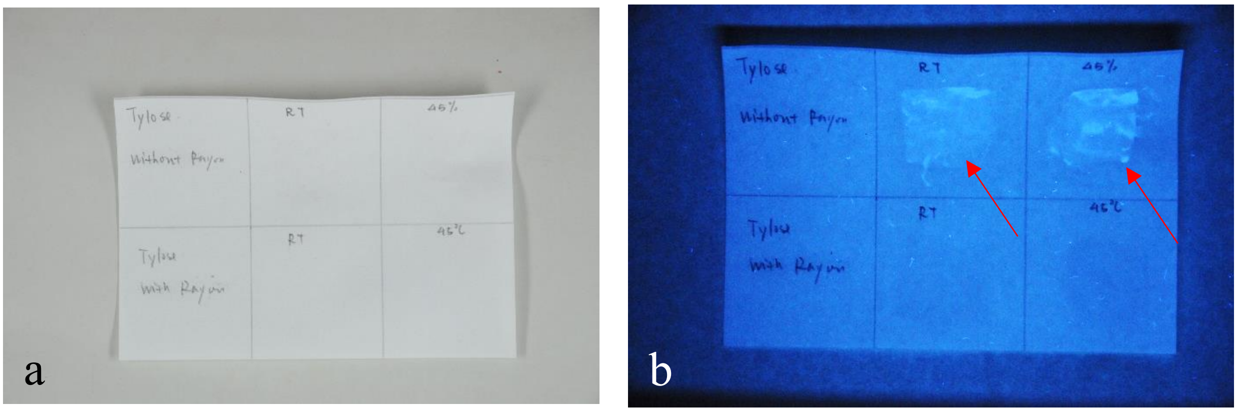


Fig. 5.20: Determination of the tideline formation after 40 minutes treating time with Tylose® MH 30000 gel in 10 wt% concentration, with and without Rayon paper, under room temperature and at 45 °C with Vis-photography (a) and UV-photography (b).

Several pieces of agarose and gellan gel were prepared, and a piece of Watesmo test paper was placed under each gel, respectively with and without Rayon paper, treated for 10 and 40 minutes, under room temperature. Agarose gel was prepared in 2 wt% – 6 wt% and gellan gel was prepared in 2 wt% – 5 wt%. A glass plate was placed on the gel to ensure a good contact (Fig. 5.21 a, d, g; Fig. 5,22 a, d, g). The results of agarose and gellan gel are shown respectively in Fig. 5.21, Fig. 5.22 and summarized as following:

a) Under room temperature: Without the presence of Rayon paper, the color of the test paper changed immediately from light blue to dark blue, which was significantly postponed by the presence of a Rayon paper in between.

   In the case of 2 wt% agarose and gellan gel, the test paper displayed a sign of direct contact with water drops after 10 minutes, even though Rayon paper was applied (see red arrows in Fig. 5.21 a and Fig. 5.22 b). In the case of 3 wt% gellan gel with Rayon paper, sign of direct contact with water drops did not occur after first 10 minutes but did occur after 40 minutes (see red arrows in Fig. 5.22 f). In the case of 3-6 wt% agarose gel and 4-5 wt% gellan gel, no sign of direct contact with water drops was shown, and the moisture introduction was carried out uniformly during the 40-minute treatment.

b) Input of thermal energy was not conducted in this experiment on agarose gel and gellan gel, but one could presume an acceleration of the moisture introduction and a more rapid penetration of water through the Rayon paper with an increase of temperature.

Risk of tideline formation of using agarose gel in concentration of 2-6 wt% and gellan gel in concentration of 2-5 wt%, with and without the presence of Rayon paper, was also detected by humidifying blotting papers with a thickness of 0.19 mm (Fig. 5.19) with agarose or gellan gel sandwich, respectively under room temperature, at 35 °C, at 40 °C and at 45 °C.

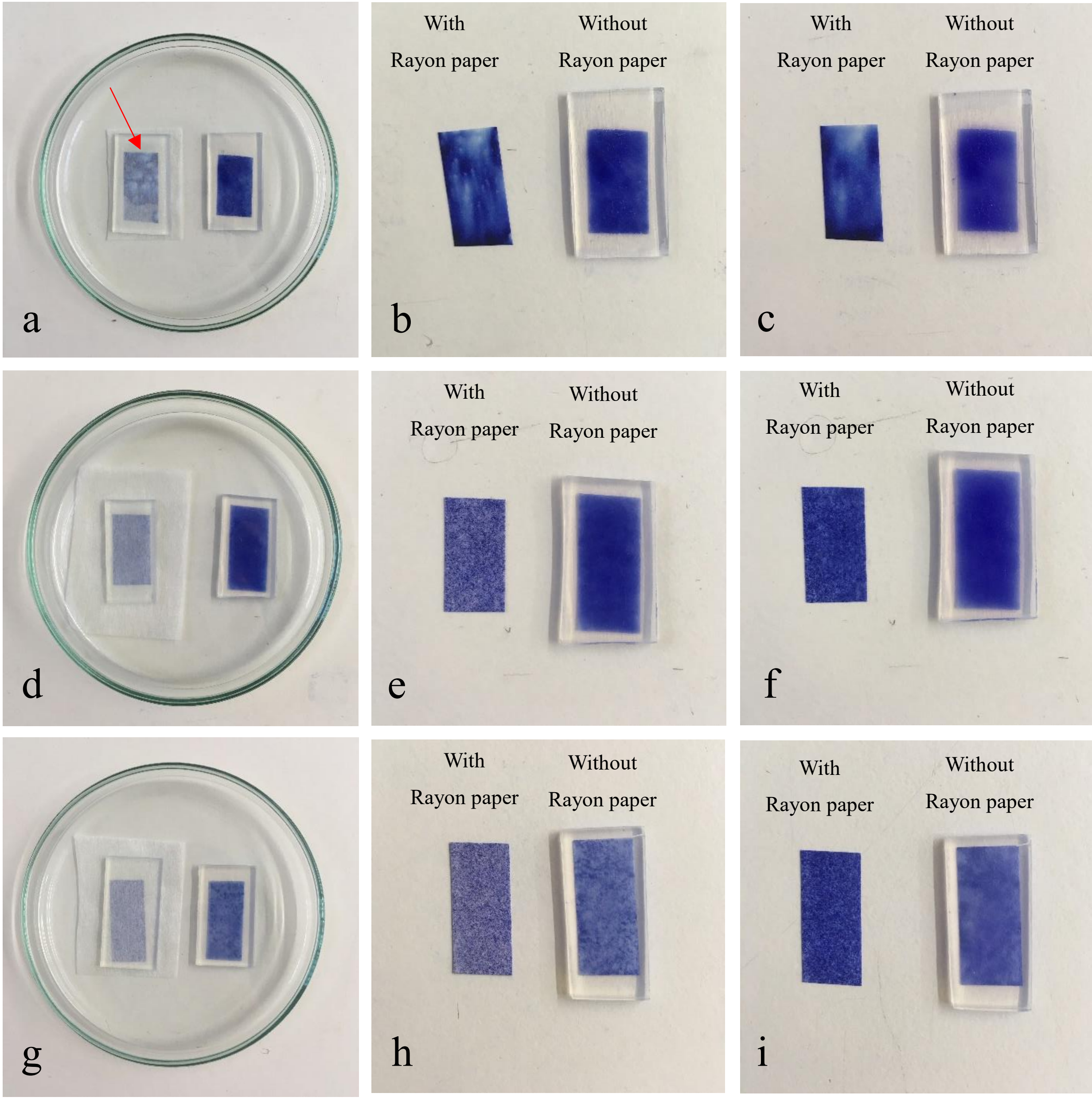


Fig. 5.21: Determination of the performance of moisture introduction through agarose gel under room temperature, respectively in 2 wt% concentration (a) after 10 min (b) and 40 min (c) treating time, in 3 wt% concentration (d) after 10 min (e) and 40 min (f) treating time, in 6 wt% concentration (g) after 10 min (h) and 40 min (i) treating time with Watesmos test papers.

The results of both gels are shown respectively in Fig. 5.23 and Fig. 5.24. The treating time was 40 minutes. With detection through ultraviolet ray with 365 nm wave length, the formation of tideline after the 40 minutes treatments could be concluded as following:

a) Under room temperature, 5-6 wt% agarose gel and 5 wt% gellan gel applied without Rayon paper as well as 2-6 wt% agarose gel and 3-5 wt% gellan gel applied with Rayon paper presented no formation of tideline.

b) At 35 °C: 5-6 wt% agarose gel and 5 wt% gellan gel applied without Rayon paper as well as 3-6 wt% agarose gel and 3-5 wt% gellan gel applied with Rayon paper presented no formation of tideline.

c) At 40 °C: 5-6 wt% agarose gel applied without Rayon paper as well as 3-6 wt% agarose gel and 3-5 wt% gellan gel applied with Rayon paper presented no formation of tideline.

d) At 45 °C n: 5-6 wt% agarose gel applied without Rayon paper as well as 3-6 wt% agarose gel and 3-5 wt% gellan gel applied with Rayon paper presented no formation of tideline.

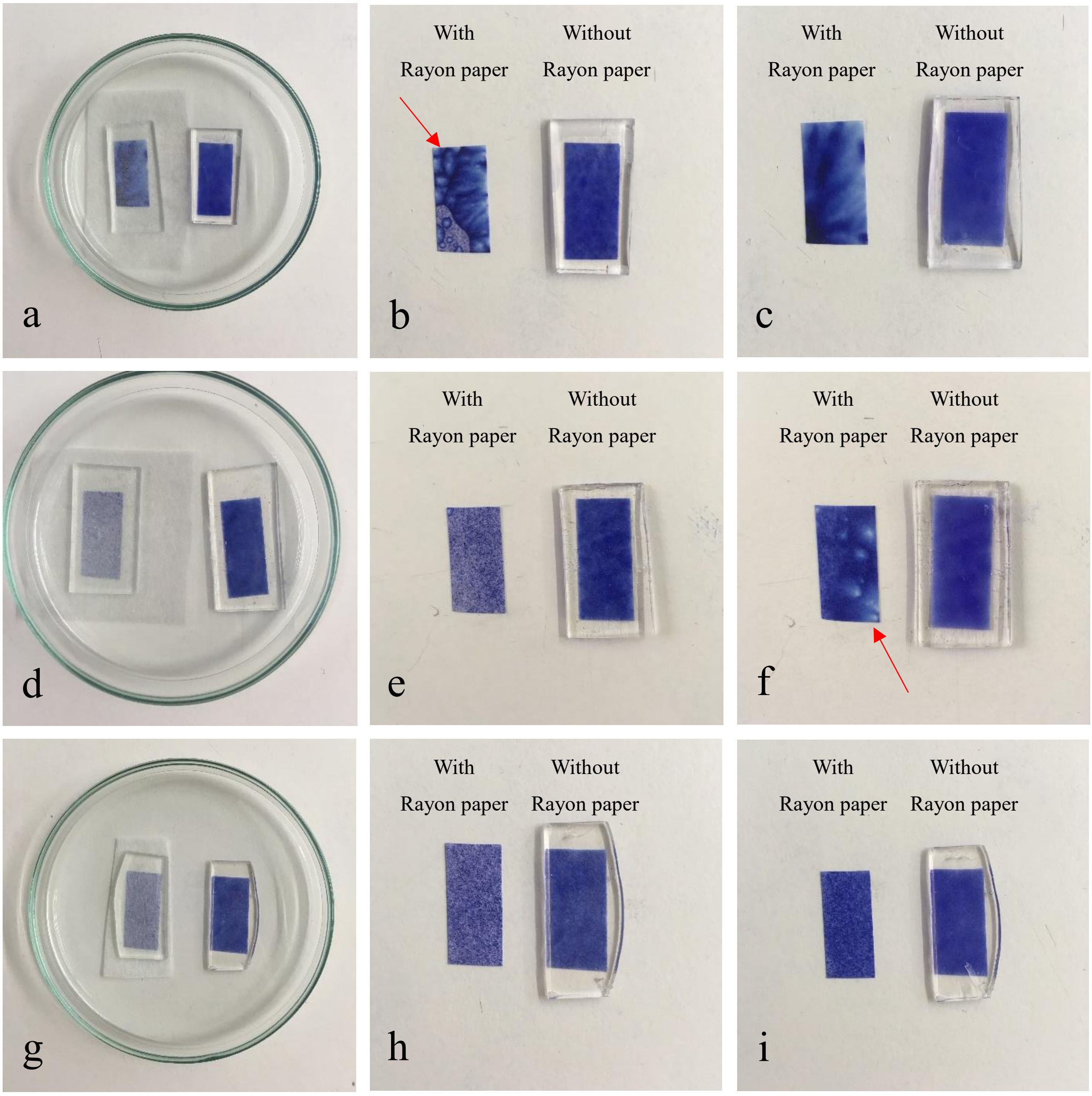


Fig. 5.22: Determination of the performance of moisture introduction through gellan gel under room temperature, respectively in 2 wt% concentration (a) after 10 min (b) and 40 min (c) treating time, in 3 wt% concentration (d) after 10 min (e) and 40 min (f) treating time, in 5 wt% concentration (g) after 10 min (h) and 40 min (i) treating time with Watesmos test papers.

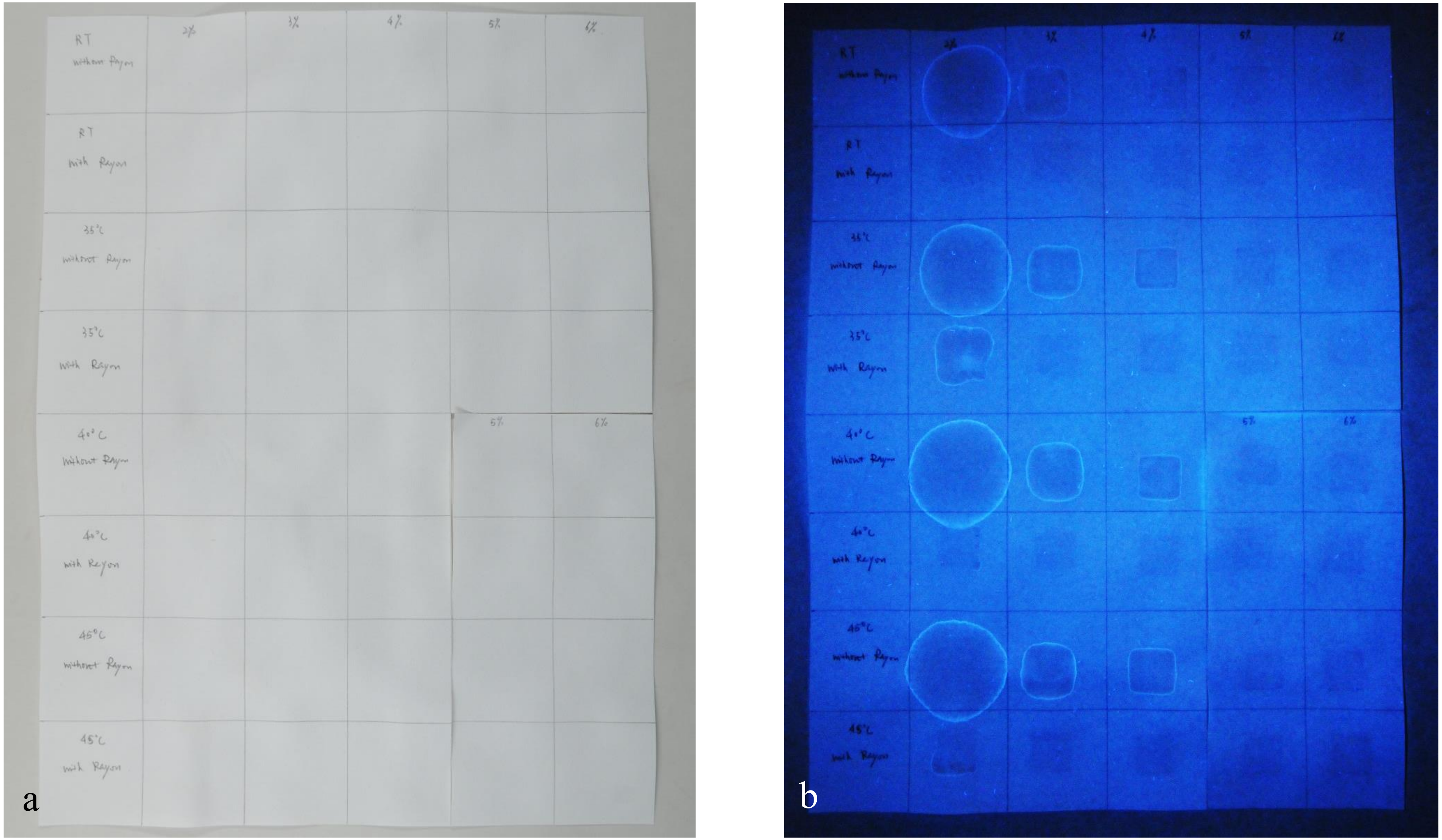


Fig. 5.23: Determination of the tideline formation after treated 40 min with agarose gel in 2-6 wt% concentration, with and without Rayon paper, under room temperature, at 35 °C, at 40 °C and at 45 °C with Vis-photography (a) and UV-photography (b).

