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Innovation in Green Materials for the Non-Contact Stabilization of Sensitive Works of Art: Preliminary Assessment and the First Application of Ultra-Low Viscosity Hydroxypropyl Methylcellulose (HPMC) by Ultrasonic Misting to Consolidate Unstable Porous and Powdery Media

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Abstract: Paintings and other works of art created with fragile and mechanically unstable powdery media present challenges to conservators. Frequently, powdery media is water-sensitive, extremely fragile, tends to delaminate, and may be altered by even the slightest physical action or interaction with liquids. Materials that can provide an efficient stabilization without unacceptably altering the optical characteristics of the delicate substrate are extremely limited. Among these, Funori, Isinglass, and Methocel A4C have become established for this use. In bench practice, consolidants are frequently applied in a non-contact way, using ultrasonic and pneumatic aerosol generators to minimize the impact of the consolidant on sensitive substrates. However, nebulizing the available materials is problematic in bench practice, because of their high viscosity and, only extremely low concentrations can be nebulized using low kinetic impact ultrasonic or pressure-based misting systems adopted from the healthcare industry. As a potential innovative solution, this study introduces novel ultra-low viscosity (ULV) cellulose ethers (ULV-HPMC) for stabilisation of unstable porous and powdery surfaces, which have been successfully applied in bench practice for the pilot treatment of Edvard Munch painting on canvas and two 19th c. Thai gouache paintings on panel. Novel ULV-HPMC materials have multiple desirable qualities for consolidation treatments in conservation, and in accelerated aging tests marginally outperformed Methocel A4C, considered to be one of the most stable consolidants in the practice of conservation. Because of the ultra-low viscosity, higher concentrations of ULV-HPMC materials can be applied as water-based aerosols in a non-contact way and in fewer applications, which is a significant advantage in the treatment of delicate water-sensitive surfaces. Notably, novel ULV biopolymers are low-cost, derive from sustainable and renewable sources, and do not raise health and environmental concerns. Such novel materials and methods seamlessly resonate with the ICOM-CC's Melbourne 2014 declaration, EU Green Deal, and the UN's Sustainable Development goals and show potential adding new sustainable materials with the exceptionally low viscosity to the conservator's tool box.

Keywords: sustainability; cultural heritage conservation; ultra-low viscosity; HPMC; cellulose ethers; ecologically sustainable materials; porous powdery media; non-contact; water-based paint consolidation; stabilization; ultrasonic misting; modern contemporary art materials

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1. Introduction

Tangible cultural heritage objects (paintings, works on paper, modern and contemporary objects, and ethnographic artifacts) containing friable and powdery materials present multiple conservation challenges. Frequently, such materials typically lack adhesion and cohesion; however, the stabilization of delicate painted surfaces (gouache, modern oils, acrylic emulsion paints), friable media (pastels, chalks, charcoal), woven and nonwoven materials (textile, paper, tracing paper), animal-sourced materials (leather, silk), and contemporary media remains challenging. Porous, powdery and mechanically unstable surfaces can be extremely sensitive to liquids or to the slightest physical contact, shock, or vibration, severely limiting their transportation, display, and accessibility to the public (Figure 1). Their stabilization is complicated by the high risk of optical changes caused by consolidation, and limited availability of treatment methods and materials. Among these, Isinglass [1], Funori, Jun-Funori, Tri-Funori [2–4], and Methocel A4C [5] have become established as effective and stable consolidants. The few other materials in occasional use, such as ethyl hydroxyethyl cellulose (EHEC), hydroxy propyl cellulose (HPC), and hydroxy ethyl cellulose (HEC), have been assessed in past studies to be of average or insufficient stability for conservation treatments [5].

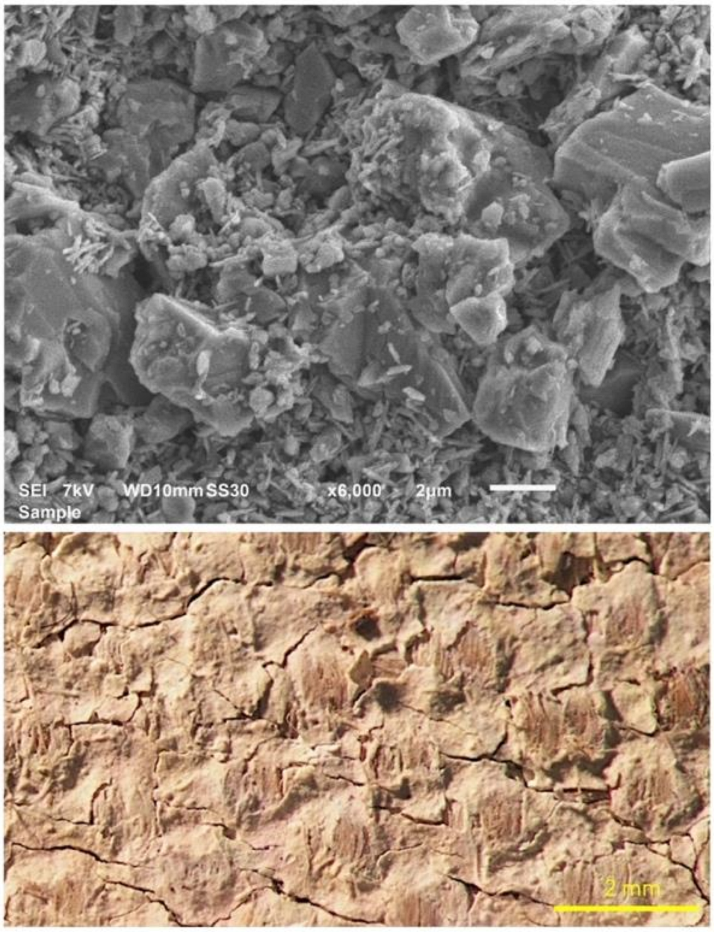

Figure 1. SEM image of natural ochre gouache paint on paper shows powdery media on the surface (top). Stereo microscope image of powdery delaminating paint of E. Munch Alma Mater figure study (1912) oil on canvas, M 881/Woll M 31, © Munch Museum, Oslo, Norway.

Consolidation treatments are essentially irreversible, and the requirements for treatment methods and materials regarding their effectiveness, stability, and minimal changes to the substrate are exceptionally high. When stabilizing delicate surfaces, consolidants are frequently applied in a non-contact way, using ultrasonically or pneumatically generated aerosols, because sensitive surfaces cannot tolerate mechanical action or the brush-application of liquids (Figure 2). However, nebulizing typical consolidants, such as Methocel A4C, Isinglass, and Funori, remains problematic because of their high viscosity. This allows only for extremely low concentrations of the biopolymers to be nebulized, which are often insufficient to stabilize the substrate. As a result, multiple aerosol applications are required, and considerable amounts of water are applied to the substrate. Water interacts with delicate and often water-sensitive substrates, which increases treatment risks, while multiple misting applications (especially when treating large-scale objects) increase treatment time and costs.