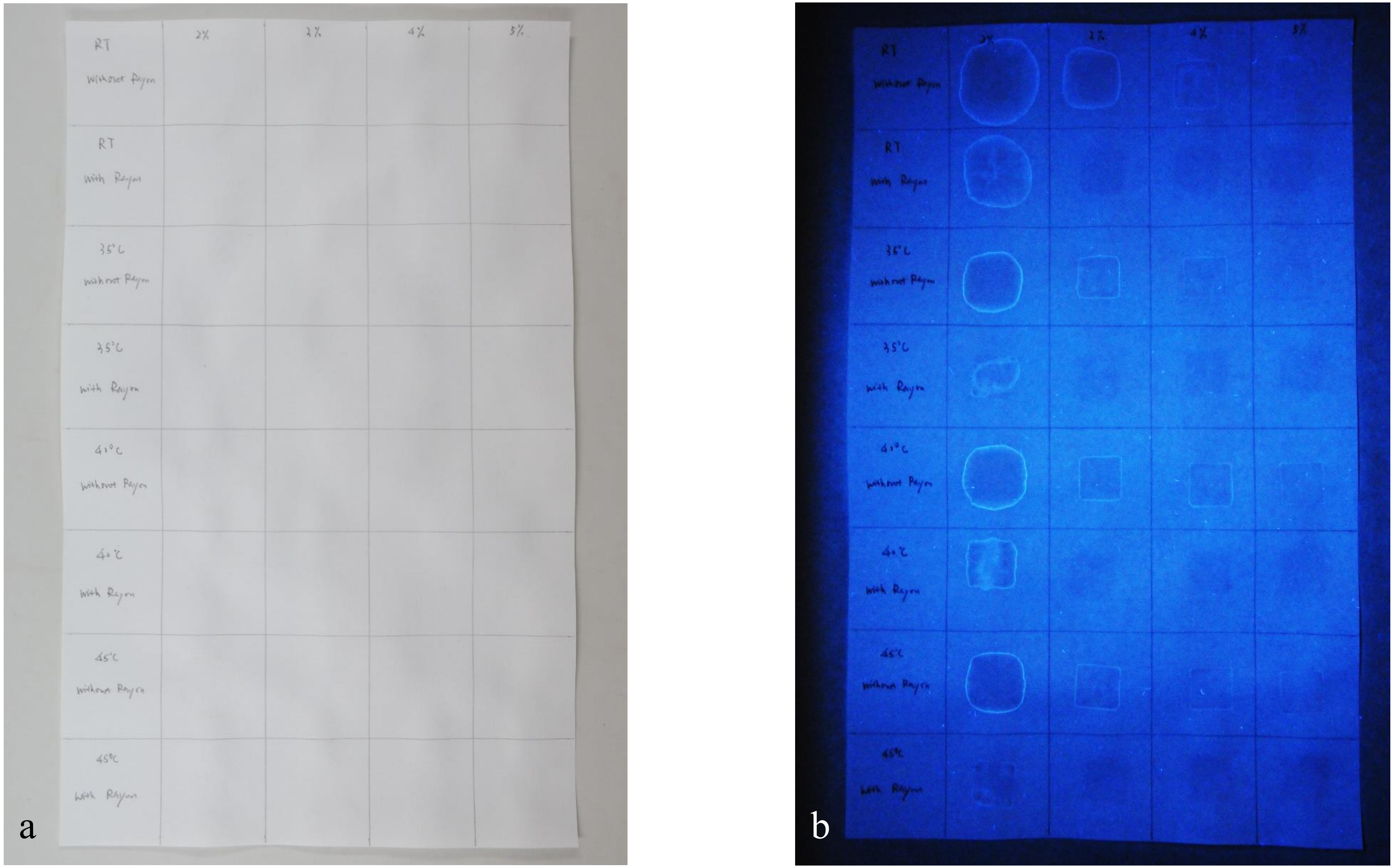


Fig. 5.24: Determination of the tideline formation after treated 40 min with gellan gel in 2-5 wt% concentration, with and without Rayon paper, under room temperature, at 35 °C, at 40 °C and at 45 °C with Vis-photography (a) and UV-photography (b).

To summarize, it is very difficult to make a clear conclusion on the performance of moisture introduction through hydrogels and it is hardly possible to propose a “surefire” method for introducing moisture through hydrogels as well. It can be presumed that the intermolecular forces between water molecule and hydrogel polymer chains as well as the mobility of bound water and free water in hydrogel play a significant role in the interaction between paper and gel. So far, only a few determinations can be made:

a) The presence of Rayon paper as a barrier between gel and object shows advantages during the introduction of moisture in several ways:

- It prevents the object, to a certain extent, from having direct contact with gel or liquid water as long as the barrier paper has not been fully saturated with water. The object has contact with the multimolecular water and capillary water inside the Rayon paper. Besides, it also generates a slower and more uniform moisture introduction. However, the saturation can be accelerated by increased temperature, external applied pressure or an extended treating time.

- The residues of the gels remained on the object can be minimized, especially in the case of Tylose® MH 30000 gel. However, a clear conclusion of the residues presence of agarose gel and gellan gel cannot be drawn in this study. Sullivan (2017) and her colleagues have determined that a Japanese tissue barrier can successfully attenuate the amount of agarose and gellan residues using the highly sensitive fluorescein-tagging technique. (Sullivan et.al, 2017, pp. 48-49).

- With the presence of Rayon paper, the aging performance of the treated and untreated areas of the object is generally similar. Nevertheless, direct contact with the gel can enhance the visual distinction of the treated and untreated areas after aging[5]. However, in this study it cannot be determined, in how many ways and how exactly the gels and the presence of Rayon paper can affect the paper aging process after a treatment.

b) The rate of moisture introduction by applying hydrogel increases with a raised treating temperature, a decreased concentration of the gel, or other applied forces such as the gravity (thickness) of the gel and external pressure.

c) When the treating temperature is not higher than 45 °C, the risk of tideline formation is very low when Tylose® MH 30000 gel in 10 wt% concentration is applied with or without Rayon paper. The risk will be amplified by external pressure and further increase of

[5] An accelerate aging test was extra carried out on four papers with different raw materials, additives, wettability and surface textures after treated with the gels under different temperature conditions. The presence of Rayon paper showed generally a positive result. However, the results could not straightforwardly present how exactly the Rayon paper influenced the aging procedure of the papers, and it raised more research questions on the topic. Therefore, this test is not summarized and discussed in detailed.

temperature.

d) When the treating temperature is not higher than 45 °C, the risk of tideline formation is low, when: 1) agarose gel is prepared in 3-6 wt% concentration and applied with Rayon paper, 2) agarose gel is prepared in 5-6 wt% without Rayon paper, 3) gellan gel is prepared in 3-5 wt% concentration and applied with Rayon paper. The risk will be amplified by external pressure, increase of the thickness of the gel sheet and further increase of temperature.

5.2.3.2 Feasibility and Efficacy of Temperature-related Optimization

Experiments were carried out on the mock-ups by applying different humidification sandwiches coupled with heat transfer followed by the arrangement demonstrated in Fig. 4.30. Each treatment was conducted under room temperature, at 35 °C, at 40 °C and at 45 °C. The results and discussions are summarized as following:

1. General temperature-related influence on protein-based adhesive

- Through an introduction of moisture combined with heat transfer, the adhesive film of mock-ups could swell far more quickly than the adhesive film treated without an input of thermal energy. The duration of the treatment could be largely accelerated. The mending paper could be easily removed from the paper substrate as a spatula could be inserted into the adhesive layer to separate the mending paper and the substrate (Fig 5.25). An insufficient swelling of the glue layer could lead to damages to the fiber of the paper substrate during the detachment (Fig 5.26).

- When too much moisture was applied, or when the temperature reached a certain degree, the swelled adhesive film could liquify (see red arrow in Fig 5.27 a). Although the liquification of animal glue could further simplify the detachment of the mending paper, it increased the risk of the penetration of glue into paper substrate, especially when the paper substrate was porous, weak sized or already degraded (see red arrow in Fig 5.27 b). This risk could be further increased by an extended treating time as well as an increase of treating temperature.

After the experiments, it could be determined that:

a) A certain swelling degree of animal glue is required during the removal of old mending papers, which can considerably benefit by an input of thermal energy through the IMAT heater.

b) An increased treating temperature can raise the risk of the penetration of glue into paper substrate during the treatment caused by the liquification of the glue and the decreased viscosity of the glue solution. Increased moisture introduction as well as an extended treating time can also increase this risk. Thus, a treating temperature over 45 °C is not recommended. A regular control of the treatment process is necessary.

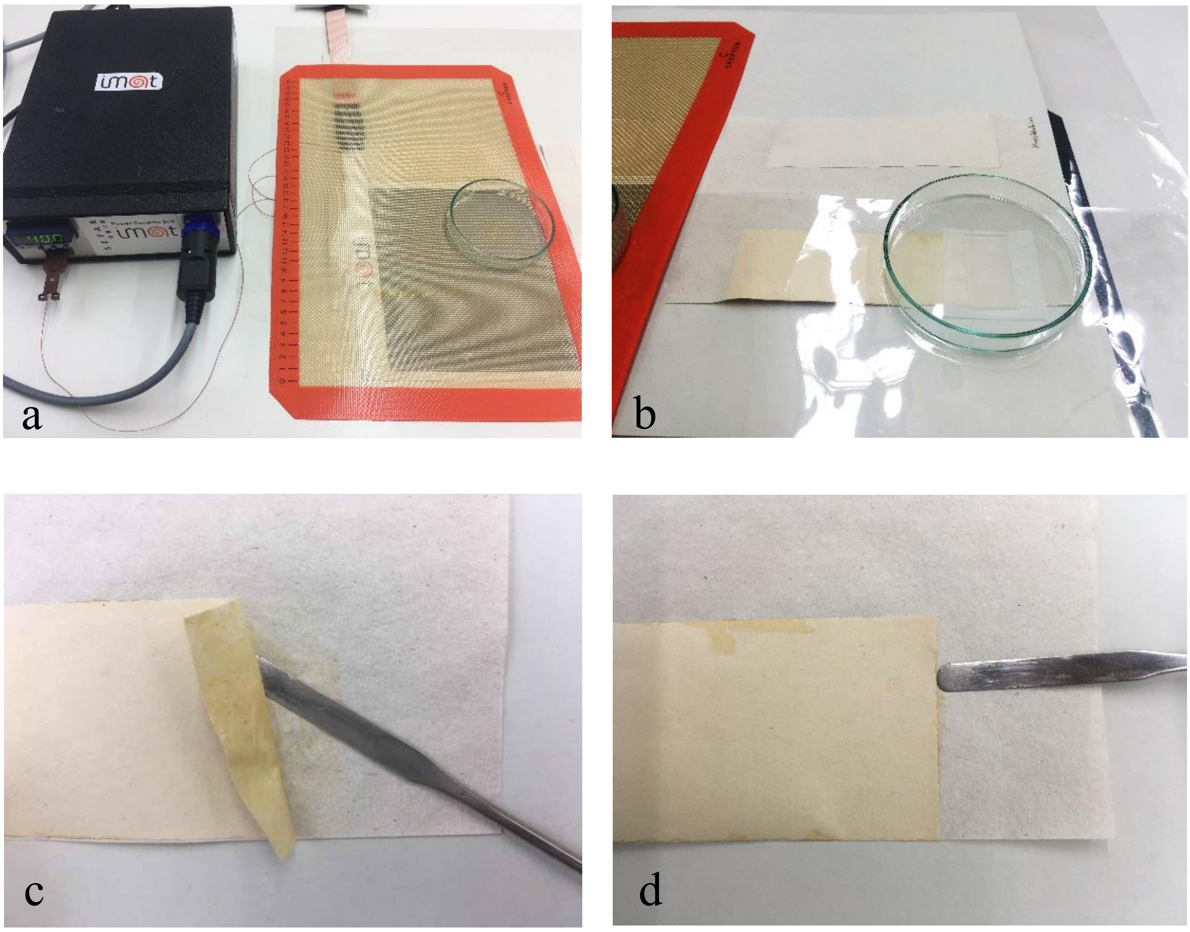


Fig. 5.25: Temperature-related optimization on the removal of mending papers carried out on mock-ups. The mends were treated with a 2mm thick 4 wt% agarose gel with Rayon paper respectively under 40 °C condition (a) and under room temperature (b). After 10 minutes, the removal of the mending paper could already be realized when treated under 40 °C condition (c), while the one treated under room temperature still showed no possibility (d).

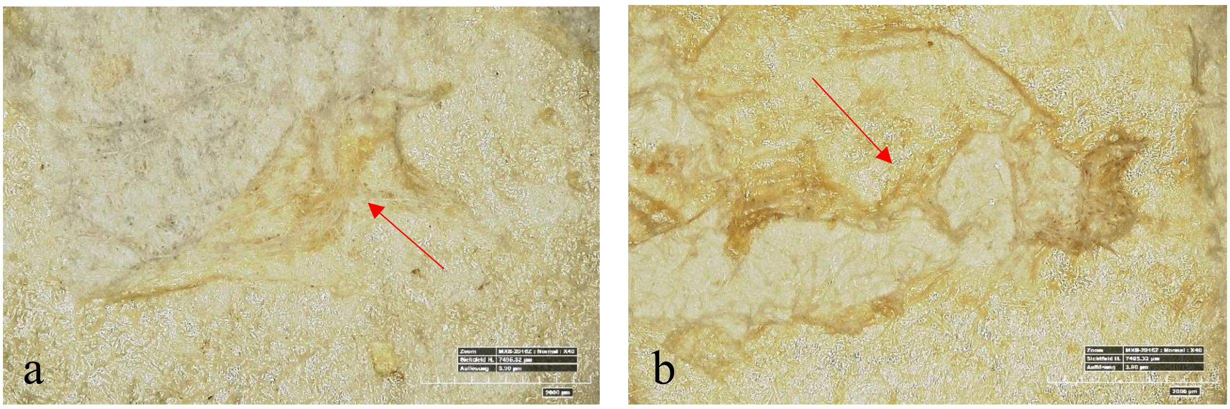


Fig. 5.26: Microscopic images for the damages of fiber (see red arrows) on the rag paper substrate (a) and on the wood pulp paper substrate (b) caused by the removal of the mending papers when the adhesive layer did not swell sufficiently.

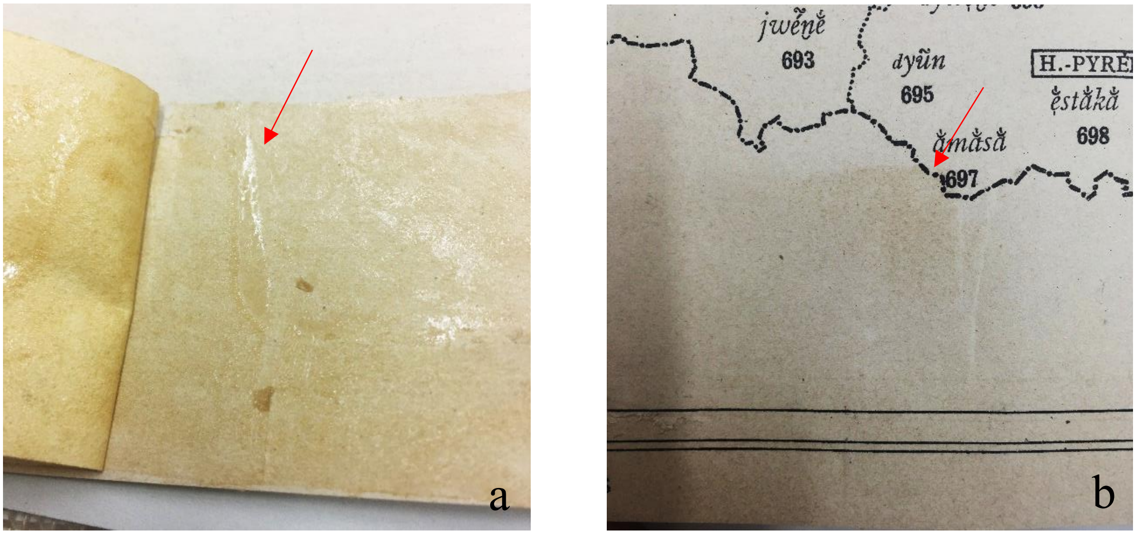


Fig. 5.27: Condition of the bone glue layer between the wood pulp paper substrate and the wood pulp mending paper after treated with a Gore-Tex sandwich under 45 °C condition for 90 minutes. The mending paper could be easily removed from the substrate, but meanwhile the bone glue was already partly liquefied (red arrow in a) that it has penetrated through the strong degraded paper substrate to a certain extent (red arrow in b).

2. Performance of the different types of glue, mending paper and paper substrate

- In this study, the bone glue required a slightly shorter treating time than the hide glue when treated with same method under identical condition, but the bone glue was also more likely to liquify so its penetration into the paper substrate was higher. This might due to the stronger denaturation of bone glue during its manufactural process. Nevertheless, the difference between both glues was not dramatic since they are both common products currently available by conservation suppliers.

  In a real conservation case, however, the properties of the glue applied during previous repairs can widely vary, of which conservators cannot be aware. Additionally, since the degree of swelling and liquification of the glue also increase with an enhanced degradation of the glue, it should also be taken into account during a conservation treatment. Therefore, one should better consider the worst situation to avoid unpredictable outcomes by, for example, always starting at a relative low treating temperature and a relative short treating period with a regular control of the treatment.

- The two types of mending paper presented not much difference during the required treating time. However, the adhesive tended to remain more on the wood pulp paper than on the rag paper, whose surface was a rather rough and whose sizing was more intact.

  However, it is hardly possible to make a comprehensive statement only from these two selected samples. Depending on different raw materials, manufacturing processes, sizing agents, surface textures and porosities of paper as well as its different degraded degrees etc., mending papers can perform in various ways during each specific treatment. A regular control of the treating process is therefore the most significant factor.

- The removal of the mending papers from the wood pulp paper substrate required much greater effort compared to the rag paper substrate. During the experiments, fibers on the surface of wood pulp paper substrate tended to stick to the adhesive layer, so the adhesive layer needs to become much softer than the rag paper. Results showed that treatments with a target temperature lower than 40 °C were inefficacious as the swelling degree of the glue was not satisfied, even after a four-hours solving time with a Gore-Tex sandwich and a two-hours solving time with a gel sandwich. However, as described above, a high degree of swelling or a liquification of the glue could accelerate the penetration of glue into paper substrate, which could also readily happen to this strong degraded paper substrate (Fig. 5.27). To achieve a balance between an “enough swelling” and an “excessive swelling” was, as a result, pretty challenging.

  In order to explain this phenomenon, the fiber morphology and the cross section of both papers were compared by means of scanning electron microscope. The wood pulp paper was generally composed of fibers with poor strength and splits (see red arrows in Fig. 5.28 b), which were pressed together with other additives (Fig. 5.28 a). It was also interesting to find in the cross-section images that some gaps which “separated” the fibers into several individual layers (see red arrows in Fig. 5.28 c and d). The bonding between the layers was weak. The poor fiber strength and the weakened fiber-fiber-bonding in the strong degraded wood pulp paper could perfectly explain why first layer of fibers tended to stick to the glue during the treatment. Besides, the interaction between the surface of the wood pulp paper substrate and the protein-based adhesive could hereby also plays an important role. When the wood pulp paper was applied with only a thin layer of animal glue, the glue could partly fill up the area between the fibers (see red arrowed in Fig. 5.28 e, f). Since the removal of the mending papers always requires a mechanical action, it was not difficult to image that damages to the fibers on the paper substrate and the penetration of glue into the paper substrate during the removal of the mending papers could readily occur.

  In the real praxis, therefore, when dealing with a mending paper glued to a degraded, brittle wood pulp paper substrate, the swelling degree of the glue should be controlled precisely, where the IMAT heater can certainly show its particular superiority.

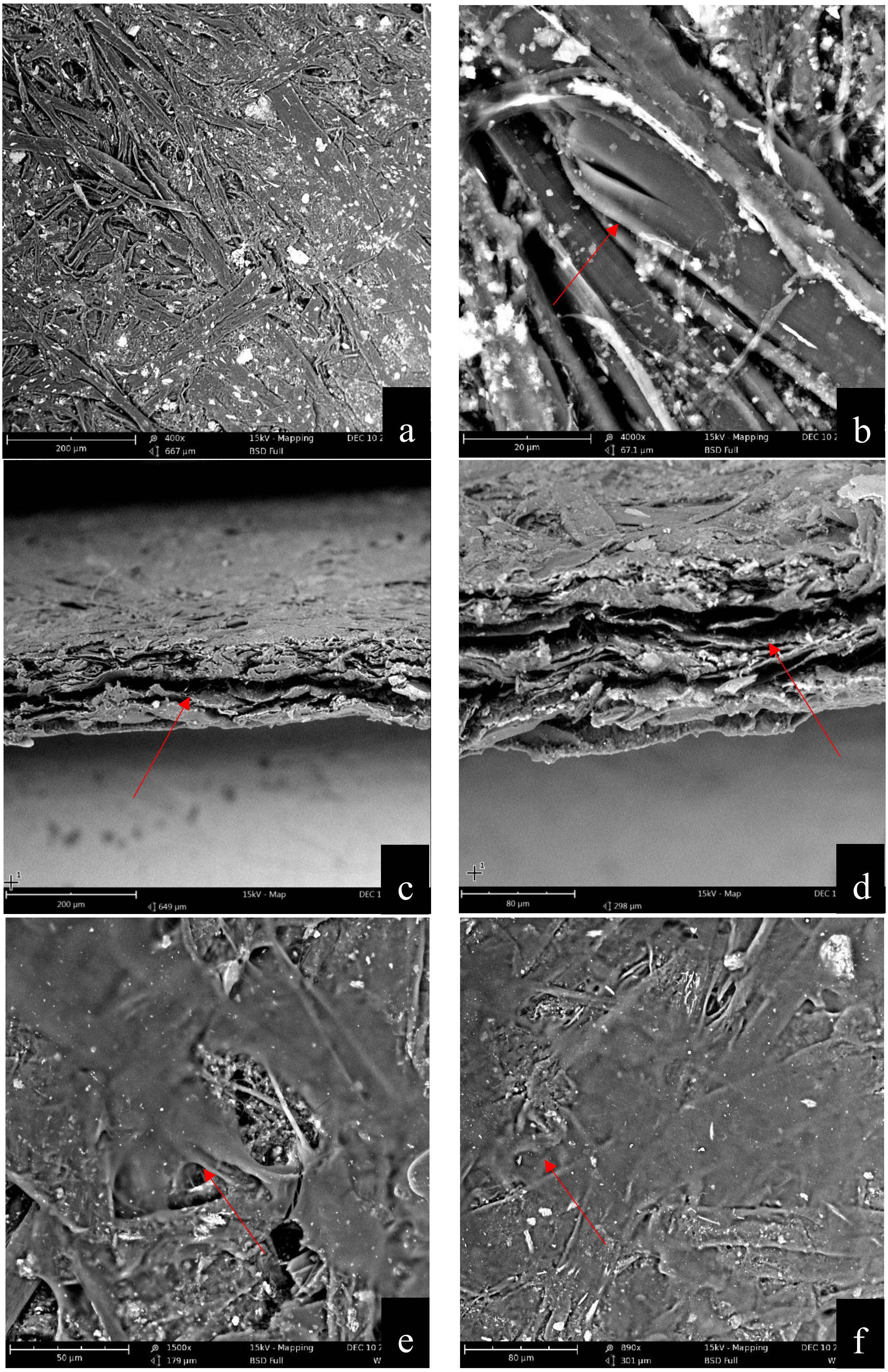


Fig. 5.28: SEM images captured for the wood pulp paper substrate: (a): Overview of the fibers; (b): Detail image for a fiber with splits; (c) and (d): Cross-sections of the paper; (e) and (f): Images captured for the paper which was applied a thin layer of bone glue.

In comparison, fibers of the rag paper were far more intact (Fig. 5.29 a). The fiber-fiber-binding in the paper was also satisfactory due to the fibrillation of the first cell wall (see red arrows in Fig. 5.29 b). The fibers were generally good interlinked in the paper (Fig. 5.29 c, d). Therefore, the removal of the mending papers glued on the rag paper substrate did not require a high swelling degree of the adhesive, through which the risk of penetration of glue into the paper substrate was also lower.

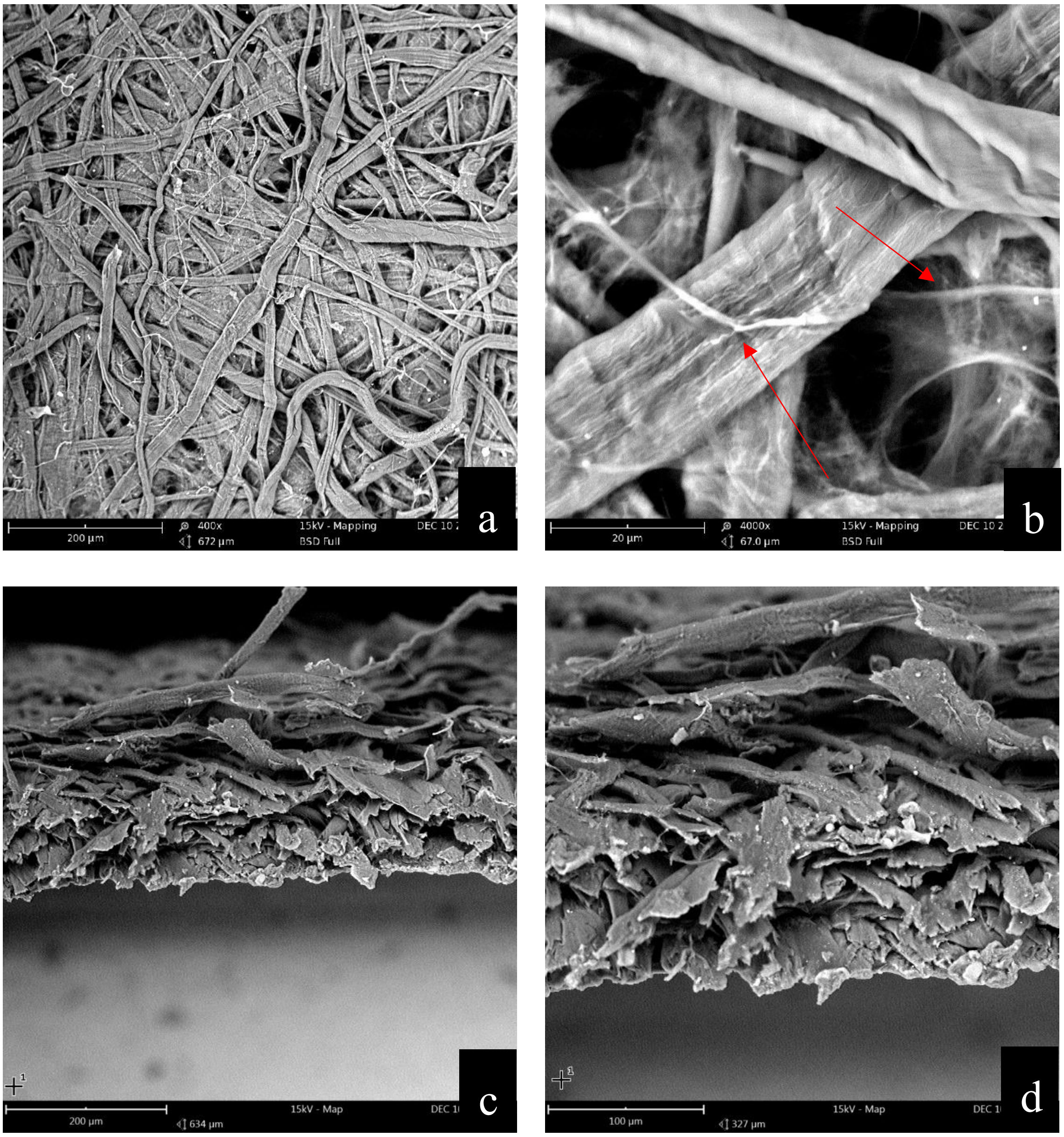


Fig. 5.29: SEM images captured for the rag paper substrate: (a): Overview of the fibers; (b): Detail image of the fibrillated fibers which enhanced the fiber-fiber-binding in the paper; (c) and (d): Cross-sections of the paper;

- After a successful removal of the mending papers, no tideline formation and penetration of glue or other damages to fibers appeared on the paper substrate (Fig. 5.30). The residues of glue remained on the wood pulp paper substrate was more than that on the rag paper substrate (Fig. 5.31). Adhesive residues on the paper substrates could be further reduced after the detachment.

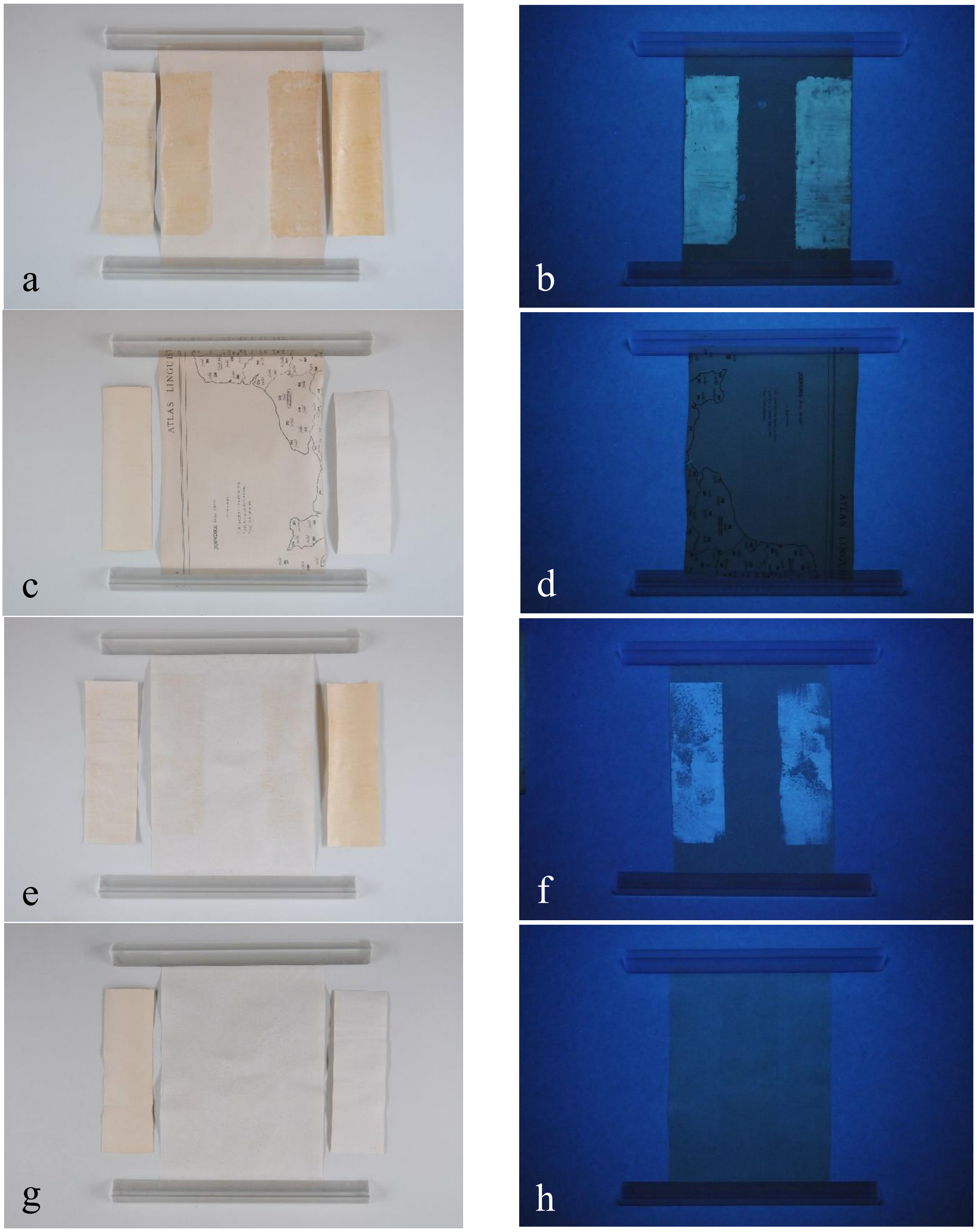


Fig. 5.30: Mock-ups after the removal of mending papers captured under with visible light and UV-light, respectively the front side (a, b) and the back side (c, d) of the wood pulp paper substrate and the mending papers; the front side (e, f) and the back side (g, h) of the rag paper substrate and the mending papers.

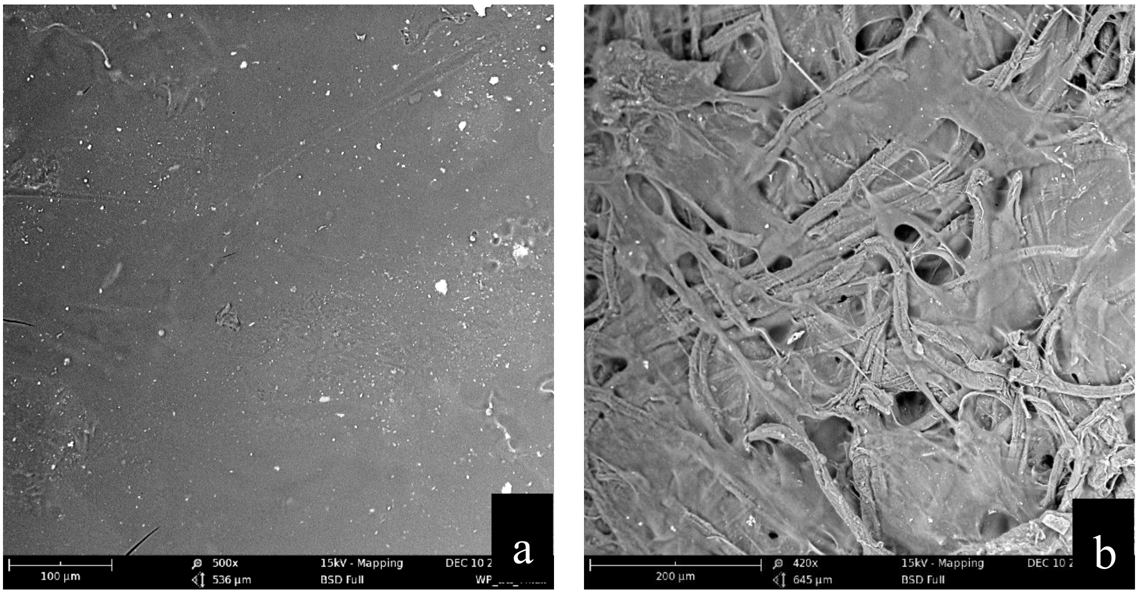


Fig. 5.31: SEM images captured for the wood pulp paper substrate (a) and the rag paper substrate (b) after a successful detachment of the mending papers

3. Comparison of different humidification sandwiches

1) Gore-Tex sandwich

- The duration of detaching a mending paper was accelerated through a heat application. Without heat application, the protein-based adhesive could not swell adequately after a 200-minutes treatment. With an input of thermal energy, the duration of the treatment lasted only 30-90 minutes depending on different target temperatures, different mending papers and different types of glues.

- Introduction of moisture through a Gore-Tex sandwich was generally even, with a low risk of a tideline formation since moisture was introduced in gas phase. Yet the absorption of moisture was not always even: edges of the mending paper could be humidified slightly quicker than the center due to more explosion to the water vapor; areas, where the mending paper was stronger degraded or where the adhesive layer was applied thinner, could equally absorb moisture more rapidly. Besides, a target humidification was difficult to be conducted with a high precision as paper substrate close to the boundary of the mends could be humidified at the same time.

- Paper substrate was exposed to a high RH level for a generally long period of time, it dwelled therefore at a high *EMC* state that the fiber of the paper contained a high amount of moisture for a long-term period, which could enhance the ability of the swelled or liquefied animal glue to travel into the substrate as well.

- A Gore-Tex sandwich was difficult to be properly arranged to humidify a mend glued in or close the spine fold of a bound volume, especially when the width of the mend was relatively narrow. However, it would be more suitable for a large area treatment.

2) Tylose® MH 30000 gel sandwich

- The duration of detaching a mending paper was accelerated through a heat application. Without heat application, the protein-based adhesive could not swell adequately after a 90-minutes treatment. With an input of thermal energy, the duration of the treatment lasted 20-50 minutes depending on different target temperature, different mending papers, different types of glues, and whether Rayon paper was applied.

- The slight fluidity and the shear-thinning property of the Tylose® gel provided both pros and cons on its working feasibility: On the one hand, Tylose® gel could conform to the surface texture of the mending paper, which promises an ideal contact between the gel and the mending paper. On the other hand, however, a target humidification was difficult to be conducted precisely as the shape of Tylose® gel could not remain stable. The gel almost always slightly flowed laterally out of the boundary of the mend during the treatment, which could be even aggravated by external pressure or an increase of temperature (Fig. 5.32). The gel thus did not have a uniform thickness throughout the treated area. Therefore, Tylose® gel was evaluated as an improper humidification agent for dealing with a mending paper glued right beside to a moisture sensitive area, such as hand-colored illustration or text written with red ink. When redundant adhesive already oozed out of the edges of the mend during the previous repair, the lateral flow of Tylose® gel could also increase the risk of penetration of glue into paper: The oozed glue might have direct contact with the gel and absorb moisture much quickly.

- Due to the different interaction between paper and moisture as well as the shorter treating time compared to the treatment with a Gore-Tex sandwich, the paper substrate did not need to be exposed to a high RH level for a long-term period during a treatment with Tylose® gel. Yet the introduction of moisture through Tylose® gel could lead to a formation of tideline on the paper substrate or penetration of glue, when too much external weight was added or the treatment lasted too long. In addition, when Tylose® gel was applied in combination with the IMAT heater, the introduction of moisture and heat was likely to be carried out unevenly due to the ununiformed temperature distribution of the Tylose® gel (Fig. 5.14 d). The mobility of water inside the gel and the rate of moisture introduction into the paper and adhesive could be significantly affected by the temperature variable. Therefore, a pre-heating of the Tylose® gel and a regular control of the shape and thickness of the gel were recommended in order to maximally avoid overheated areas and unreasonable rate of moisture introduction.