Figure 2. The author in the process of consolidation using ULV-HPMC and ultrasonic misting under the stereomicroscope in the treatment of Edvard Munch's unvarnished painting "Alma Mater" (1911–16), Munch Museum, Oslo. Paintings conservator Carolina Jimenez Gray in the process of the consolidation of unvarnished traditional Thai Thotsachat gouache paintings on panel using a pneumatic aerosol generator and HPMC, Victoria and Albert Museum, London.

Moreover, Funori and Isinglass are products from the seaweed and sturgeon farming industries, that have begun to increasingly raise environmental and sustainability concerns [6]. High-density sturgeon farming operations often require significant amounts of water and are energy-intensive. Furthermore, the discharge of nutrient-rich effluents leads to water pollution and promotes the spread of diseases among the fish, which in turn results in the use of antibiotics and other pharmaceuticals, the development of antibiotic-resistant pathogens, and drug pollution in the water. Seaweed farming disrupts local ecosystems, displaces native species, and pollutes water with fertilizers, pesticides, and antifouling chemicals, which has detrimental effects on the environment [7]. It is also worth considering economic sustainability. ULV-HPMC materials, investigated in this paper, have been commercialized, but are not offered by conservation materials suppliers. However, it is reasonable to expect that the retail price range will be affordable to conservators, similar to other cellulose ethers. The cellulose ethers and ULV-HPMC investigated in this paper are made from a sustainable and renewable resource, cellulose, are water-soluble, biodegradable, non-toxic, odourless, stable, biocompatible, low-cost, and are easily accessible to conservators. While the scope of this paper is restricted to the preliminary assessment of novel green ULV-HPMC materials for non-contact stabilization treatments, first presented by the author in 2019 as a conference presentation [8], further studies, and adoption in the bench practice, would allow for the nebulizing of low molecular weight ULV-HPMC materials at higher concentrations and limit the exposure of sensitive substrates to water. Thanks to their low molecular weight, ULV-HPMC materials can diffuse more effectively within porous substrates and can stabilize fragile painted surfaces and other cultural heritage materials with a reduced risk of inadvertent physical and optical changes. Altogether, ULV-HPMC could contribute for safer, greener, and more effective stabilisation treatments.

2. Materials and Methods

The samples of ULV-HPMC Tylose MOBS 3P4 (Pharmacoat 603®) and MOBS 6P4 (Pharmacoat 606®) were provided by the Shin-Etsu SE Tylose GmbH & Co. KG in Wiesbaden, Germany. Funori, Isinglass, and Methocel A4C® were obtained at Kremer Pigmente GmbH & Co. KG, Aichstetten, Germany. SEM image was obtained using scanning electron microscopy (SEM) JEOL JSM-6010PLUS. The samples were aged in a Binder KBF 115 constant climate chamber at 80 °C and 65% RH over 90 days. Gloss measurements were performed at 85° using Rhopoint Novogloss glossmeter. Colour measurements were carried out using a Konica Minolta 2600d spectrophotometer, using CIE standard illuminant D65 and a CIE 1964 10° standard observer. The perceived colour change was calculated using CIEL*a*b* ΔE^*_{76} coordinates with values indicated in (L^* a^* b^*). ULV-HPMC aerosol was generated using an ultrasonic AGS 2000 nebulizer, ZFB-Zentrum für Bucherhaltung GmbH, and pressure-based Pari Boy V0000 Type 038 (1.6 Bar), PARI Medical Ltd., Byfleet, UK.

3. Novel Ultra-Low Viscosity (ULV) Cellulose Ethers for the Consolidation of Powdery Media

3.1. The Role of Ultra-Low Viscosity in the Consolidation of Media, Using Ultrasonic Misting

In treatments that aim to consolidate unstable porous powdery media using ultrasonic misting, the low viscosity of the consolidation medium is an important factor for an optimal penetration of the medium within the paint matrix and for a reduction in the risk of unwanted optical changes [9–13]. The role of low viscosity has been emphasized in Michalski's physical model for the consolidation of matte powdery media [9]. Generally, the effectiveness of a consolidation treatment requires an optimal fluid transport within the paint matrix, which in turn depends on capillary penetration, among other factors. The diffusion of the consolidation medium within the powdery paint or another porous substrate is similar to the fluid dynamics in tubes, where capillary pressure increases at reduced fluid viscosity and with a smaller diameter of pores. Low molecular weight biopolymers appear to possess the required qualities for this purpose: they are more agile, the viscosity of their aqueous solutions is low, and they diffuse better within the paint matrix than the high molecular weight polymers. ULV cellulose ethers are particularly interesting as a medium for ultrasonic misting treatments because of their capacity to diffuse well and because of the low impact to the air gaps within the porous and powdery paint matrix. Filling the air gaps with bulky, high molecular weight polymers may change the light scattering at the air–pigment interface, resulting in unwanted colour saturation and change, as first pointed out by Michalski, who in 1989 pioneered his ultrasonic atomization method for the consolidation of powdery media. His apparatus, the "CCI mister" directed the emission of micro-droplets of consolidation medium from an acoustically and pneumatically excited liquid–air interface to the surface undergoing treatment [10]. Since then, conservators have used both ultrasonic and pneumatic aerosol generation instruments (Figure 2), summarized by multiple authors [10–20].

The prototype "CCI Mister" apparatus, by Michalski and Dignard, employed ultrasound oscillation and an air pump was used to create a gentle flow of mist. Later on, conservators adopted several medical nebulizers, which use either ultrasonic oscillation (AGS-2000, Hico Ultrasonat 810) or air pressure, as well as DIY pneumatic, ultrasonic or hybrid devices, which remain of marginal use. Ultrasonic misting has enabled conservators to minimize the direct physical interaction with extremely fragile matte powdery paint. Yet another advantage is related to the size of the micro-droplets of the consolidation medium: c. 5–10 µm, (Hico Ultrasonat 810: 0.5–6 µm) which was within the pigment particle size range of c. 0.1–10 µm [9]. Smaller micro-droplets, produced by the ultrasonic oscillation, tended to have a lower impact on the optical properties of matte powdery media, compared with the larger droplets produced by the pneumatic nebulizers c. 10–300 µm [9,10] or by the brush application of liquid phase consolidation media.