- A Tylose® MH 30000 gel sandwich was relatively easy to be arranged to humidify a mend glued in the spine fold of a bound volume.

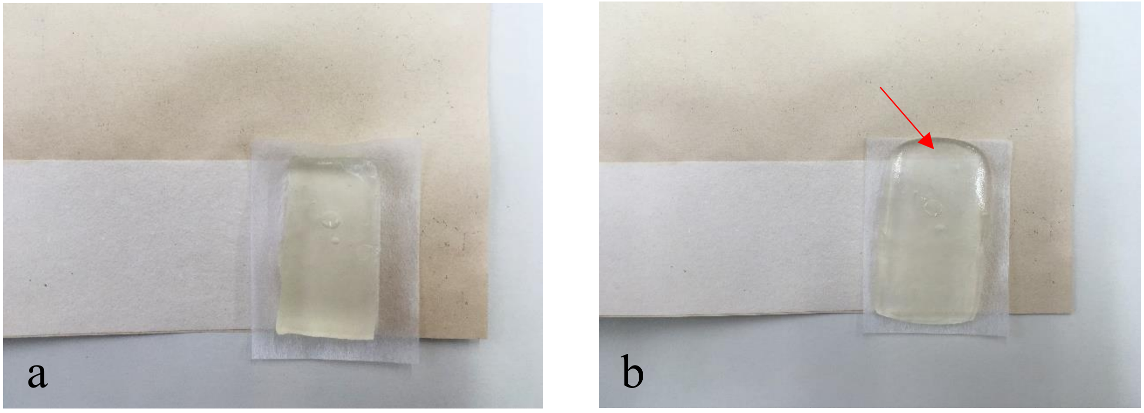


Fig. 5.32: Detachment of the mending paper on a mock-up carried out with a Tylose® gel sandwich under 40 °C condition. At the beginning (a) the gel was cut into the shape with the same width as the mend had. After a 30-minutes treatment (b), however, the gel flowed laterally out of the boundary of the mend (see the red arrow), which is pretty risky when the area would be water sensitive or covered with adhesive which was preciously oozed out of the boundary.

3) Agarose and gellan gel sandwich

The feasibility and efficacy of using a 2mm thick agarose gel and 2mm thick gellan gel were similar due to their comparable chemical structure and physical properties, which are therefore summarized together as following:

- The duration of detaching a mending paper was accelerated through heat application. Without a heat application, the protein-based adhesive could not swell adequately after a 60-minutes treatment. With an input of thermal energy, the duration of the treatment lasted 5-30 minutes depending on different target temperatures, different mending papers, different types of glues, different gels concentration and whether Rayon paper was applied.

- The rigidity of agarose gel and gellan gel also provided both pros and cons on their working feasibility: On the one hand, a target humidification can be conducted fairly precisely as the shape of agarose and gellan gel could remain stable due to their restricted lateral flow. The shape of the gel only shrank slightly after a period of time due to syneresis (Fig. 5.33). The gel could be cut into the shape with the same width as the mending paper had, which showed almost no risk of direct contact with the paper substrate. On the other hand, however, the stiffness of both gels, especially when they were prepared in a concentration higher than 4 wt% and in combination with a barrier paper, could not always promise an ideal contact between the gel and the mending paper (Fig. 5.34). This could result in an uneven introduction of moisture. Extra application of weight such as sand bags on the top of the sandwich could optimize the contact, while one should bear three issues in mind:

  a) Heat loss though the sand bag during the treatment should be prevented. This could be achieved by placing a sheet of polyester wadding or a sheet of relatively thick and flexible polyester non-woven fabric between the mat and sand bag (Fig. 5.35). Compared to a normal silicone sheet, the polyester wadding or the polyester non-woven fabric showed a better heat-isolation effect while possessing more softness and flexibility, through which a better contact between the sand bag, the gel and the mending paper could be realized. Additionally, the polyester wadding could be expediently cut into a desirable shape for each specific circumstance.

b) Agarose gel or gellan gel should not be cut into a large piece. A satisfactory contact between the gel and the mending paper could always be achieved more easily when gel was cut into a rather small piece. A sand bag could still be futile when a piece of gel was applied to an irregular and strongly distorted surface. An optimal size of the gel should better be individually determined and tested under each specific circumstance.

c) Rate of moisture introduction of each gel prepared in a certain concentration should be reconsidered since the external weight could enhance the risk of tideline formation as well as a penetration of adhesive, especially when thermal energy was introduced. It was necessary to find a balance between "enough weighting" and "excessive weighting" during the treatment.

- Once an ideal contact was achieved, introduction of moisture and thermal energy could be carried out uniformly. Yet the weight on the sandwich should be relatively uniformly distributed throughout the treated area, partially over-pressed area should be averted. Besides, the moisture absorption of the mending paper and the adhesive layer was not always identical either. Areas, where the mending paper or its sizing was stronger degraded as well as where the adhesive layer was applied thinner, could absorb moisture more rapidly.

- A 2 mm thick agarose or gellan gel sandwich could easily be arranged to humidify a mend glued in the spine fold of a bound volume.

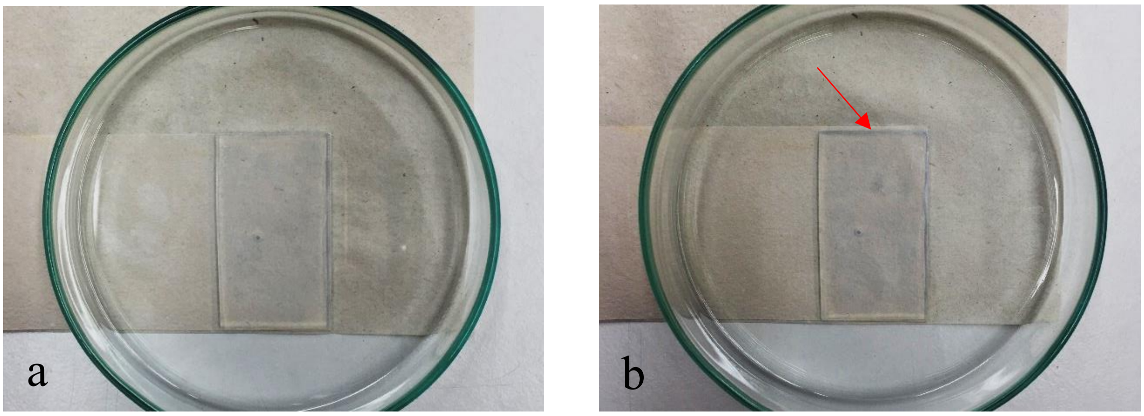


Fig. 5.33: Detachment of the mending paper on a mock-up carried out with an agarose gel sandwich. At the beginning (a) the gel was cut into the shape with the same width as the mending paper had. After a 30-minutes humidification (b), the gel shrank circa 1mm due to syneresis (see the red arrow).

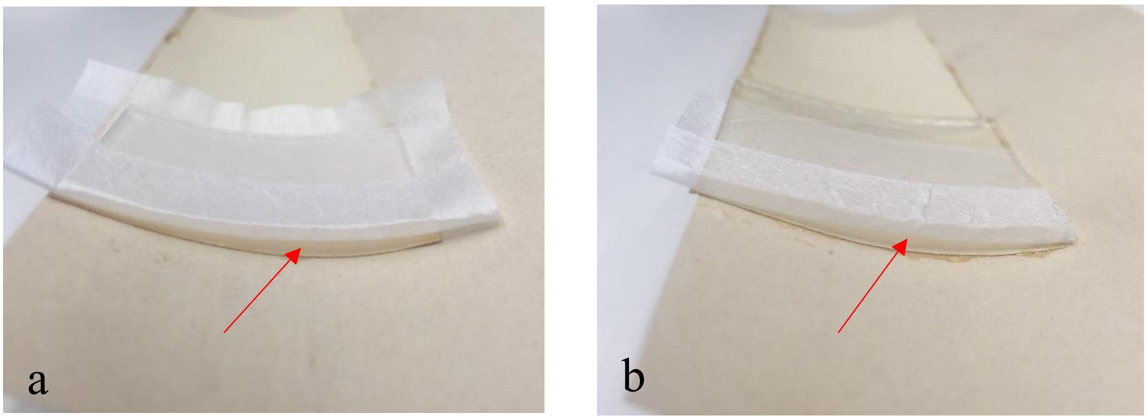


Fig. 5.34: Application of a 2mm thick agarose gel (a) and of a 2mm thick gellan gel (b) with Rayon paper on the mock-ups. Both gels were prepared in 5 wt%. The contacts between the gel and the mending papers were poor due to the distortion of the mock-ups and the stiffness of the gel.

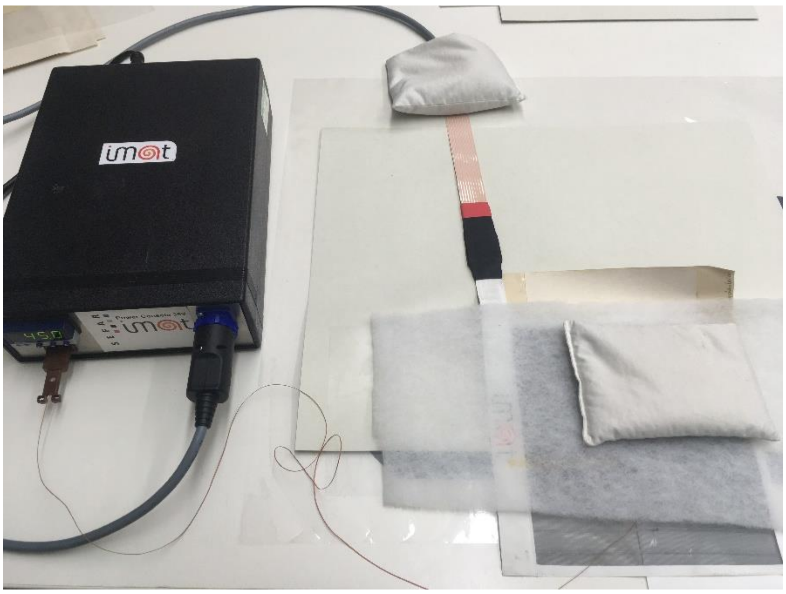


Fig. 5.35: Application of a sheet of polyester wadding between the mat and sand bag during the treatment using an agarose/gellan gel sandwich.

6 Applications on Originals

6.1 Detaching Old Mends Glued in the Spine Fold of a Manuscript from the 15th Century (Munich, Bavarian State Library, Clm 18199)

6.1.1 Description of the Work and the Damages Caused by the Old Mending

The Latin manuscript (Munich, Bavarian State Library, Clm 18199) is an anthology with a title of "Tractatus de volutione rotarum. Eusebius Pamphilus de evangelica praeparatione a Georgio Trapezuntio traductus. Epistola una ex omnibus epistolis B. Pauli compilate per Dionysium Carthusiensis ord. Commendatio uitae solitaries. Vicentini ord. praed. libri de uenatione diuini amoris" (Halm et al., 1878, p. 142). The manuscript was written in the 15th century on paper with hand-colored illustrations. The text block was bound in wood boards covered with alum tanned sheep leather (Fig. 6.1), which was partly scratched and rubbed. The bosses and fastenings were missing.

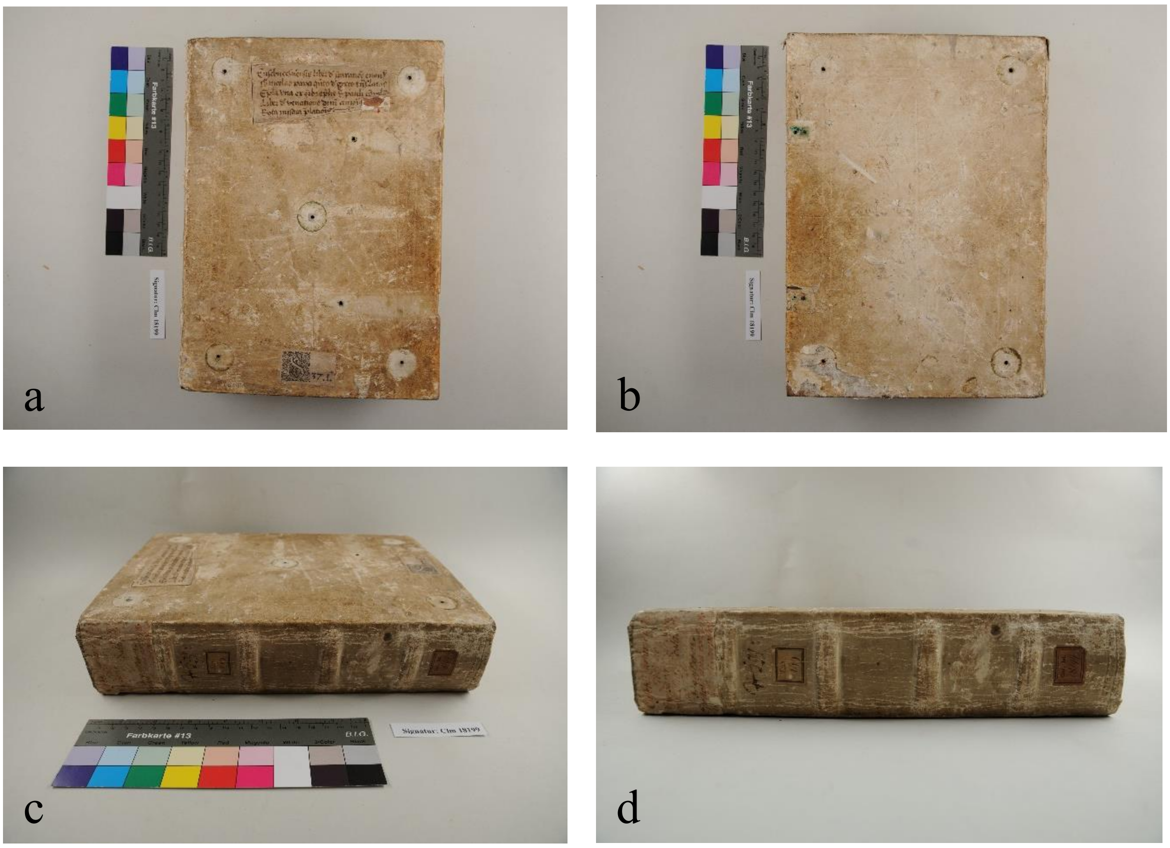


Fig. 6.1: Condition of the medieval manuscript (BSB, Clm 18199): front board (a), back board (b) and spine (c, d).

Old mends in the spine fold of the first section were found, whose adhesive was identified as protein-based glue. Due to the shrinkage, stiffness and inflexibility of the aged glue, heavy distortions appeared on several pages (Fig. 6.2 a, b). The inner fold of the section was partly torn. Additionally, some mending papers also covered part of the illustrations. Therefore, a detachment of the old mends was decided.

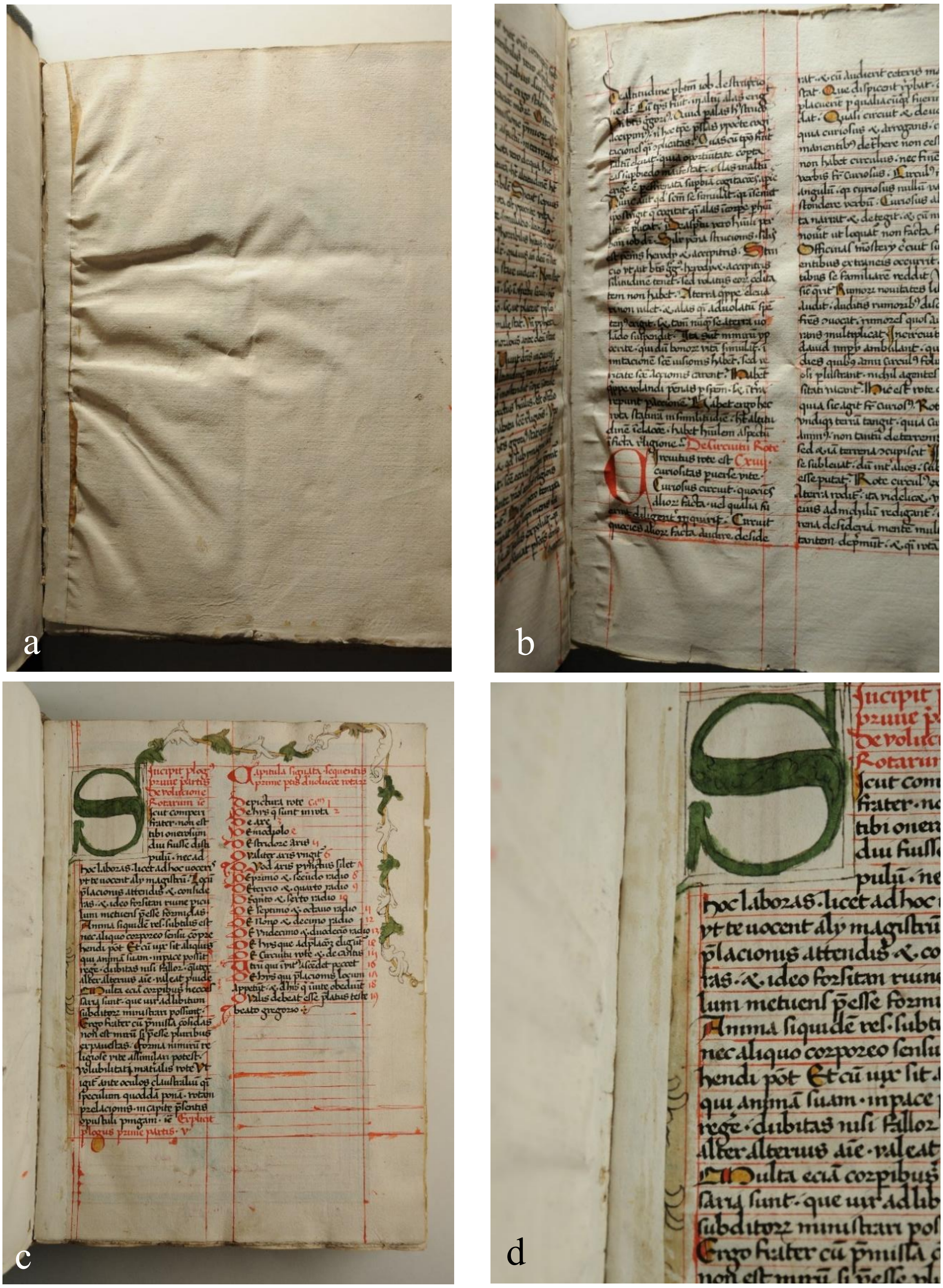


Fig. 6.2: Detail photos of the medieval manuscript (BSB, Clm 18199). Heavy distortions on page 0r (a) and page 8r (b) caused by the shrinkage of the mending glue. The illustration on page 1r is covered by an old mending paper strip glued to the spine of the first section of the manuscript (c, d).