Before going further, this part requires an explanation. Smaller micro-droplets in an aerosol generated by ultrasonic misting allow the delivery of smaller volumes of consolidation medium than does brush application of a consolidant in a solution. When consolidating sensitive powdery materials, the challenge is to determine the optimal amount of consolidation medium. When a drop of consolidation medium hits the paint surface, it breaks down, and then diffuses into the substrate, and forms a film, as water evaporates. When applied in excess, the medium will not have enough time to diffuse in a porous substrate by the time that the evaporation leads to the formation of a film on the surface. This film may cause colour change of the substrate and big drops will deliver too much solution, which diffuses in the substrate, fills up the capillaries and air gaps, and changes optical properties, and hence, the colour of the substrate as a consequence. Misting small quantities allows one to control the amount of the consolidant delivered. Moreover, smaller aerosol droplets, upon hitting the paint surface, diffuse better in the substrate porosities and present less of a risk of perturbing or displacing the loose paint fragments or particulate matter on the surface. Thus, smaller aerosol droplets are advantageous for stabilization and consolidation treatments. When using ultrasonic misting, the droplet size decreases at lower viscosity [20,21], which can be explained from Equation (1) for the threshold amplitude (A) given by Mercer [22]:

$$A = 4n/fl \tag{1}$$

where A = threshold amplitude; n = viscosity of liquid; f = frequency of acoustic signal; and l = capillary wavelength

However, when using the available high viscosity consolidation materials, the aerosol droplets size increases, and nebulization of concentrated solutions is highly complicated. Viscous media dampens the acoustic waves, and, above a certain threshold, the consolidation medium cannot be nebulized at all. Generally, ultrasonic nebulization requires a lower viscosity than the jet atomizers, where pneumatically driven air is forced through a small orifice and creates a sub-atmospheric pressure at the top of a capillary tube immersed in water. As a result, ultrasonic misting produces smaller droplets than jet atomizers, where stronger air flow tends to agglomerate the micro-droplets [21]. Achieving low viscosity has always been problematic in consolidation media, because the materials that are customarily used as consolidants, such as MC A4C (400 mPa·s) or Funori (11.5 mPa·s, 121.3 mPa·s) [23], have a relatively high viscosity. The viscosity of Isinglass and gelatine obtained from different fish species may have different values, depending on raw materials, production processes, molecular weights, and degrees of polydispersity. The reported typical viscosities vary in a range of 4–22 mPa·s, with extremes at 0.66 and 112.6 mPa·s [24] and can reach up to 2000 mPa·s in purified Isinglass [25]. However, the standard conditions by which to measure the viscosity of gelatine (6.67 wt% 60 °C) are different from those of the standard viscosity test for the cellulose ethers (2 wt% 20 °C). Gelatine viscosity depends on the concentration of solution, temperature and bloom value, and in practical applications, the effective gelatine viscosity at room temperature ~ 21 °C will be different from the reported standard mPa·s values at 60 °C.

To overcome the issue of the high viscosity, in bench practice conservators tend to use an ultra-low concentration of A4C (up to 0.5 wt%), Jun-Funori (0.1–0.25 wt%), gelatine (up to 1 wt%) and other consolidants (typically 0.25–1 wt%) misted multiple times [13]. On the positive side, this approach allows for the gradual increase in the amount of the consolidant in the substrate, avoiding an excess which could cause unwanted optical changes in the substrate. On the negative side, powdery and friable substrates are typically porous and water-sensitive, and repeated misting increases the exposure to water (and to the organic solvents used in consolidation treatments) which may swell and shrink the substrate, displace particulate matter, facilitate migrations of leachable components though osmotic pressure, and altogether contribute to unwanted physical and optical changes in the substrate. Therefore, it is desirable to limit the amount of water and the number of misting applications to the minimum necessary. To achieve this objective, ULV cellulose ethers may offer valuable advantages over the available materials, such as generate aerosols using more concentrated solutions, which require fewer misting applications, and have a potential to diffuse better in the substrate thanks to their low molecular weight.

3.2. New Ultra-Low Viscosity HPMC Consolidation Medium for Ultrasonic Misting Treatments

In this study, a new approach was tested using previously unreported ULV cellulose ethers. The methylcellulose (MC) and hydroxypropyl methylcellulose (HPMC) cellulose ethers considered were Metolose SM4 (MC) (4 mPa·s) by Shin-Etsu, Methocel E3 Premium LV (HPMC) (2.4–3.5 mPa·s), and Methocel E5 Premium LV (HPMC) (4–6 mPa·s) by Dow Chemical Company. For the early-stage testing two Shin-Etsu HPMC grades MOBS 3P4 (Pharmacoat 603®) (2.4 mPa·s) and MOBS 6P4 (Pharmacoat 606®) (4.7 mPa·s) were selected.

3.2.1. Ultra-Low Viscosity Hydroxypropyl Methylcellulose (ULV-HPMC) MOBS 3P4 (Pharmacoat 603®) and 6P4 (Pharmacoat 606®): Chemical and Physical Properties Relevant to Conservation

Since the 1960s, HPMC has been widely used in the pharmaceutical and cosmetics industries as a thickener, binder, and film former. The ultra-low molecular weight grades were developed for tablet coating, where a low viscosity is needed for the nebulization. HPMC is a semi-synthetic, inert, viscoelastic and thermoplastic polymer (Figure 3). Chemically, it is methylcellulose modified with a small amount of propylene glycol ether groups. Both MC and HPMC have the polymeric backbone of cellulose, but contain different ratios of hydroxypropyl to methoxyl substitution, which influence their hydrophilicity, gelling behaviour, rheology, surface activity, and film properties.

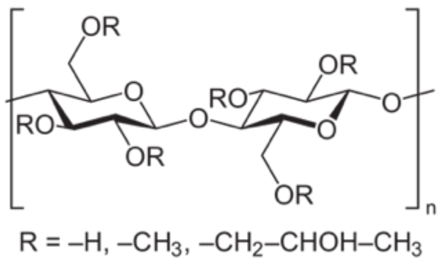

Figure 3. Chemical structure of hydroxypropyl methylcellulose $C_{56}H_{108}O_{30}$.

HPMC contains 28% to 30% of methoxyl -OCH_3 groups and 7% to 12% of hydroxypropyl -$OCH_2CH(OH)CH_3$ groups. In case of the investigated MOBS 3P4 and 6P4 grades, the methoxyl content is 29% and hydroxypropyl content is 8.9% [26]. Pharmaceutical literature describes HPMC as chemically inert and having excellent film-forming properties [25,27–32]. HPMC is produced with a broad viscosity range: from 2.4 mPa·s to 200.000 mPa·s (at 2% 20 °C) [30–33]. The high viscosity grade HPMC has been mentioned by Feller [5], but ultra-low viscosity grade HPMC has not been previously reported in conservation literature. In this context MOBS 3P4 and 6P4, with an ultra-low viscosity of 2.4 and 4.8 mPa·s, respectively, are particularly interesting for the consolidation of matte powdery media using ultrasonic misting. In addition, HPMC water solutions have good wetting properties, with surface tensions ranging from 42 to 56 mN/m, better than A4C at 64 mN/m. HPMC pH between 6 to 7 is similar to that of Isinglass and Funori. In this case, the pH of HPMC MOBS 3P4 was measured at 6.5 and 6P4 at 6.9. HPMC is stable in the broad pH range of 3–11. It is soluble in water and ethanol, isopropanol containing water.

The viscosity of HPMC is proportional to the molecular weight or chain length of the specific type. MOBS 3P4 (Pharmacoat 603®) (2.4 mPa·s) and MOBS 6P4 (Pharmacoat 606®) (4.7 mPa·s) have the lowest viscosity among all HPMC grades manufactures by Shin-Etsu, which allows for the generation of aerosols from solutions with a higher concentration of consolidant. (Figure 4). Like MC, HPMC exhibits a thermal gelation property and at critical temperature forms a reversible gel. The critical temperature for HPMC at 75–90 °C is higher than the critical temperature of 40–55 °C for A4C, which means that HPMC can remain at a low viscosity at higher temperatures. However, the thermal gelation temperature is not fixed and decreases at increased concentration of HPMC, but in case of MOBS 3P4 (Pharmacoat 603®) remains around 55–60 °C [5] at 10 wt% or higher at lower concentrations. This aspect is important in ultrasonic misting applications, as, in the ultrasonic mister, consolidation medium is warmed by the transducer in the water container and there is a heat transfer to the nebulized content in the heated hose (AGS 2000, Hico 810 models). The increase of temperature may increase the viscosity and disrupt the misting process. Practical applications of HPMC MOBS 6P4 and 3P4 suggest that the misting process appears to be more stable at room temperature (~21 °C) without the heated hose, which can be disconnected in the AGS 2000 model.

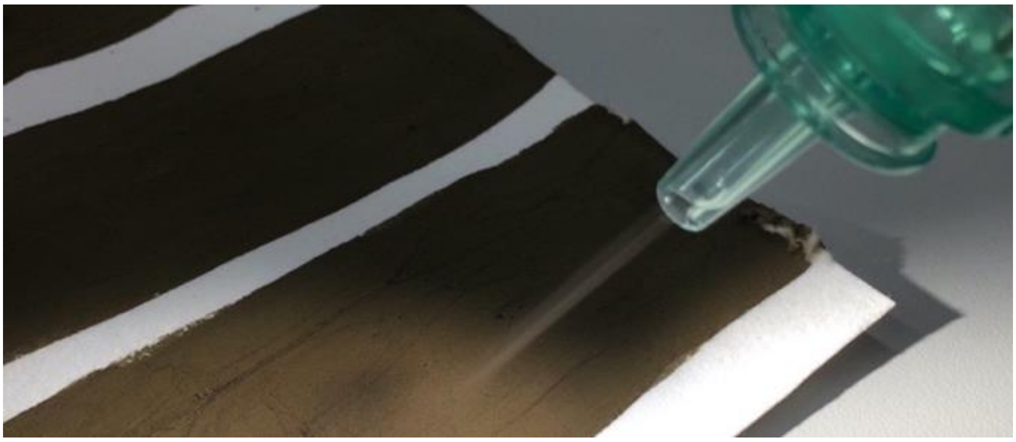

Figure 4. MOBS 3P4 aerosol generation test using ultrasonic nebulizer AGS 2000.

Among other desirable properties, it can be noted that HPMC is resistant to microbiological activity, and to thermally induced discoloration, as demonstrated by Fellers [5]. The higher molecular weight HPMC grades generally possess improved resistance, extensibility, and toughness related to the greater level of physical entanglement arising from the longer chains [5,33]. However, these need to be assessed in relation to the actual treatment needs. To consolidate an underbound paint composed of lightweight powdery matter, strong adhesion and high tensile strength are typically not required, while other properties, such as low viscosity, optimal diffusion in the substrate, ability to be used in non-contact applications, and low impact on the optical properties of the substrate are essential for successful treatment.

3.2.2. ULV-HPMC Stability, Optical Changes and Preliminary Accelerated Aging Testing

While ULV-HPMC has many desirable properties as a consolidant, it is unreported in the conservation literature and in bench practice. 1990 Feller's study on cellulose ethers characterized HPMC as having excellent stability and aging properties "equal or better than methylcellulose" [5]. To be noted, Feller tested high molecular weight HPMC with viscosity of 4000 mPa·s. In a 1992 paper, C. Baker made a claim that low molecular weight and low viscosity cellulose ethers may degrade faster than higher molecular weight grades [34]. However, no specifics were provided on the conditions (i.e., polymer, solution, dry powder, film) pertaining to the claim, which was unsupported by experimental data or literature. On the contrary, MOBS 3P4 and 6P4 manufacturer Shin-Etsu confirmed that there is no difference between low and high molecular weight HPMC in terms of its aging at the molecular level. The effect of aging in solution, however, is different, and the viscosity of higher molecular weight HPMC grades will decrease faster [35], which pertains to the stability of higher molecular weight HPMC and is not relevant for practical consolidation treatments, as the consolidant solution is typically prepared and used fresh within a short period.

3.3. Experimental: Testing and Assessing ULV-HPMC Stability and Effectiveness

3.3.1. Hygro-Thermal Accelerated Aging

Consolidation treatments of porous friable materials are typically irreversible and the consolidant cannot be removed from the substrate. Therefore, long-term stability and resistance to discoloration are essential for conservation applications. To study the colour changes of MOBS 3P4 and 6P4 samples, a hygro-thermal accelerated aging study was carried out. The new materials were compared with more commonly used consolidants: Funori, Isinglass, Methocel A4C and MOBS 6P4 at 5 wt%, both as cast films and brushed on Whatman filter paper with α-cellulose content > 98%. Half of the paper substrate was coated with the consolidant, and the other half was left uncoated for control. For repeatability, 5 samples of each consolidant were produced and aged. The samples were aged in a climatic chamber at 80 °C and 65% RH for 90 days. A second set of samples was kept in the dark at standard museum ambient conditions (21 °C and 51% RH). To assess changes, colour measurements were carried out using a Konica Minolta 2600d spectrophotometer, based on a CIE standard illuminant D65 and a CIE 1964 10° standard observer. For repeatability, measurements were carried out 3 times and the average value was calculated. Confidence levels were estimated over 95% because the measured area is relatively small and because we can reasonably assume that the 3 measurements are representative of the entire surface. The perceived colour change was calculated using CIEL*a*b* coordinates with values indicated in (L* a* b*) and ΔE^*_{76} Equation (2):

$$\Delta E^*_{ab} = \sqrt{(L^*_2 - L^*_1)^2 + (a^*_2 - a^*_1)^2 + (b^*_2 - b^*_1)^2} \tag{2}$$

Notably, chamber aging caused yellowing of the filter paper substrate (ΔE^*_{76} exceeded 5, mostly due to an increase of b*). To avoid the interference of the yellowing of the paper, the ΔE^*_{76} colour difference of the aged consolidant related to the aged paper was calculated. Aging in dark ambient conditions produced little effect on the colour of the paper and consolidant. (Table 1). After the accelerated aging (Figures 5 and 6) the colour changes of both A4C and 6P4 were minimal: ΔE^*_{76} = 1.25 and 0.3, respectively, which is below the perceptible change (PC) threshold ΔE^* = 1.5 [36]. Isinglass and Funori samples underwent noticeable colour changes: ΔE^*_{76} = 7.91 and 14.0, respectively, mostly due to yellowing and darkening. The ΔE table (Table 1) shows the change values, where HPMC MOBS 6P4 changed 11 times less than MC A4C in the thermal aging test (ΔE^*_{76}: 6P4: 0.3 vs. A4C: 1.25).

Table 1. Colour change of the samples after aging (dark ambient and accelerated aging in climatic chamber).