6.1.2 Conservation Concept

After a preliminary test, it was determined that a heat transfer could optimize on the removal of the old mends in the manuscript. A temperature condition at 40 °C showed a satisfactory result. Based on this knowledge, a conservation concept was established:

1) Selection of humidification sandwich:
   Since the mends were glued in the spine fold, a gel sandwich was chosen.
   Since some of the mending papers were also glued right beside some illustrations as well as some text written with red ink, which were extremely sensitive to moisture, agarose gel was selected due to its restricted lateral flow. It was prepared in the concentration of 4 wt% and casted in 2mm. A sheet of Rayon paper was also applied to generate a more uniform moisture introduction and to minimize the possible existence of agarose residue on the mending paper.

2) Selection of mat and temperature:
   Since the mending papers were glued in the spine fold, an IMAT mat, which could be heated up till the edges, was demanded. Therefore, the small, breathable but not transparent mat was selected. The temperature was set at 40 °C.

3) The arrangement of the sandwich was presented in Fig. 6.3

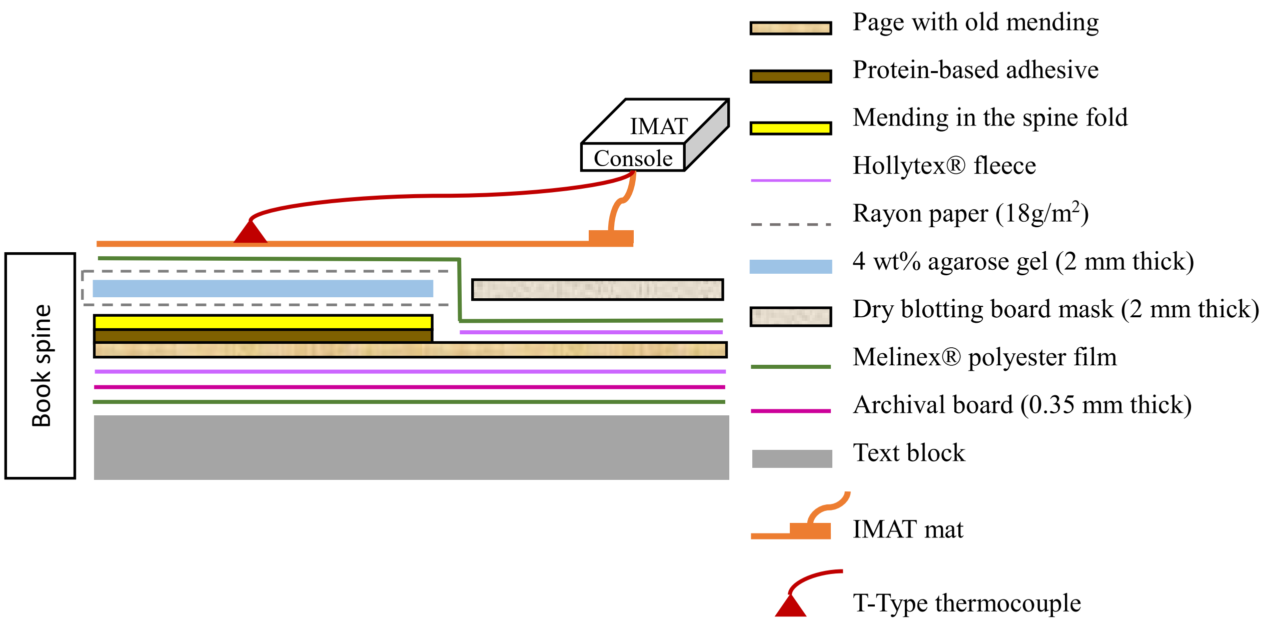


Fig. 6.3: Schematic diagram of the humidification sandwich with heat transfer for the detachment of the old mending papers in the medieval manuscript (BSB, Clm 18199).

6.1.3 Conservation Treatment

1) Surface cleaning of the edges and margins of the pages was firstly conducted by a natural rubber sponge to remove loose dust and dirt. Tears and cracks on the edges and corners

were rejoined and reinforced by the thin Japanese paper Gossamer Tissue (2 g/m^2) and wheat starch paste.

2) 4 wt% agarose gel was casted in 2mm thick and cut into a rectangle shape with the same width as the mending papers and a length of 2 cm. The humidification sandwich combined with heat transfer was arranged according to the demonstration shown in Fig 6.3. The adhesive layer could swell after treated for 3-5 minutes, the mending papers could be removed by a microspatula piece by piece (Fig. 6.4).

3) The old mending papers were successfully detached from the pages. The residues of the proteinaceous glue could be further cautiously reduced with Tylose® MH 300 gel in 7 wt% concentration. After the treatment, the tension of the area was considerably reduced, and the distortions on the pages were minimized. The previously concealed illustration was revealed (Fig. 6.5). The tears in the spine area of the section could be rejoined and reinforced with Japanese paper and wheat starch paste.

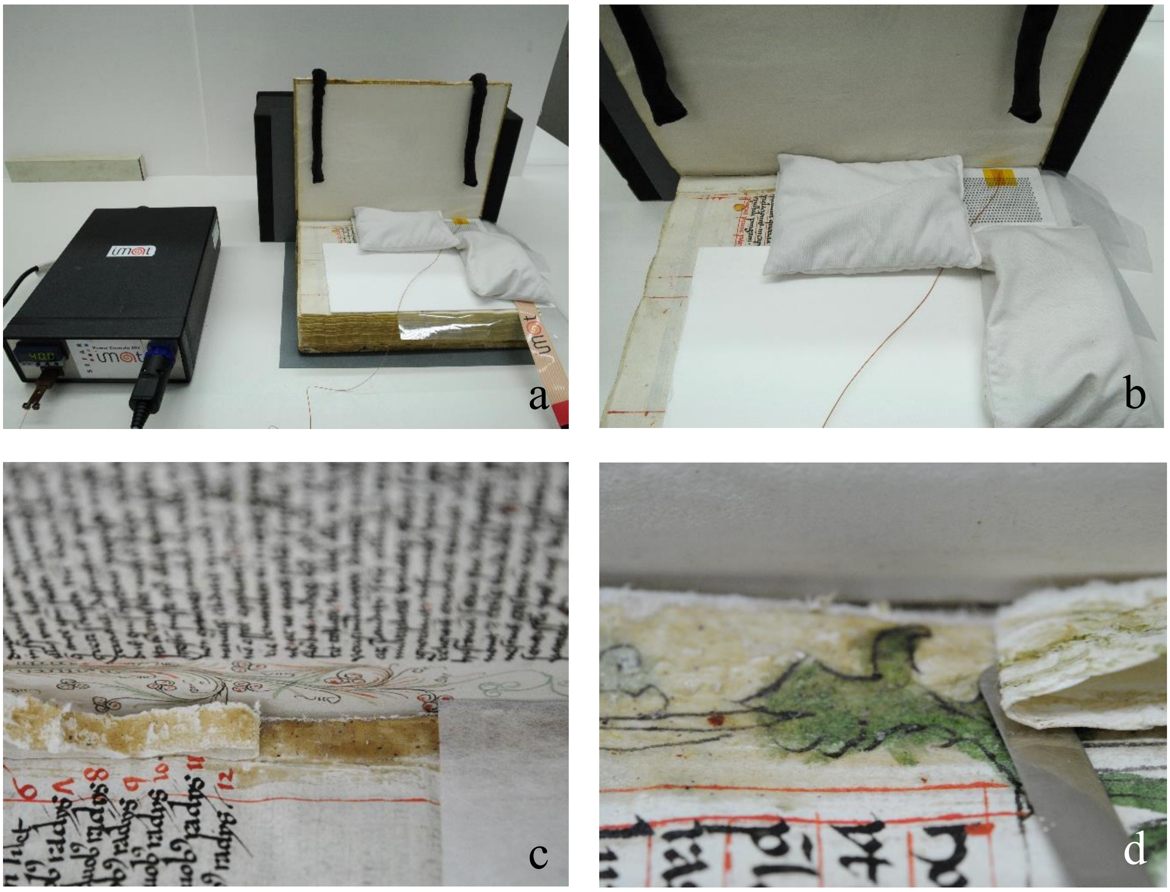


Fig. 6.4: Images during the conservation treatment on the medieval manuscript (BSB, Clm 18199). The humidification sandwich combined with heat transfer through the IMAT prototype was arranged (a, b). After several minutes of treatment, the protein-based adhesive could swell and the mending paper could be detached by a microspatula (c, d). The hand-colored illustration which had been covered by the mending paper could be exposed (d).

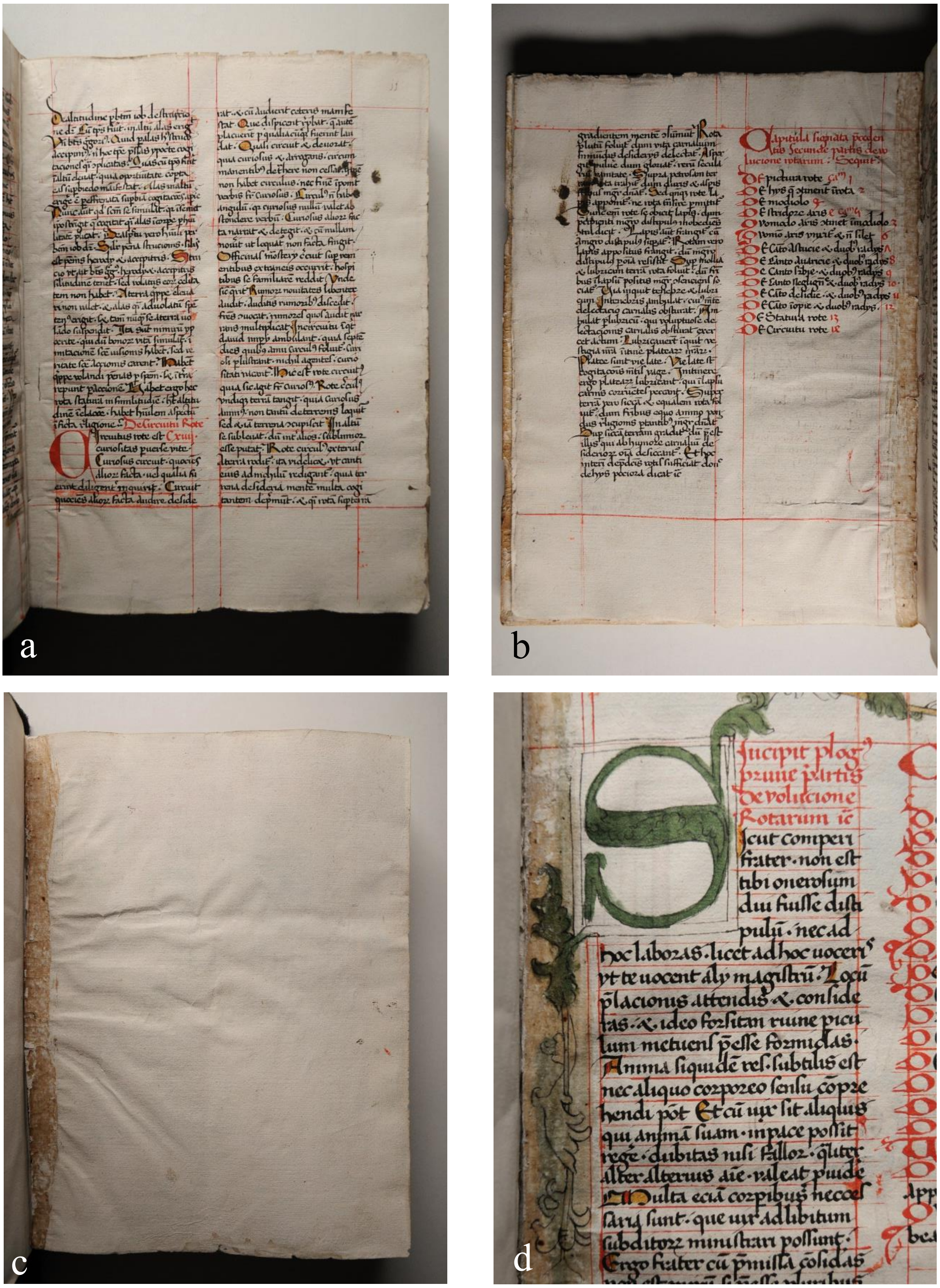


Fig. 6.5: Pages (BSB, Clm 18199) after the conservation treatment. The old mending papers were successfully removed. Distortions and tensions on page 0r (c) and page 8r (b) and 8v (c) caused by the shrinkage of the glue were reduced. The illustration on page 1r was revealed (d).

6.2 Possible Applications for Other Goals in Book and Paper Conservation

Since the application of the IMAT heater for the removal of old mending in bound manuscripts and rare books presented a satisfactory temperature-related optimization, this innovative heat transfer method is considered to be able to apply in other conservation cases. In this chapter, two possible applications for achieving other goals in book and paper conservation are presented.

6.2.1 Detaching the Old Backing from a Woodcut Map of Venice in the *Peregrinatio in Terram Sanctam* (Munich, Bavarian State Library, 2 Inc.c.a. 1726 a)

6.2.1.1 Description of the Work and the Damages Caused by the Old Backing

The *Peregrinatio in Terram Sanctam* is an incunable account of a pilgrimage to Jerusalem undertaken by the canon of Mainz Cathedral Bernhard von Breydenbach and the artist Erhard Reuwich together with other companions in the year of 1483 to 1484. It was published under the name of Breydenbach in 1486 with the illustrations drawn by Reuwich, which was also the first printed illustrated travel-book. The book was widely spread followed by numerous reprints and was translated into several languages in the 15th century. The German translation from Latin was carried out by Martin Roth using the manuscript records of Paul Walther von Guglingen. The book featured several large fold-out woodcut panoramas of cities in Europe including Venice and Modon as well as a map of Jerusalem, Palestine and Egypt. Reuwich's views served as models for depictions in the Nuremberg Chronicle (Hertrich, 1991). This copy (BSB, 2 Inc.c.a. 1726 a) was printed on paper and bound in wooden boards covered with brown vegetable tanned sheep leather decorated with blind tooling, which was torn at the joint of the book spine. The leather was partly scratched, rubbed and darkened. The bosses and fastenings were missing (Fig. 6.6).

One of the fold-out woodcut panoramas in the incunable – the woodcut map of Venice (Fig. 6.7 a) – was backed with two papers (Fig. 6.7 b). Several missing areas, splits and tears were found on the original map, which was reinforced by the first backing – a waste paper whose text side was glued to the back of the map (Fig. 6.8 a, b). During the previous application of glue, however, the glue had already penetrated into the map surface in many places, where dark yellow, transparent stains were presented (see red arrow in Fig. 6.8 c). This backing was later reinforced once more with a grey-colored paper. Some tears and cracks appeared in the folds (see red arrow in Fig. 6.8 d). Due to the aging of the glue, the whole map became stiff and already lost its flexibility. New tears appeared on the edges and the fold areas of the map (see blue arrow in Fig. 6.8 c). In addition, the yellowed glue and the text from the first backing also interfered with the integrity and the appearance of the map. Therefore, a detachment of the backings was required.

Fig. 6.6: Condition of the incunable (BSB, 2 Inc.c.a. 1726 a): front board (a), back broad (b), and spine (c, d).

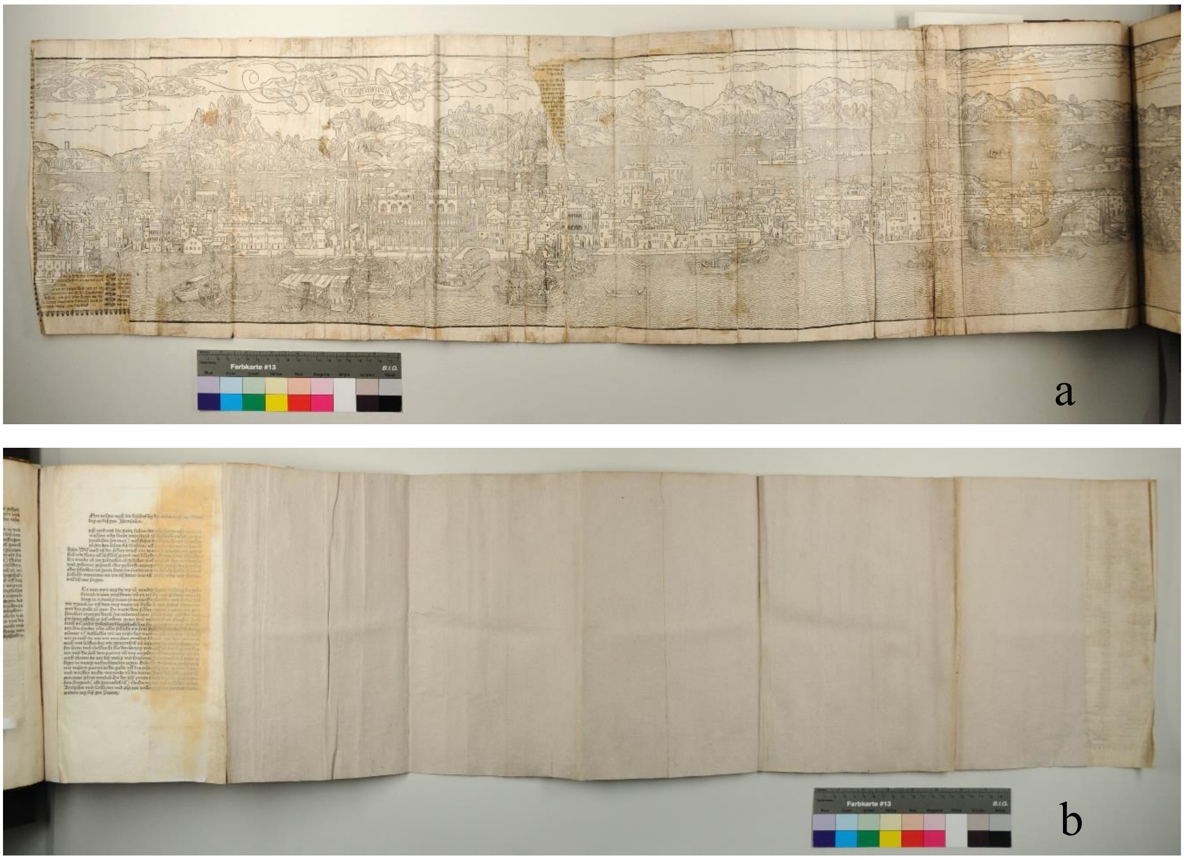


Fig. 6.7: The woodcut map of Venice folded out of the incunable (BSB, 2 Inc.c.a. 1726 a): Condition of the front page (a), condition of the two backings on the back page of the map (b).

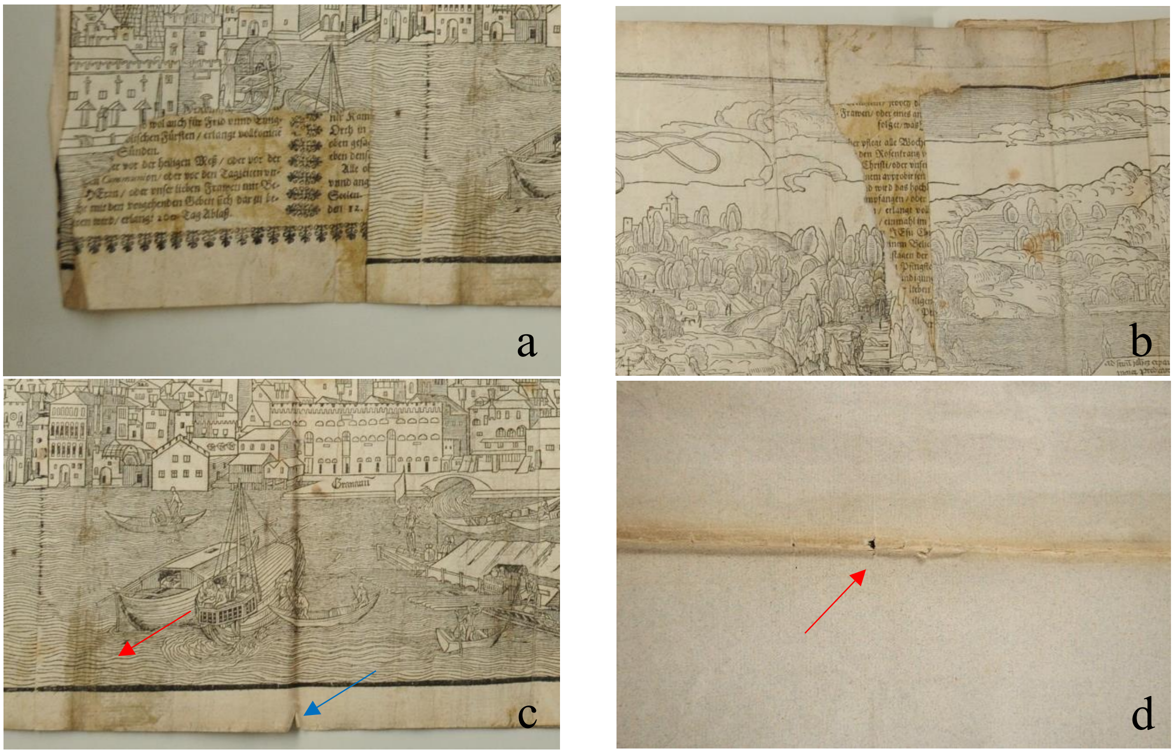


Fig. 6.8: Detail photos of the woodcut map of Venice (BSB, 2 Inc.c.a. 1726 a). Several missing areas and splits on the map were reinforced by the first backing (a, b). Dark yellow, transparent stains were presented where glue had already penetrated through the map, with new tears in the folds (c, d).

6.2.1.2 Conservation concept

After a preliminary test, it was determined that the first backing was glued with proteinaceous adhesive, while the second backing was glued with a starch-based paste. Therefore, a separate removal of the two backings was considered as the first choice. However, the ability of water absorption of the starch-based paste was not satisfactory. In order to avoid a long-term humidification, which could increase the risk of further penetration of glue through the map, the two backings were decided to be detached simultaneously by combining moisture introduction with input of thermal energy. Based on this knowledge, a conservation concept was established:

1) Selection of humidification sandwich:
   After testing agarose gel and Gore-Tex sandwich, the latter was selected for the detachment of the backings: The humidification through a Gore-Tex sandwich combined with heat transfer was in this case more even due to the large size and high stiffness of the backings. However, as discussed in Chapter 5.2.3.2, the ability of moisture absorption of the paper could not always be evenly distributed throughout the whole area. In order to keep the treated area under control, the humidification and heat application were still carried out in a rather narrow area, where the backings could be removed piece by piece. An overall humidification of the whole map was considered to be too risky.

2) Selection of mat and temperature:
   Since the width of the backings was circa 30 cm, the small mat and the meshed mat could not cover the target area. Therefore, the large, transparent mat was selected. The temperature was set to 40 °C.

3) The arrangement of the sandwich was presented in Fig. 6.9

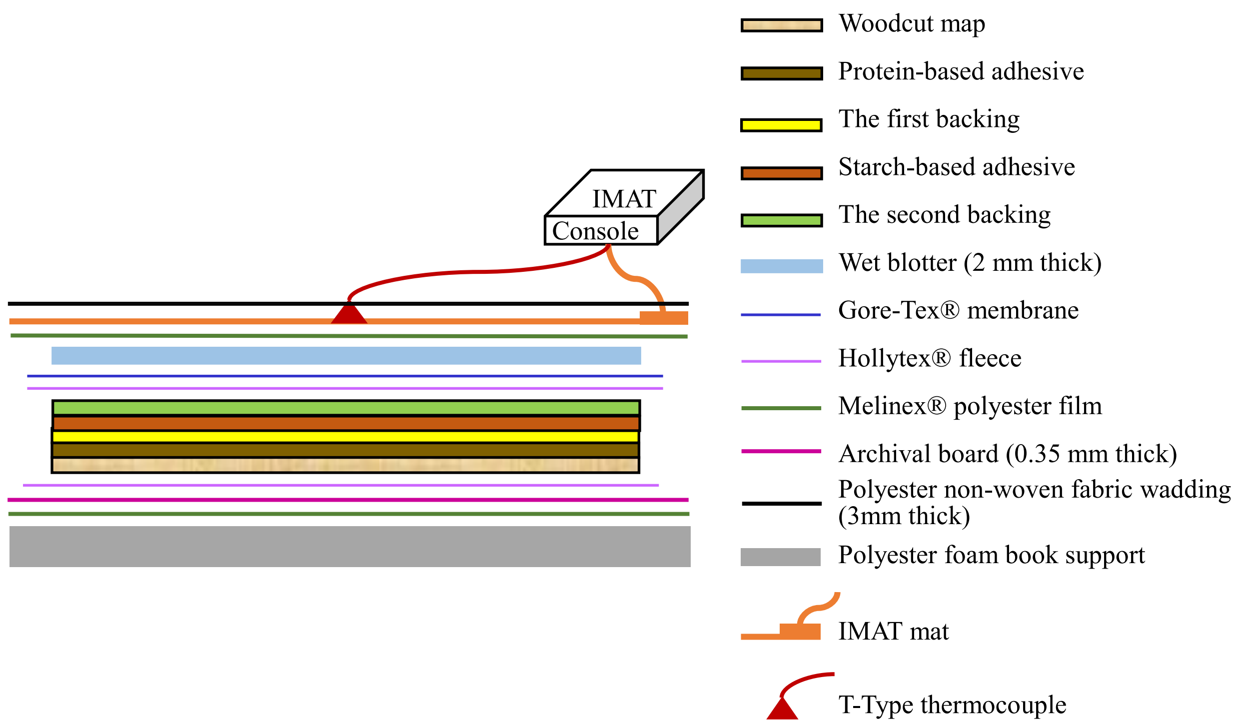


Fig. 6.9: Schematic diagram of the humidification sandwich with heat transfer for the detachment of the backings from the woodcut map of Venice (BSB, 2 Inc.c.a. 1726 a).

6.2.1.3 Conservation Treatment

1) Surface cleaning of the edges and margins of the pages was firstly conducted by a natural rubber sponge to remove loose dust and dirt.

2) Blotting board with a thickness of 2 mm was cut into a rectangle shape, whose length was the same as the width of the backing; width was circa 10 cm (Fig. 6.10 a). The humidification sandwich combined with heat transfer was arranged according to the demonstration shown in Fig 6.9. Since the treated area was quite narrow (Fig. 6.10 b) and the size of the mat was much larger, sand bags were placed direct onto the area where the mat had contact only to the polyester foam book support and air to avoid the mat from being partially overheated. Two sand bags were also placed onto sandwich to ensure an ideal contact between the mat and the Gore-Tex sandwich throughout the whole treated area (Fig. 6.10 c). A sheet of polyester non-woven wadding was placed in between to prevent heat loss.

3) The adhesive layer could swell after treating for circa 20 minutes, and the mending could

be readily removed piece by piece (Fig. 6.10 d) without damages on the fibers of the map and a further penetration of glue into the map (Fig. 6.11).

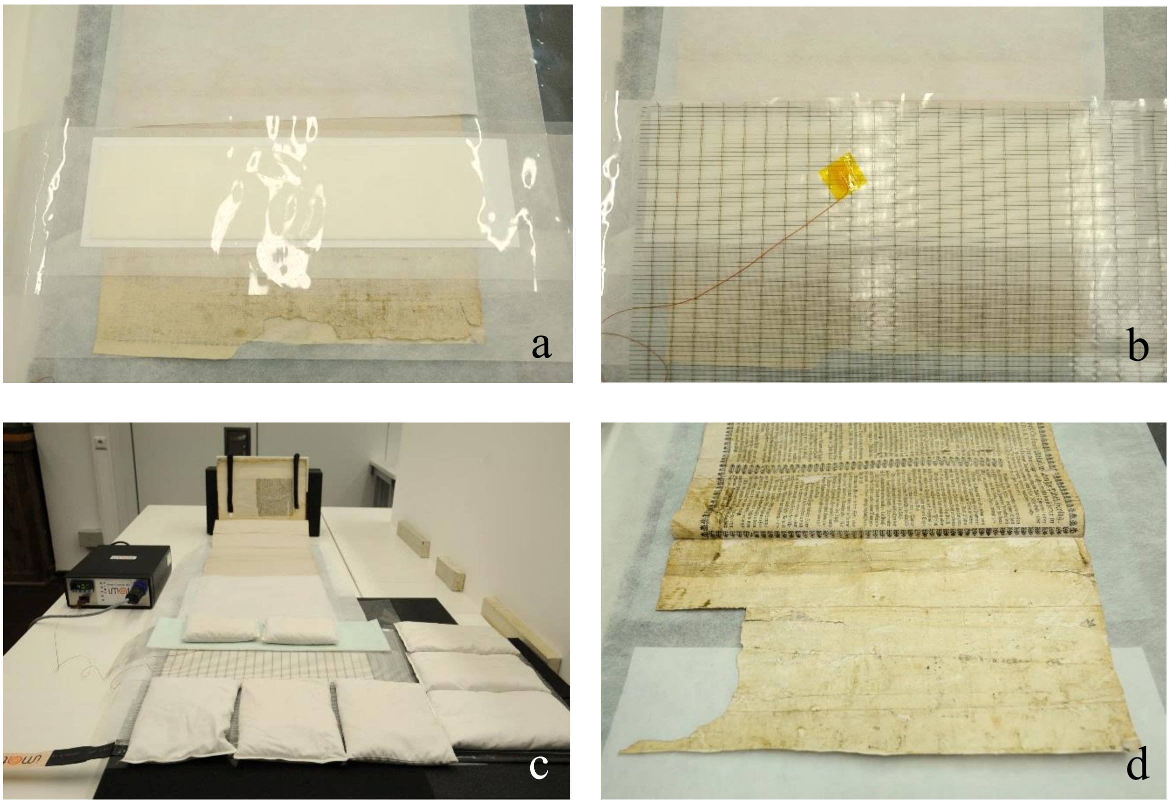


Fig. 6.10: Images during the conservation treatment (BSB, 2 Inc.c.a. 1726 a). A Gore-Tex sandwich was arranged (a), a large, transparent mat was placed onto the sandwich (b). Two sand bags were placed onto the sandwich with a polyester non-woven fabric in between; other sand bags were placed directly onto the mat (c). The backings were successfully detached (d).

Fig. 6.11: The front side of the map after detaching part of the backings (BSB, 2 Inc.c.a. 1726 a).

6.2.2 Detaching the Paper Cover from the Text Block of a Dissertation Printed in 1780 (Munich, Bavarian State Library, Diss. 849 d,16)

6.2.2.1 Description of the Work and the Damages on the Spine

The dissertation (Munich, Bavarian State Library, Diss. 849 d,16) with a title of "Dissertatio de aestimanda perfectione machinarum ad mechanicam solidorum pertinentium" was authored by Franz Seraphin von Zallinger zum Thurn and published in the year of 1780 (Zallinger zum Thurn & Hallerstein, 1780). The book was printed on paper, with some fold-out technical drawings. The spine of the text block was directly glued to a light-colored paper cover, which is a patterned paste paper, with a protein-based adhesive (Fig. 6.12).

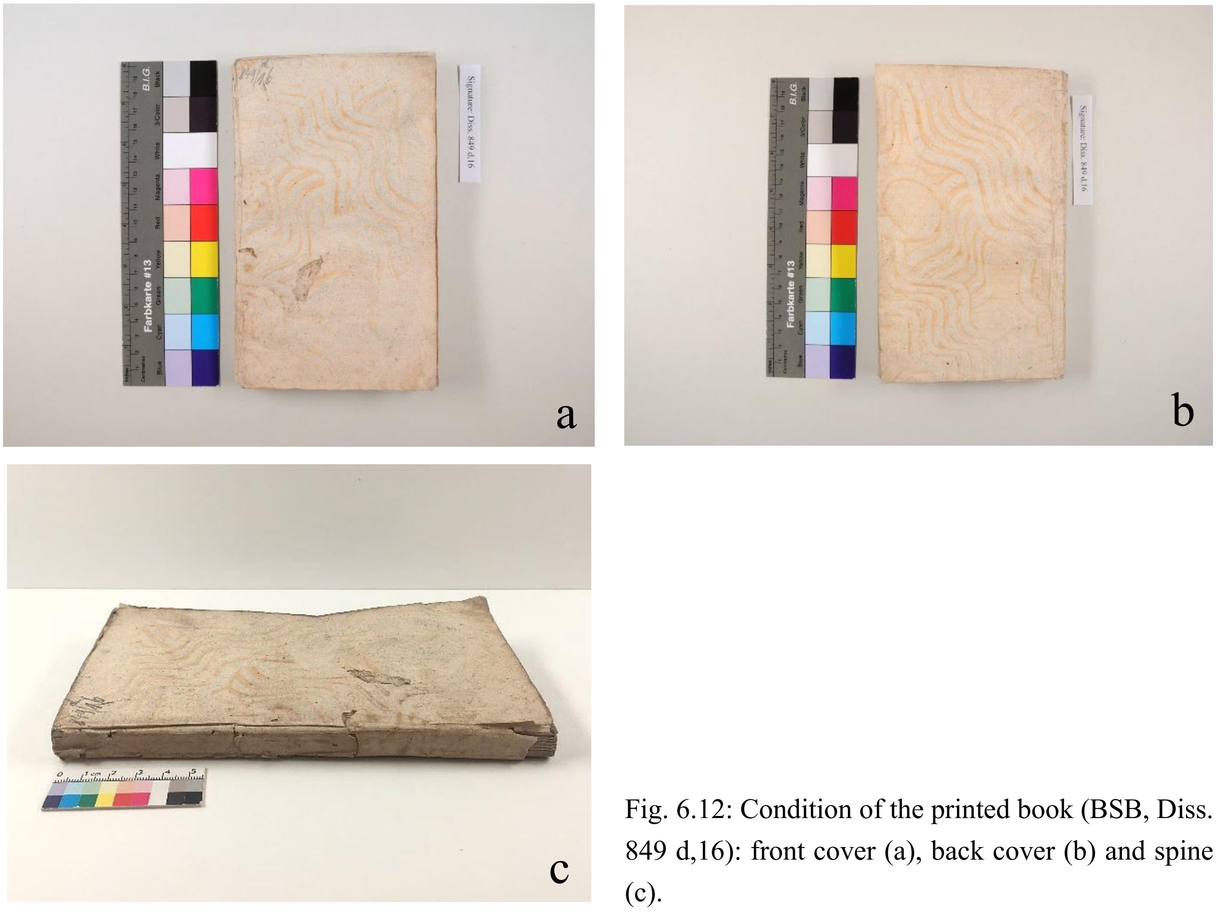


Fig. 6.12: Condition of the printed book (BSB, Diss. 849 d,16): front cover (a), back cover (b) and spine (c).

The cover on the spine was partly torn and split. Several missing parts were found at the head and foot as well as the joint of the spine (Fig. 6.13 a). The cover was partial detached from the text block (see red arrow in Fig. 6.13 b). Besides, several sections were also missing, because of which the spine was weakened and the book cover could be potentially damaged to a further extent. In order to solve the problem, it was decided that the paste paper cover should be completely detached from the text block before further conservation treatments were conducted.