Aging Method and Consolidant	ΔE^*_{76} Aged vs. Unaged Paper	ΔE^*_{76} Unaged Coating vs. Unaged Paper	ΔE^*_{76} Aged Consolidant vs. Aged Paper
Ambient: MOBS 6P4	0.14	0.15	0.47
Ambient: Methocel A4C	0.18	0.29	0.54
Ambient: Isinglass	0.59	0.98	0.48
Ambient: Funori	0.17	1.86	1.92
Chamber: MOBS 6P4	5.53	0.16	0.30
Chamber: Methocel A4C	5.79	0.36	1.25
Chamber: Isinglass	5.73	0.98	7.91
Chamber: Funori	5.83	2.01	14.00

Another important optical perceptive factor–gloss change was examined before and after the aging. Changes in gloss after both ambient and chamber aging did not seem to be necessarily linked to the consolidant, as the blank paper often shows similar or higher gloss change after aging. The gloss change of paper was included in the table to demonstrate how much the actual change was influenced by the gloss change in paper substrate (Figure 7).

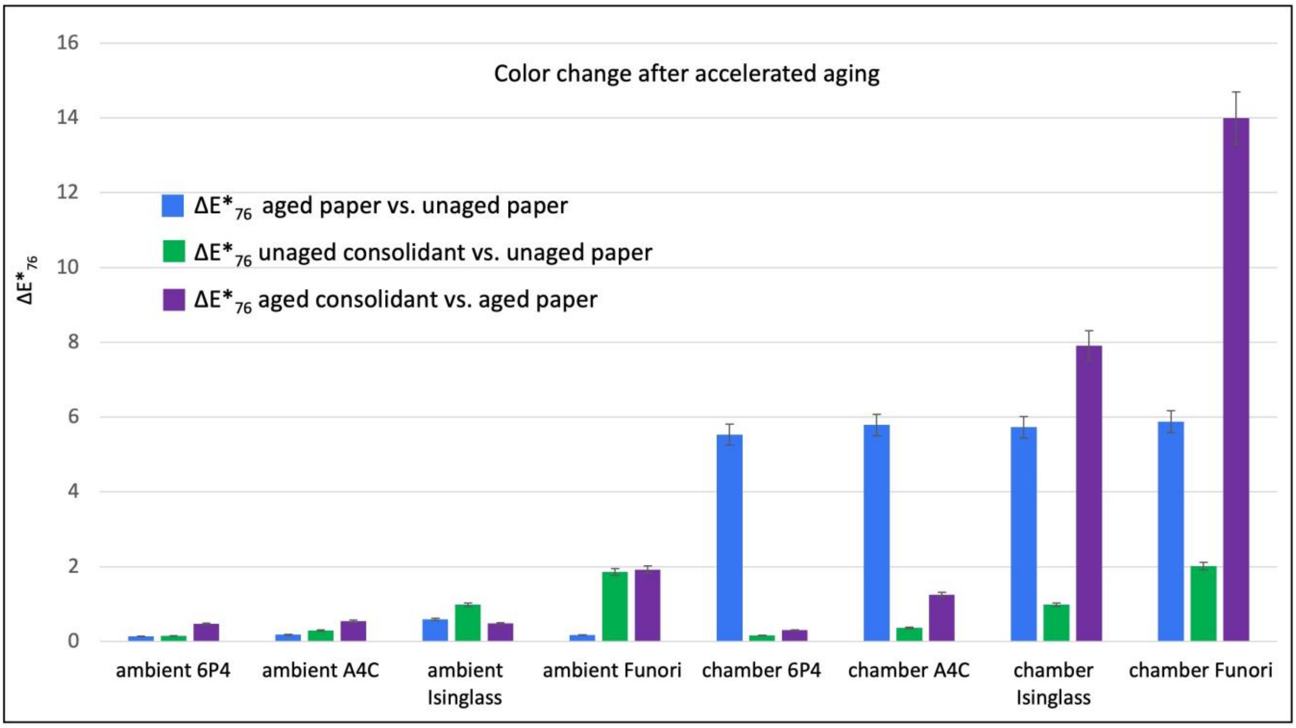

Figure 5. Colour change of the samples after aging (dark ambient and accelerated aging in climatic chamber).

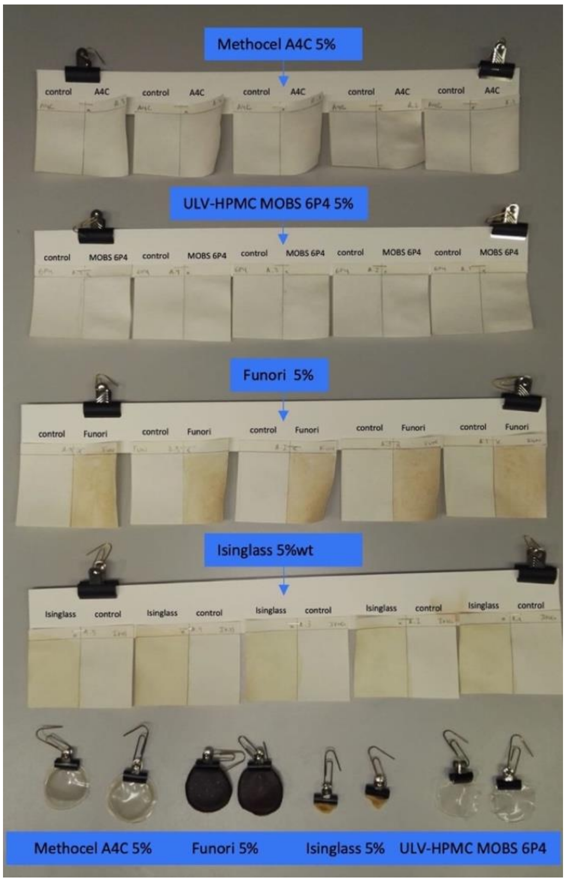

Figure 6. Image after aging: MC Methocel A4C, ULV-HPMC MOBS 6P4, Isinglass, Funori samples. Image: Lora Angelova.

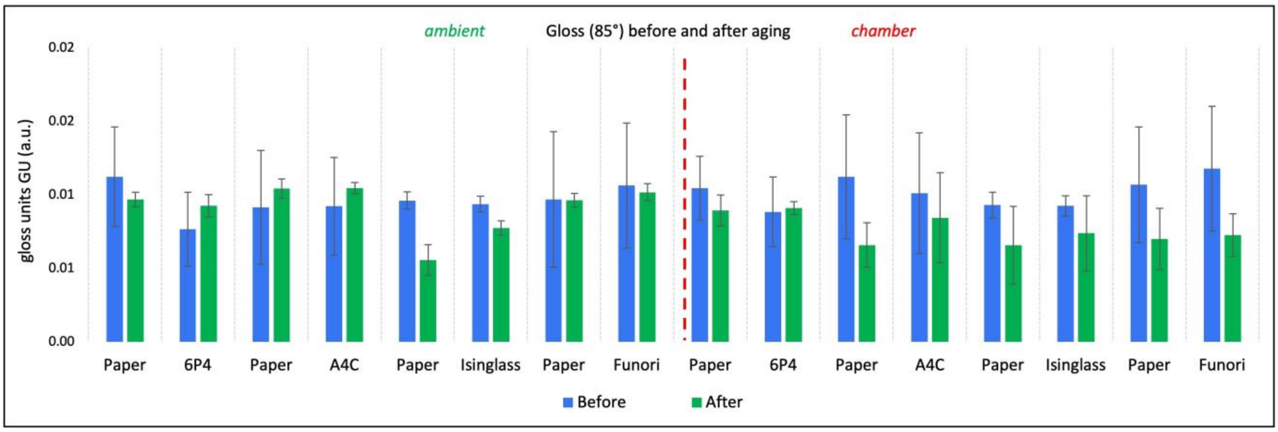

Figure 7. Gloss change (measured in gloss units (GU) along the vertical axis) of the samples after the application of the consolidation medium on paper before (blue) and after (green) aging (dark ambient—**left**; accelerated aging in climatic chamber—**right**).

It should be noted that dramatic Isinglass and Funori darkening in the hygro-thermal aging may be incommensurable with the thermal aging results of the cellulose ethers, and that a different testing methodology is needed. Similar dramatic changes of Funori have been reported in a previous thermal aging study [37] without explaining the darkening mechanism and reasons. Arguably, the dramatic darkening of Funori may be explained by the Maillard "cooking" reactions, which take place between the carbohydrates and proteins at elevated temperatures (similar "cooking" reactions make butter croissants brown). Funori is a polysaccharide, but contains around 12% and Jun-Funori 1.3% of proteins [38], which may play an important role in discoloration. Typically, the Maillard reactions require around 120 °C dry, however in this testing, 80 °C combined with an extended period of time and an elevated humidity (90 days, 80 °C, 65% RH) might have sufficed for the Maillard reactions to take place [39–41]. This may explain the dramatic discoloration of Funori, suggesting that light-based (non-thermal) aging would be appropriate. However, like all artificial aging studies, the results need to be viewed as relative and potential, rather than absolute and certain, as currently available methodologies do not allow the translation of artificial aging to aging under natural conditions [5,42].

3.3.2. Assessment of Consolidation Treatment

To assess optical changes related to consolidation treatment, mock-up samples were prepared using soft Cobalt blue pastel (not analysed) on 100% Cotton Archival Rag Endleaf paper (Figure 8). Pastel was selected as a model, because ultrasonic misting is frequently used to stabilize pastels and other friable media, and pastel presents readily available powdery material with high pigment volume concentration (PVC) and particulate matter (PM) mass, which allowed the revealing of colour, gloss, and mass changes, as well as an assessment of the effectiveness of the treatment.

Three consolidants (Methocel A4C, MOBS 3P4, MOBS 6P4) were applied by brushing (2 wt% and 4 wt%) and misting (1.5 wt% and 3.5 wt%) using a pneumatic (1.6 Bar) nebulizer, and A4C was only brush-applied, as it could not be nebulized at 1.5 and 3.5 wt%. (Figure 9). Application with a brush invariably led to the removal of some pigment particles and deposition of the misted consolidant sometimes was uneven, as seen under the microscope. Colour and gloss measurements were taken with the instruments described above (Section 2). The application of three consolidants slightly modified the colour (increase in b*, decrease in L*) (Figure 10) and increased the gloss (Figure 11).

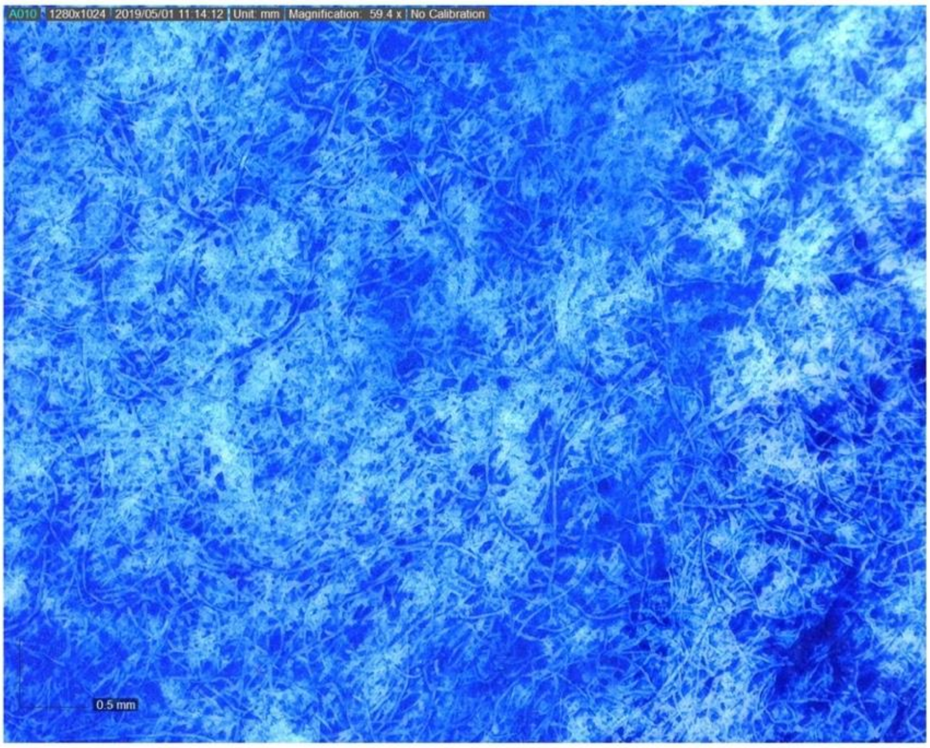

Figure 8. Stereo microscope image of cobalt blue pastel (not analysed) on 100% Cotton Archival Rag Endleaf paper after consolidation using MOBS 3P3 3.5 wt%. Image: Lucia Pereira Pardo.

Figure 9. Methocel A4C, MOBS 3P4, and MOBS 6P4 were applied by brushing (2 wt%, 4 wt%) and misting (1.5 wt%, 3.5 wt%), A4C was only brush-applied (2 wt%, 4 wt%). Image: Lucia Pereira Pardo.

Peeling tests were performed on the paint samples to assess the efficiency of the consolidation, by weighting the amount of pigment removed after the peeling of a 1 × 4 cm generic paper pressure sensitive tape, adhered to the surface of the sample (Figure 12). The consolidation media was brush applied, as misting A4C at 2 wt% is not possible. Both 3P4 and 6P4 were efficient at improving the adhesion of the pigment and performed better than A4C. After consolidation with 2 wt% 3P4 the tape removed 0.5 mg of powdery pigment and 1.4 mg after the consolidation with A4C at 2 wt%.