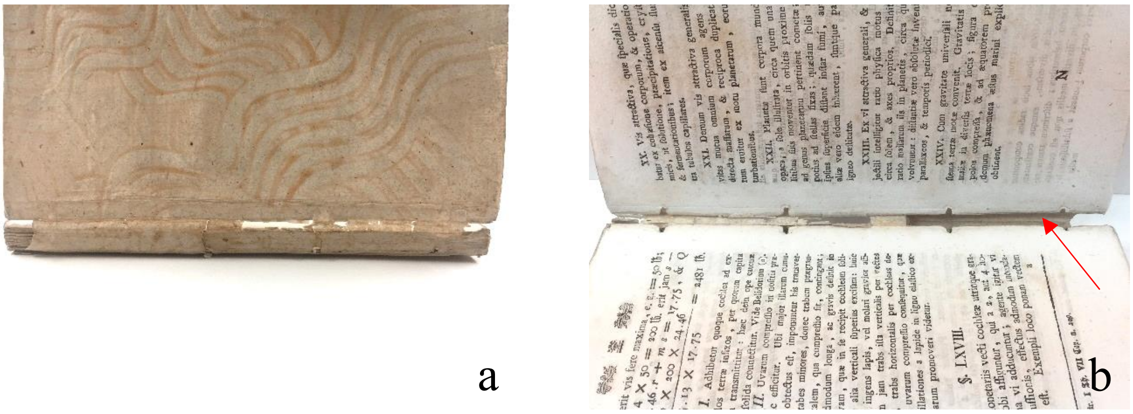


Fig. 6.13: Images of the damages on the spine (BSB, Diss. 849 d,16).

6.2.2.2 Conservation Concept

After a preliminary test, it was determined that a heat transfer could optimize the detachment of the cover from the text block. A temperature condition of 42 °C showed a satisfactory result. Based on this knowledge, a conservation concept was established:

1) Selection of humidification sandwich, mat and temperature
   Since the spine of the book was irregular and uneven, a Tylose® MH 30000 gel sandwich was selected in order to better conform the surface. The small mat was applied for the treatment, by which the temperature was set to 42 °C.

2) The arrangement of the sandwich was presented in Fig. 6.14

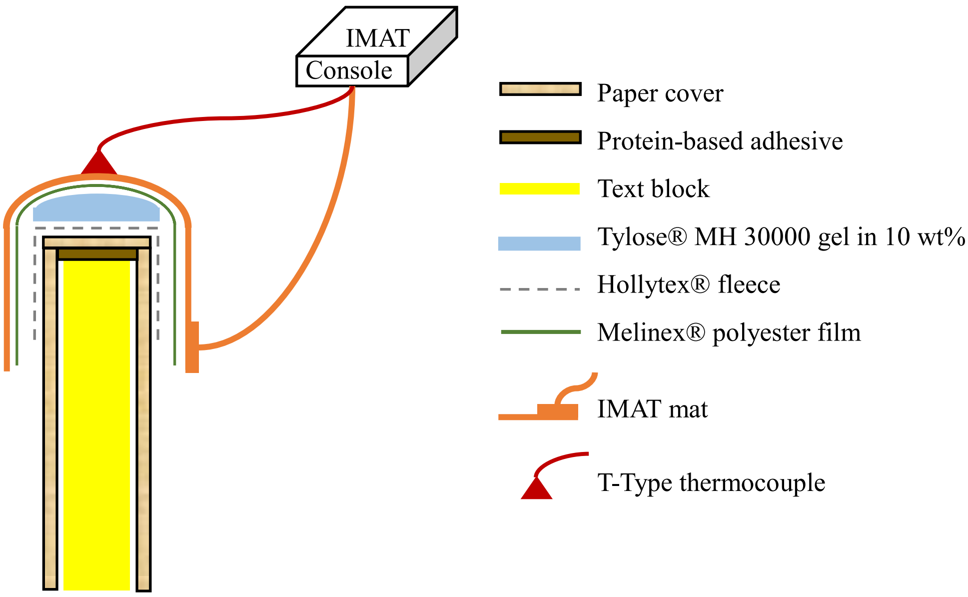


Fig. 6.14: Schematic diagram of the humidification sandwich with heat transfer for the detachment of the paste paper cover from the text block (BSB, Diss. 849 d,16).

6.2.2.3 Conservation Treatment

1) Surface cleaning of the paste paper cover was firstly conducted by a natural rubber sponge to remove loose dust and dirt. Tears and cracks on the edges and corners of the page were joined and reinforced by the thin Japanese paper Gossamer Tissue (2 g/m^2), RK-00 (3.6 g/m^2) and wheat starch paste.

2) Tylose® MH 30000 gel was cut into a cube shape, whose width is the same as the width of the spine, and whose length and thickness were circa 3 cm and circa 3 mm respectively. It was first pre-heated with the mat. The shape of the gel was generated again after the pre-heating, and the humidification sandwich combined with heat transfer was arranged according to the demonstration shown in Fig 6.14. Two lead snakes were placed right beside the Tylose® gel to make sure an ideal contact (Fig. 6.15).

3) The adhesive layer could swell after treating for circa 10 minutes, and the paper cover could be readily removed from the spine of text block piece by piece. The tears on the over were then rejoined, and the unstable areas were reinforced using by the thin Japanese papers Berliner Tissue (2 g/m^2) and RK-00 (3.6 g/m^2) as well as wheat starch paste. The photo after the treatment is shown in Fig. 6.16.

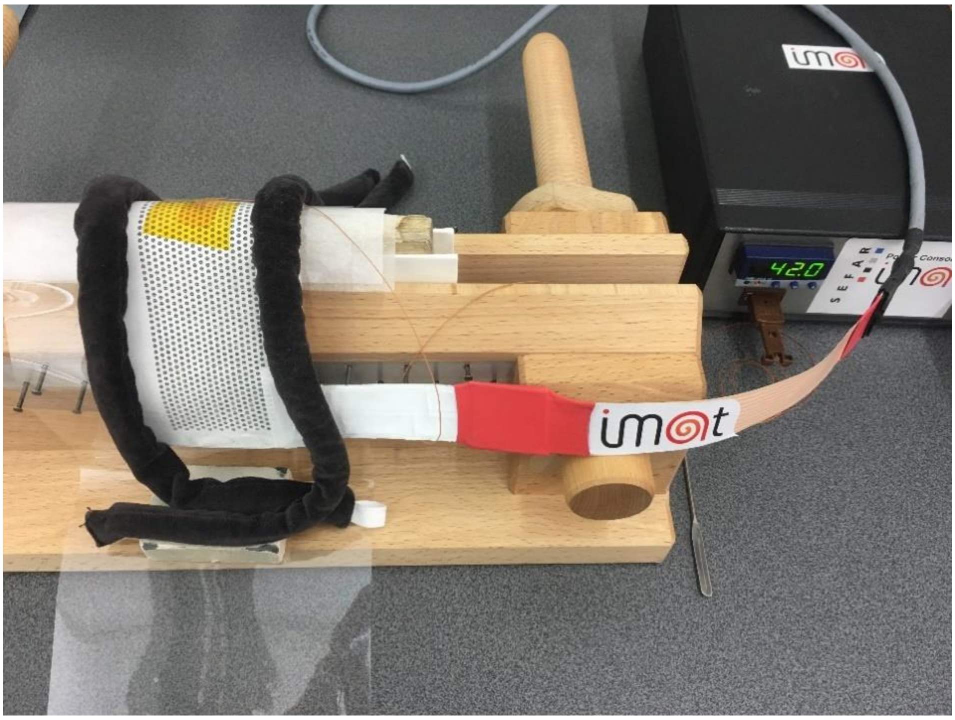


Fig. 6.15: Images during the conservation treatment on the spine (BSB, Diss. 849 d,16).

Fig. 6.16: After detaching of the paper cover from the text block (BSB, Diss. 849 d,16).

7 Conclusions and Outlook of Further Researches

In this study, a considerable temperature-related optimization on the removal of old mends glued with protein-based adhesives in bound manuscripts and rare books utilizing the IMAT heater is verified. An optimal working pattern of combining heat transfer with moisture introduction using the IMAT heater and various humidification sandwiches is suggested for the future conservation work. Besides, performance of each treatment variation correlated with different humidification sandwiches and treating temperatures is characterized. Finally, conservation treatments on three historical documents from the collections of the Bavarian State Library are successfully conducted: a medieval manuscript (BSB, Clm 18199), an incunable from the early years of printing (BSB, 2 Inc.ca 1726 a) and a printed book from the 18th century (BSB, Diss. 849 d, 16).

This chapter summarizes all the significant conclusions drawn in this study, followed by a suggested working procedure for dealing with old mending in the future conservation work and an outlook of future researches.

7.1 Suggested Working Pattern Combining Heat and Moisture

7.1.1 The Arrangement of the Humidification Sandwiches with Heat Transfer

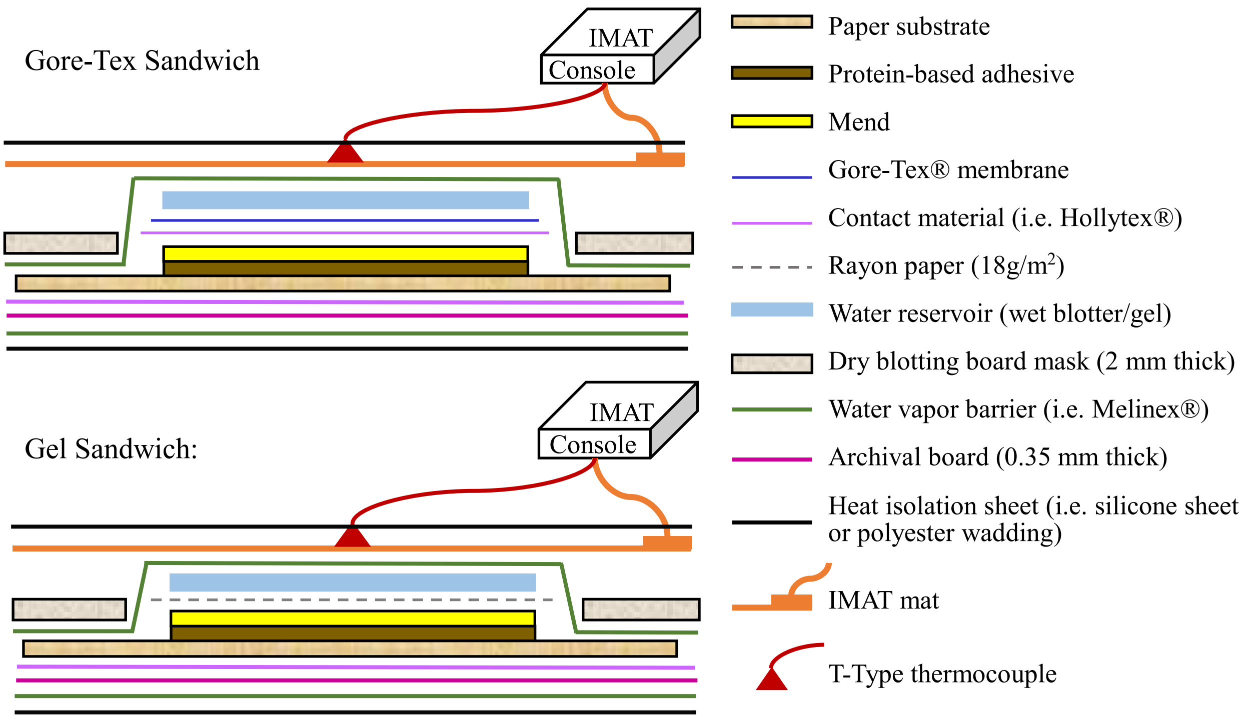


Fig. 7.1 Schematic diagrams of the arrangement of humidification sandwich with heat transfer.

- Description of the sandwiches:

a) Principle: Thermal energy travels through the water reservoir and heats the water inside. Mend is humidified with warm water or warm water vapor.

b) Direction of heat transfer: from top to bottom

c) Direction of moisture migration: from top to bottom

d) Function of the Rayon paper: It prevents the object to a certain extent from having direct contact with gel or liquid water as long as the barrier paper has not been thoroughly saturated with water. Besides, it also generates a slower and more uniform moisture introduction.

e) Function of the dry blotting board mask: During a heating process, part of the mat has no contact with the humidification sandwich, so they can be overheated since the heat capacity of the water reservoir is much higher than that of the air or the paper substrate. A mask of the humidification sandwich made from a dry blotting board can absorb a considerable amount of thermal energy provided by the mat, which not only prevents some area of the paper substrate from being overheated but also protects the mat from being partly overheated beyond its limitation.

f) Function of the archival board: The saturation vapor pressure inside the sandwich is always higher than the saturation vapor pressure under room temperature. Water vapor travels through the paper substrate will condense at the surface of the polyester film due to a lower temperature. Therefore, it is necessary to place an archival board between the paper substrate and the polyester film to prevent the paper substrate from having direct contact with the condensation water.

g) Function of the heat isolation sheets: Heat loss can occur through the surroundings during a heating process. Two thin silicone sheets or polyester wadding placed on and under the sandwich can help to minimize the heat loss through the environment. When sand bags are placed on the sandwich, a sheet of polyester wadding or a sheet of relatively thick and flexible polyester non-woven fabric are recommended as heat isolator.

(Related chapters: 4.3; 5.2.3)

7.1.2 Creating a Heat Transfer Condition as Ideal as Possible

a) A conduction heat transfer should be ensured: In the case of using a Gore-Tex sandwich, air pocket between the mat, the polyester film and the blotting paper should be avoided; in the case of using a gel, air pocket between the mat, the polyester film, the gel, the barrier paper and the mending should be avoided.

b) The thermocouple should detect the temperature of the system – the humidification sandwich: Make sure the thermocouple is fixed on the area of the mat, where the water reservoir is placed below.

c) The heat loss and the thermal gradient inside the sandwich should be minimized: The material of each layer in the humidification sandwich should be as thermally conductive as possible; without affecting the humidification effect, the thickness and the heat capacity of each layer should be chosen or made as slight as possible.

d) The heat loss through the surroundings should be minimized through silicone sheets or polyester wadding, which is yet not always required, especially when the accessibility to the working area is limited.

(Related chapters: 3.2; 5.2.2)

7.1.3 Advantages of Using the IMAT Heater in Conservation Treatment

a) The heater is portable and mobile, which permits a heat application for a localized treatment of different target areas.

b) The slight thickness and high flexibility of the mat optimize the accessibility to the working area.

c) The heater features a fast-thermal response, a precisely controllable and steady heat regulation as well as a uniform heat distribution. Thermal energy can continuously flow into the system due to the electric energy provided by the IMAT console when heating with the IMAT mat. Thermal energy which is required to keep the temperature of the system at a certain degree can be obtained when heat transfer condition is ideally created, especially when a heat application is carried out in a long-term process.

d) The customized size from a few square centimeters to several square meters can be suitable for objects with various dimensions. The transparency or semi-transparency allows an accurate arrangement of the heating area and visual monitoring of the treatment process. The optional breathability offers a permeability to airflow or water vapors when it is demanded.

(Related chapters: 3.1; 5.2.3.2)

7.1.4 Problems need to be improved

The heating performance of the mats shown in this study are partly acceptable since these prototypes are not final products, which were not designed and produced with high resilience from the beginning. Once this IMAT heater becomes commercially available, the manufacturer should pay high attention to the durability, the aging resistance as well as the insolation of the mat. It would be much more practical and safer if conservators are able to notice as soon as possible when an error inside the mat occurs. Additionally, a regular maintenance for the mat may also be required.

(Related chapters: 5.2.1)

7.2 General Temperature-related Influence on the Protein-based Adhesives

a) Input of thermal energy can enhance the swelling degree of glue by accelerating its loosening entangled molecular network during an introduction of moisture. When too much moisture was applied, or when the temperature reached a certain degree, the swelled adhesive film could be liquified. The viscosity of the liquified glue decreases when temperature increases.

b) During the removal of old mending papers, a certain swelling degree of animal glue is required, which can be considerably benefited by an input of thermal energy through the IMAT heater.

c) An increased treating temperature can raise the risk of the penetration of glue into paper substrate during the treatment caused by the liquification of the glue and the decreased viscosity of the glue solution. A treating temperature over 45 °C is not recommended.

(Related chapters: 2.2; 5.2.3.2)

7.3 Comparison of Several Treatments under Different Temperature Conditions for Removing Old Mends Glued with Protein-based Adhesives

Table 7.1 Characterization of the preparation of different sandwich materials

Sandwich	***Preparation of the sandwich materials***
Gore-Tex sandwich	Blotting boards are easy to be prepared. e-PTFE Gore-Tex® membrane with no colorants is now almost not commercially available, but it can be replaced by Sympatex® or Polartec® NeoShell® membranes as alternative products.
Tylose® MH 30000	Preparation of Tylose® MH 30000 takes about 2 days, but it can be stored in a glass container in refrigerator for a long period of time once it is prepared. Risk of mold growth is low.
Agarose	Preparation of 2mm agarose gel is generally easy in all concentrations (2-6 wt%). But agarose gel should always be freshly made since the gel can only be kept in refrigerator for 3-4 days due to risk of mold growth.
Gellan gum	Preparation of 2mm gellan gel in concentration of 5 wt% is extremely unpractical due to its high viscosity and rapid gelling process. Preparation of 2mm gellan gel in concentration of 3-4 wt% is easier, but a continuous gel sheet is hard to casted due to its "snap-set" property. Gel in concentration of 2 wt% is easy to cast. Gellan gel should always be freshly made since the gel can only be kept in refrigerator for 3-4 days due to risk of mold growth.

(Related chapters: 4.2.2; 4.2.3)

Table 7.2 Characterization of the moisture introduction through different sandwiches

<table>
<tr><th>Sandwich</th><th>Performance of moisture introduction</th></tr>
<tr><td>Gore-Tex sandwich</td><td>With an increasing treating temperature, humidification process carried out by a Gore-Tex sandwich is accelerated.

The risk of tideline presence during a treatment with Gore-Tex sandwich with a treating temperature not more than 45 °C after 1 hour treating time is extremely low. Further increase of temperature and treating time can raise the risk of tideline formation.</td></tr>
<tr><td>Tylose® MH 30000</td><td rowspan="3">The rate of moisture introduction through hydrogels increases with a raised treating temperature, a decreased concentration of the gel as well as other applied forces such as the gravity (thickness) of the gel and external pressure.

When the treating temperature is not higher than 45 °C, the risk of tideline formation is very low when Tylose® MH 30000 gel in 10 wt% concentration is applied with and without Rayon paper. The risk will be amplified due to external pressure and further increase of temperature.