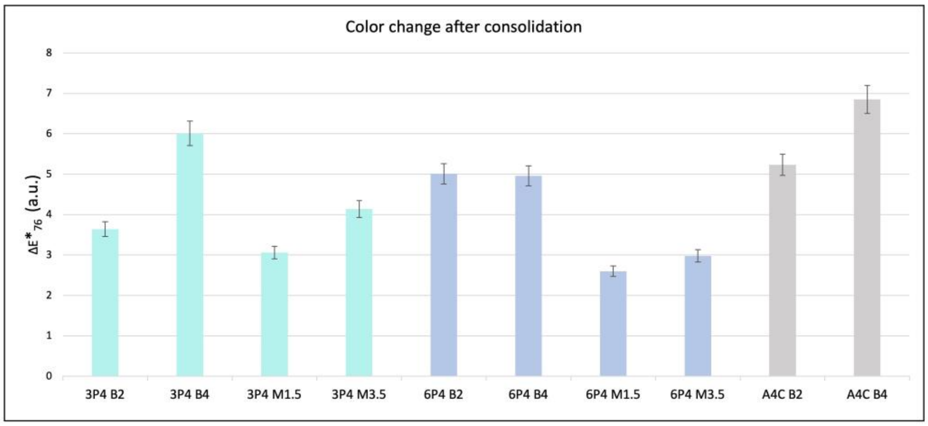

Figure 10. Colour change of the mock-up paint samples after consolidation (B2: brushed 2 wt%; B4: brushed 4 wt%; M1.5: misted 1.5 wt%; M3.5: misted 3.5 wt%).

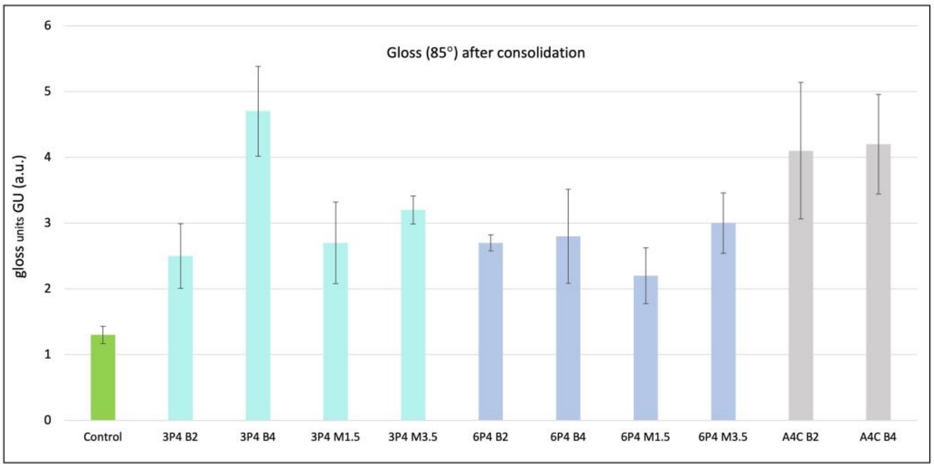

Figure 11. Gloss change after consolidation (B2: brushed 2 wt%; B4: brushed 4 wt%; M1.5: misted 1.5 wt%; M3.5: misted 3.5 wt%).

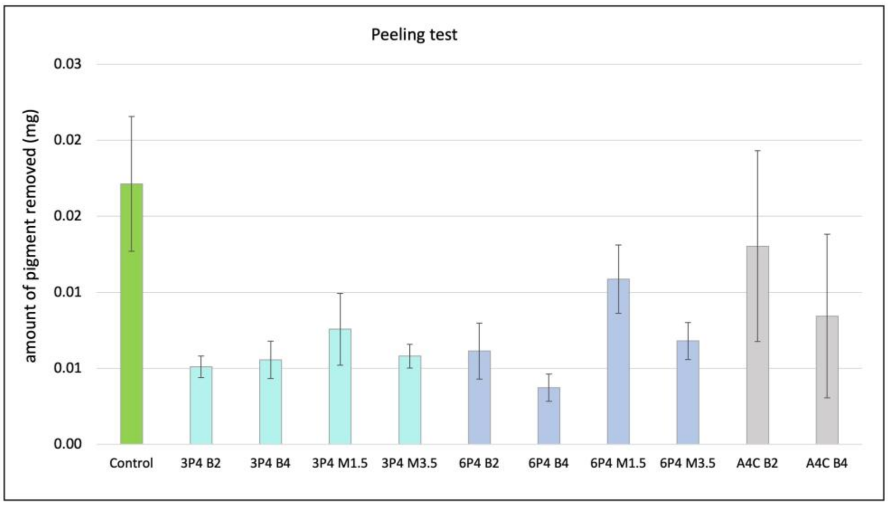

Figure 12. Results of the peeling test (mg of pigment removed): B2: brush applied 2 wt%; B4: brush applied 4 wt%, M1.5: misted 1.5 wt%, M3.5: misted 3.5 wt%.

The testing method (manually applying and peeling the pressure-sensitive tape) is simple and practical for conservators, but is limited, as it is difficult to reproduce with a high degree of accuracy because the force applied when pressing and peeling the tape manually, will vary to some degree. For more repeatable result, the same test was repeated three times, and the average value was used. Additionally, only one pastel material was tested, and other pigments and paints may produce different results, which should be addressed in future studies.

4. Two Case Studies: Consolidation Treatments Using Novel ULV-HPMC Materials

In further discussed conservation treatments, MOBS 6P4 was used at 3.5 wt% in water (1:1 mixture with Isinglass 0.7 wt%) and 3P4 at 5 wt% (nebulized) and 2.5 wt% (brush applied). However, in actual treatments, the wt% of HPMC-ULV medium needs to be established empirically and tailored for each case.

4.1. Edvard Munch's Alma Mater Study

The "Alma Mater" (1912–14), oil on canvas, 122.1 × 101 cm, M 881/Woll M 311, Munch Museum), treated by the author at the Munch Museum in 2017, presented particular consolidation challenges. When Edvard Munch bequeathed his collection to the city of Oslo in 1944, many of the artworks were in poor condition, caused by Munch's experimental techniques, the lack of storage facilities, and the artist's negligence, much commented on by his friends. The poor condition of some paintings in the collection was exacerbated by Munch's practices known as the "kill-or-cure remedy," which is understood as an intentional weathering [43–45]. Diverse Edvard Munch paintings in the collection are extremely fragile, with matte, underbound, and water-sensitive surfaces, which require frequent consolidation treatments, and the Munch Museum conservation department has a long history of successful consolidation practices using Isinglass, Funori, and ultrasonic misting.

Edvard Munch's Alma Mater study is painted on a medium weight plain weave linen canvas. The painting has thin white ground, applied by the artist. The ground is matte and porous (not analysed) and under the microscope resembles the typical white grounds used by Munch, where animal glue and linseed oil, and zinc white, lead white, and chalk were identified [3]. Loose, freehand underdrawing was executed with a dry medium, probably charcoal, and is visible in the figure areas where the paint was skipped. The painting medium appears visually to be oil. The paint was loosely applied in opaque brushstrokes and washes. The painting is unvarnished. The off-white ground is underbound and has extensive micro-flaking. The areas covered with the paint are in better condition. The surface has stains from pre-existing water damage which likely occurred while the painting was at Munch's studio, and thus deemed inherent to the painting. The Alma Mater study ground and the white paint was exceptionally friable, exhibiting extensive micro-flaking. Even minimal physical contact with the surface could have led to the displacement of flaking paint fragments. Moreover, the white ground was water sensitive, and there were concerns that extensive contact with water may stain the white surface by leaching coloured materials from the canvas. It was decided, therefore to consolidate the paint with a minimal amount of water-based consolidation media, using an AGS 2000 ultrasonic nebulizer with a fixed droplet size of around 5 µm. The treatment started by testing MOBS 6P4 on mock-ups, brush-applied and misted, using an AGS 2000 ultrasonic nebulizer. Diverse concentrations in water were tested empirically, using mixtures of water, ethanol, and isopropanol. For the benchmarking of MOBS 6P4 for the treatment, several alternative consolidants (Funori, Isinglass, Aquazol®-200, Lascaux® medium for consolidation) were used.