When the treating temperature is not higher than 45 °C, the risk of tideline formation is low when agarose gel prepared in 3-6 wt% concentration is applied with Rayon paper or in 5-6 wt% without Rayon paper; and when gellan gel in 3-5 wt% concentration is applied with Rayon paper. The risk will be amplified due to external pressure, increase of the thickness of the gel sheet and further increase of temperature.</td></tr>
<tr><td>Agarose</td></tr>
<tr><td>Gellan gum</td></tr>
</table>

(Related chapters: 5.2.3.1)

Table 7.3 Characterization of the thermal response and the working properties of different sandwiches

<table>
<tr><th>sandwich</th><th>Time to reach the thermal equilibrium</th><th>Working properties</th></tr>
<tr><td>Gore-Tex sandwich</td><td rowspan="4">Gore-Tex sandwich using blotter which is immersed in warm water bath before treatment <

Agarose/Gellan sandwich <

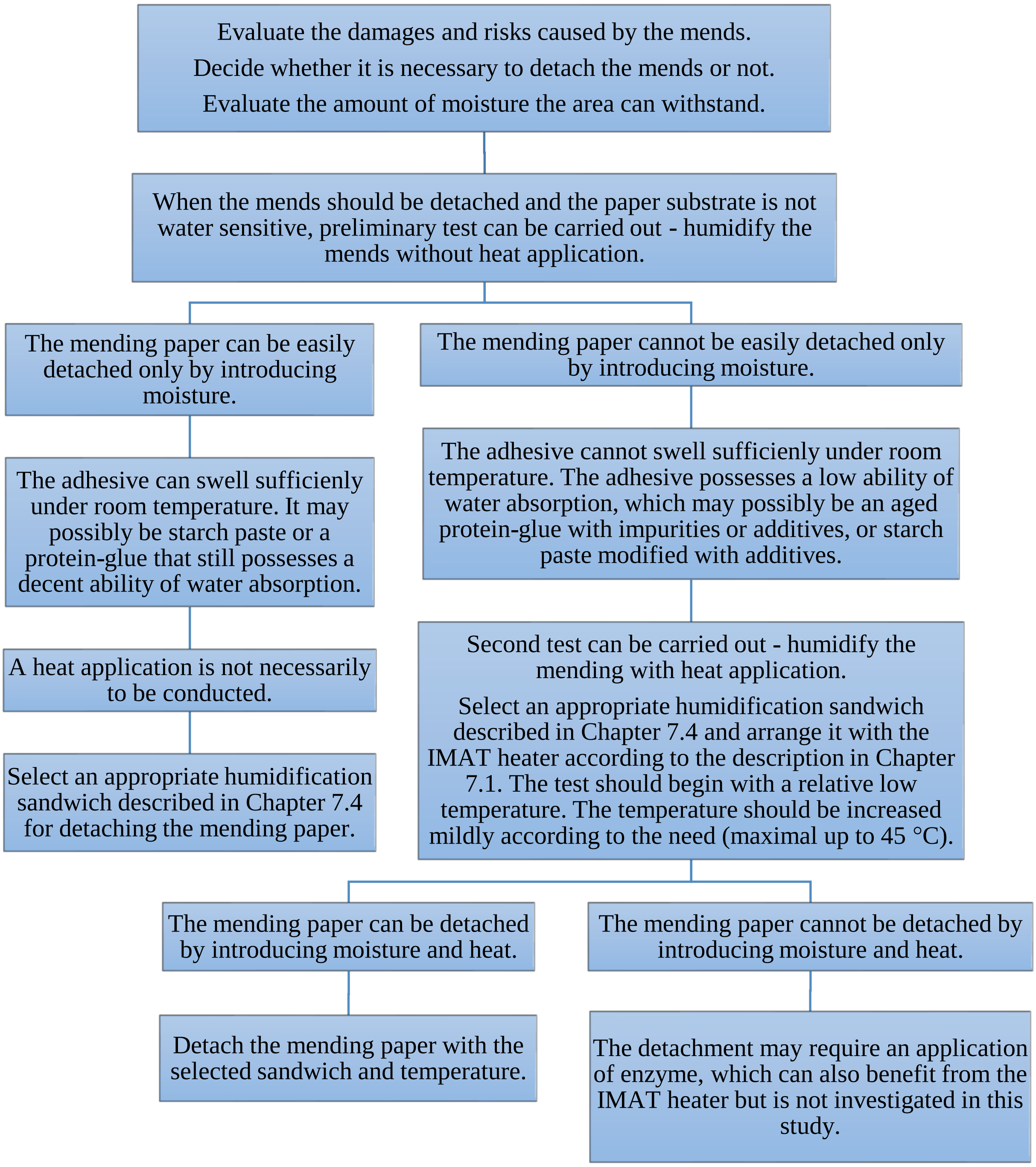
Gore-Tex sandwich using blotter which is immersed in cold water bath before treatment <

Tylose® MH 30000 sandwich</td><td>◆ The detachment of a mend takes generally longer than a gel sandwich.
◆ A target humidification is difficult to be conducted with high precision as paper substrate close to the boundary of the mends can be humidified at the same time.
◆ Introduction of moisture and thermal energy is generally even. However, the absorption of moisture is not always even: edges of the mending paper can be humidified slightly quicker than the center; areas, where the mending paper is stronger degraded or where the adhesive layer is applied thinner, can absorb moisture more rapidly.
◆ Paper substrate is exposed to a high RH level for a generally long period of time, which can enhance the ability of the swelled or liquefied animal glue to travel into the substrate as well.
◆ Difficult to be properly arranged to humidify a mend glued in or close to spine fold, but more suitable for a large area treatment.</td></tr>
<tr><td>Tylose® MH 30000</td><td>◆ Tylose® gel can conform to the surface texture of mending paper, which can promise an ideal contact between the gel and the mending paper.
◆ A target humidification is difficult to be conducted precisely as the shape of Tylose® gel cannot remain stable. The gel can slowly flow laterally out of the boundary of the mend during the treatment, which can be accelerated by external pressure or an increase of temperature.
◆ Introduction of moisture and heat can be uneven due to the ununiform temperature distribution of the gel. The mobility of water inside the gel, the rate of moisture introduction into the paper and adhesive can significantly affected by the temperature variable. A pre-heating of the gel and a regular control of its shape and thickness is recommended.
◆ A Tylose® MH 30000 gel sandwich is relatively easy to be arranged to humidify a mend glued in or close to spine fold.</td></tr>
<tr><td>Agarose</td><td rowspan="2">◆ A target humidification can be conducted fairly precisely as the shape of agarose and gellan gel can remain stable due to their restricted lateral flow, which only shrinks slightly after a period of time due to syneresis.
◆ The stiffness of both gels, especially when they are prepared in a concentration higher than 4 wt% and applied in combination with a barrier paper, cannot always promise an ideal contact between the gel and the mending paper. Extra application of weight such as sand bags on the top of the sandwich can optimize the contact (see 5.2.3.1)
◆ Once an ideal contact is achieved, introduction of moisture and thermal energy can be carried out uniformly. Yet the weight on the sandwich should be relative uniformly distributed throughout the treated area, partially over-pressed area should be averted. Besides, moisture absorption of the mending paper and the adhesive layer are not always identical either. Areas, where the mending paper or its sizing is stronger degraded as well as where the adhesive layer is applied thinner, can absorb moisture more rapidly.
◆ A 2 mm thick agarose or gellan gel sandwich can easily be arranged to humidify a mend glued in or close to spine fold.</td></tr>
<tr><td>Gellan gum</td></tr>
</table>

(Related chapters: 5.2.2; 5.2.3.2)

7.4 Suggested Working Procedure

This study has focused on the removal of old mends glued with protein-based adhesives. In real praxis, however, it is hard for one to be aware of what kind of adhesive was used to glue the mending before the mends is partly detached. In other words, a conservation concept – whether moisture, heat or other conservation materials (i.e. enzymes) are required for the treatment – cannot be decided at once when old mends are found in a bound volume. Therefore, a working procedure is suggested as follows:



7.5 Outlook of Further Researches

Although the introduction of a mild and precise heat transfer through the IMAT heater presents a breakthrough in the removal of old mends, this study raises many further research questions, such as:

a) The quantitative influence of temperature to the viscosity, the capillary action, the water mobility and molecular mobility of different gels in different concentration. The relationship between these factors and the exact interaction between paper and gels are also noteworthy.

b) The determination of agarose and gellan residues under different treating temperatures and treating time. If residues exist, how were them introduced into the paper? Which role does a barrier paper play? In which part of the paper do the residues locate? Does it interfere with the aging performance of the paper?

c) The aging properties of the agarose and gellan gels.

d) The measurement of the thermal conductivity of different gels and the possibility to enhance it.

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- **Adhesives**

Bone Glue (#40105)
GMW - Gabi Kleindorfer - a brand of Wilhelm Leo´s Nachfolger GmbH
Seerosenstraße 9
72669 Unterensingen, Germany
Tel.: +49 (0) 70 22 217 20 212
Fax: +49 (0) 70 22 2 62 9110
Email: gmw@gmw-gabikleindorfer.de
www.gmw-gabikleindorfer.de

Hide Glue (#40205)
GMW - Gabi Kleindorfer - a brand of Wilhelm Leo´s Nachfolger GmbH
Seerosenstraße 9
72669 Unterensingen, Germany
Tel.: +49 (0) 70 22 217 20 212
Fax: +49 (0) 70 22 2 62 9110
Email: gmw@gmw-gabikleindorfer.de
www.gmw-gabikleindorfer.de

Wheat Starch Powder (#3850-012)
Schmedt GmbH & Co. KG
Dwengerkamp 1
21035 Hamburg， Germany
Tel.: +49 (0) 40 734 744 0
Fax: +49 (0) 40 734 744 30
Email: info@schmedt.de
https://www.schmedt24.de/en/

- **Hydrogel Products and Accessory Material**

Agarose Standard (#3810.3)
Carl Roth GmbH + Co. KG
Schoemperlenstraße 3-5
76185 Karlsruhe, Germany
Tel.: +49 (0) 721 5606 0
Fax: +49 (0) 721 5606 149

Email: info@carlroth.de
https://www.carlroth.com/de/en

Calcium Acetate Hydrate (#21056-50G-F)
Sigma-Aldrich Chemie GmbH
Eschenstraße 5
82024 Munich, Germany
Tel.: +49 (0) 89 6513 0
Fax: +49 (0) 89 6513 1169
Email: deukundenservice@sial.com
https://www.sigmaaldrich.com/germany.html

KELCOGEL® CG LA Gellan Gum
CP Kelco US, Inc.
3100 Cumberland Boulevard Suite 600
Atlanta, Georgia 30339 USA
Tel.: +1 (800) 535 2687
Fax: +1 (678) 247 2797
https://www.cpkelco.com/

Tylose® MH 30000 YP4
SE Tylose GmbH & Co. KG
Rheingaustr. 190-196
65203 Wiesbaden, Germany
Tel.: +49 (0) 611 962 04
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Email: info@setylose.com
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Mariannenplatz 2
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RK-00 (3.7g/m²)
Paper Nao
4-37-28 Hakusan Bunkyo-ku
Tokyo 112-0001, Japan
Tel.: +81 (0) 3 3944 4470
Fax: +81 (0) 3 3944 4699
http://www.papernao.com/

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Archivkarton Hellgrau 300g/m² (#00080127)
Römerturm Feinstpapier GmbH & Co. KG
Alfred-Nobel-Straße 19
50226 Frechen, Germany
Tel: +49 (0) 2234 95595 0
Fax: +49 (0) 2234 95595 55
Email: service@roemerturm.de
www.roemerturm.de

Blotting Boards – 700 g/m² Qualitative and Technical Filter Paper on Pallet (#11830300)
Th. Geyer GmbH & Co. KG
Dornierstr. 4 - 6
71272 Renningen, Germany
Tel: +49 (0) 7159 1637 823
Fax: + +49 (0) 7159 1637 710
Email: sales@thgeyer.com
www.thgeyer.de

Mould Made Printing and Fine Art Paper, laid (#8181/2)
Papierfabrik Zerkall Renker & Soehne GmbH & Co.KG
Gustav-Renker-Strasse 5
52393 Huertgenwald-Zerkall, Germany
Telephone: +49 (0) 24 27 94 06 0
Telefax: +49 (0) 24 27 94 06 79
E-Mail: info@zerkall.com
http://www.zerkall.com/

Handgeschöpfte Restaurier-Papiere (#2058, #2061, #2061)
Anton Glaser

Theodor-Heuss-Straße 34a
70174 Stuttgart, Germany
Tel.: +49 (0)711 29 78 83
Fax: +49 (0)711 226 18 75
Email: webmaster@anton-glaser.de
http://www.anton-glaser.de/

Rayon paper (18g/m^2) (#36618, item not available now)
GMW - Gabi Kleindorfer - a brand of Wilhelm Leo´s Nachfolger GmbH
Seerosenstraße 9
72669 Unterensingen, Germany
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Fax: +49 (0) 70 22 2 62 9110
Email: gmw@gmw-gabikleindorfer.de
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CROFTON® Backmatte mit Silikonbeschichtung
ALDI SÜD Dienstleistungs-GmbH & Co. oHG, Unternehmensgruppe ALDI SÜD
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45476 Mülheim an der Ruhr, Germany
Fax +49 (0) 1803 252722
Email: mail@aldi-sued.de
https://unternehmen.aldi-sued.de/de/

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GMW - Gabi Kleindorfer - a brand of Wilhelm Leo´s Nachfolger GmbH
Seerosenstraße 9
72669 Unterensingen, Germany
Tel.: +49 (0) 70 22 217 20 212
Fax: +49 (0) 70 22 2 62 9110
Email: gmw@gmw-gabikleindorfer.de
www.gmw-gabikleindorfer.de

Gore ePTFE Membrane on Polyester Non-woven Fabric (#39444, item not available now)
GMW - Gabi Kleindorfer - a brand of Wilhelm Leo´s Nachfolger GmbH
Seerosenstraße 9
72669 Unterensingen, Germany

Tel.: +49 (0) 70 22 217 20 212
Fax: +49 (0) 70 22 2 62 9110
Email: gmw@gmw-gabikleindorfer.de
www.gmw-gabikleindorfer.de

Polyester Film, Crystal Clear, 50 µm Thick (#38500)
GMW - Gabi Kleindorfer - a brand of Wilhelm Leo´s Nachfolger GmbH
Seerosenstraße 9
72669 Unterensingen, Germany
Tel.: +49 (0) 70 22 217 20 212
Fax: +49 (0) 70 22 2 62 9110
Email: gmw@gmw-gabikleindorfer.de
www.gmw-gabikleindorfer.de

Polyester Fleece “Avos” – Wadding (#99897)
Hans Schröder GmbH
Erich-Kessler-Str. 4
76689 Karlsdorf-Neuthard, Germany
Tel.: +49 (0)7251 34 88 00
Fax: +49 (0) 7251 34 88 07
Email: info@archiv-box.de
https://archivbox.com/en/

"WALLMASTER" Natural Rubber Sponge, Flat (#22401)
GMW - Gabi Kleindorfer - a brand of Wilhelm Leo´s Nachfolger GmbH
Seerosenstraße 9
72669 Unterensingen, Germany
Tel.: +49 (0) 70 22 217 20 212
Fax: +49 (0) 70 22 2 62 9110
Email: gmw@gmw-gabikleindorfer.de
www.gmw-gabikleindorfer.de

Watesmo Test Paper Reel of 5 m Length, 10 mm Wide (#90609)
Wagner & Munz GmbH
In der Rosenau 4
81829 München, Germany
Tel.: +49 (0) 89 451023 0
Fax: +49 (0) 89 451023 33

Email: office@wagnermunz.com
http://www.wagnermunz.com/

- **Equipment**

3D Digital Microscope HIROX RH-2000 with MXB-2016Z Zoom Lens
Hirox Europe
300 Route Nationale 6
Le bois des côtes, Bat. A
69760 Limonest, France
Tel.: +33 (0) 426 25 03 40
Fax: +33 (0) 426 23 68 13
Email: info@hirox-europe.com
https://www.hirox-europe.com/

FLIR SC660 High Performance Infrared Inspection System
FLIR Systems, Inc.
27700 SW Parkway Avenue
Wilsonville, OR 97070, USA
E-Mail: webmaster@flir.de
https://www.flir.com

Handheld Data Logger Thermometer with Graphic Display (#OM-EL-ENVIROPAD-TC)
OMEGA Engineering GmbH
Daimlerstraße 26
75392 Deckenpfronn, Germany
Tel.: +49 (0) 7056 9398 0
Fax: +49 (0) 7056 9398 29
Email: info@omega.de
https://www.omega.de/

Polyimide High Temperature Resistant Tape (#EL-CP-022)
ELEGOO
A205, Weidonglong Business Building
Meilong Avenue, Longhua District,
518109, Shenzhen, China
Tel.: +49 (0) 755 66693461
Email: service@elegoo.com
www.elegoo.com

IMAT Heater (Prototypes)
Supplied by Tomas Markevicius, co-leader of IMAT Project
Email: tmarkevicius@imatproject.eu
http://www.imatproject.eu/en

Nikon D700 with Nikon AF-S Nikkor 16-85mm Zoom Lens
Nikon GmbH
Tiefenbroicher Weg 25
40472 Düsseldorf, Germany
Tel.: +49 (0) 211 9414 0
Fax: +49 (0) 211 9414 300
https://www.nikon.de/

Phenom ProX Desktop SEM
Phenom-World BV
Dillenburgstraat 9E
5652 AM Eindhoven, The Netherlands
Tel.: +31 (0) 40 259 73 60
https://www.phenom-world.com/

PROclamp MINI Standard Glass Plates (#3548.1)
Carl Roth GmbH + Co. KG
Schoemperlenstraße 3-5
76185 Karlsruhe, Germany
Tel.: +49 (0) 721 5606 0
Fax: +49 (0) 721 5606 149
Email: info@carlroth.de
https://www.carlroth.com/de/en

Ready-Made Insulated Thermocouples (#5TC-TT-TI-40-1M)
OMEGA Engineering GmbH
Daimlerstraße 26
75392 Deckenpfronn, Germany
Tel.: +49 (0) 7056 9398 0
Fax: +49 (0) 7056 9398 29
Email: info@omega.de
https://www.omega.de/

Rotiphorese® Unit PROclamp MINI complete set (#3501.1)
Carl Roth GmbH + Co. KG
Schoemperlenstraße 3-5
76185 Karlsruhe, Germany
Tel.: +49 (0) 721 5606 0
Fax: +49 (0) 721 5606 149
Email: info@carlroth.de
https://www.carlroth.com/de/en

UV Analysis Lamps (Hand Lamps with Dual Wavelengths) (#2950740)
Herolab GmbH Laborgeräte
Ludwig-Wagner-Str. 12
69168 Wiesloch, Germany
Tel.: +49 (0) 6222 5802 0
Fax: +49 (0) 6222 5802 34
E-Mail: info@herolab.de
www.herolab.de