Consolidants were first applied on a mock-up, prepared with natural yellow ochre and Isinglass at 4 wt% paint, which was applied diluted on canvas (Figure 13). While protein binder had been used by Edvard Munch for his grounds [3], the mock-up did not aim to reproduce a historically accurate paint sample. The aim was to produce an effective "testing ground" with high pigment volume concentration (PVC) to allow for the identification of optical changes after consolidation. For this purpose, the pigment volume concentration PVC in the mock-up must exceed the critical pigment volume concentration (CPVC). High PVC paint typically appears matte and has voids due to the insufficient amount of polymer compared with pigments and tends to change optically when the void spaces between pigment particles are filled with consolidation media [46]. In the choice of the pigment, it was considered that, as the pigment density increases, CPVC decreases. Therefore, to produce an effectively high PVC paint mock-up, a less dense pigment, such as yellow ochre (c. 2.3 g/cm^3) would be an optimal choice, as it changes more than denser zinc white (c. 5.61 g/cm^3), when the same volume of medium is added, and allows for the identification of the consolidant and application method which would produce the least changes.

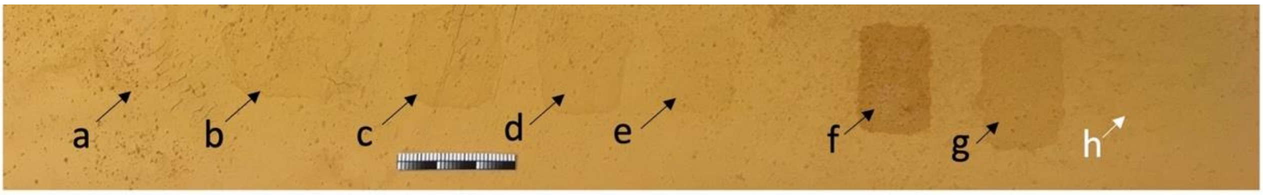

Figure 13. Consolidation tests on matte powdery natural yellow ochre and Isinglass glue tempera paint mock-up. Testing consolidation materials—a: Funori in water 3 wt% brushed, b: Isinglass in water 0.7 wt% brushed, c: MOBS 3P4 in water 3.5 wt% brushed, d: MOBS 3P4 3.5%/Isinglass 0.7 wt% in water, brushed, e: MOBS 3P4 3.5 wt%/Isinglass 0.7 wt% in water, misted, f: Lascaux® medium for consolidation in water, brushed, g: Aquazol-200 4 wt% in ethanol, brushed, h (marked white): MOBS 6P4 4 wt% in water, misted (result deemed optimal for the treatment).

The highest concentration of MOBS 6P4 in water that was possible to nebulize using the AGS2000 tool was 6%. MOBS 6P4 was tested alone and mixed with a small amount of Isinglass. Diverse concentration and proportions between MOBS 6P4 and Isinglass were tested. The stability of the paint flakes after the consolidation was tested physically under the microscope (by gently touching with a thin wooden stick). Based on visual observation and physical testing under the microscope, the optimal formula for the treatment was found at around 3.5 wt% of MOBS 6P4 mixed with 0.7 wt% of Isinglass in water (1:1 ratio). Misting treatment was carried out under the microscope. A grid made out of red threads and small pending weights was used to divide the painting into sections and to track the progress (Figure 14). The micro-flaking was typically stabilized in 1–2 applications, without visible changes to the paint. Mixtures of water and ethanol were reported to reduce the size of size droplets in ultrasonic misting [47], but in this testing, the addition of ethanol did not produce noticeable improvements, and the misting tended to be stable at room temperature, without the use of a heated hose.

Figure 14. Edvard Munch Alma Mater, figure study (1912) oil on canvas M 881/Woll M 311 © Munch Museum. Edvard Munch "Alma Mater" (**left**), application of ULV-HPMC using ultrasonic misting on "Alma Mater" (**centre**) of the grid coordinate system, used to map the consolidation process (**right**).

4.2. Two 19th C. Unvarnished Traditional Thai Thotsachat Gouache Paintings on Panel, Thai Thotsachat, 57.4 × 46.7 cm, Gouache and Gilding on Panel (IS.43-2005), Victoria & Albert Museum, London

The treatment was carried out in 2019 by paintings conservator Carolina Jimenez Gray on two 19th c. unvarnished gouache paintings on panel, depicting scenes from the last ten of the Buddha's former lives (Figure 15) [48]. In both paintings the preparatory layers consisted of white ground and thinly applied blue priming. The paint was applied in thin flat layers with finely drawn lines and some gilded elements. Both paintings were in poor condition, the ground and paint were extremely fragile, were tenting and delaminating, and would disintegrate with the slightest touch. The treatment started with the use of a pressure-based Pari Boy nebulizer and ethylhydroxyethylcellulose (EHEC) (Bermocoll e230fq, viscosity 260-360 mPa·s at 2% 20 °C) at 1 wt% in deionized water and ethanol, but, according to the conservator, the results were unsatisfactory.

Figure 15. Thai Thotsachat, 57.4 × 46.7 cm, gouache and gilding on panel (IS.43-2005), Victoria & Albert Museum, London. Overall view before stabilization treatment (**left**), a detail of upper right quadrant before (**centre**) and after consolidation (**right**). © Victoria and Albert Museum, London, United Kingdom. Images: Carolina Jimenez Gray.

The new approach was taken using ultra-low viscosity MOBS 3P4. The treatment included pre-misting with ethanol and water 1:1, followed by misting 3P4 at 5 wt% in water. The paint was left to dry under pressure, and the further consolidation continued using local brush applications of 3P4 at 2.5 wt%. While adding ethanol to the MOBS 3P4 did not produce a noticeable improvement, the pre-misting with a mixture of water and ethanol (1:1) seemed to improve the penetration of HPMC into and within the powdery layer in a second step. The treatment was successful, 3P4 did not alter the colour and gloss in both brushed and misted applications, and it was possible to nebulize ULV-HPMC at higher concentration (5 wt%) than traditional materials, which can be typically nebulized at 0.1–1 wt% [10,13,14].

5. Results and Discussion

This study introduced a new group of ecologically sustainable conservation materials, ultra-low viscosity cellulose ethers for the consolidation of matte powdery media and conducted pilot testing on two HPMC (MOBS 3P4 and 6P4) materials. Two challenging consolidation treatments were successfully carried out at the Munch Museum and the V&A Museum by misting novel, ultra-low viscosity HPMC-based solutions. In contrast with traditional consolidation media, such as Isinglass or A4C, the ULV-HPMC materials can be nebulized at considerably higher concentrations [49]

The new approach, using green ultra-low viscosity materials, allows one to limit the exposure to water and reduce the risks related to repeated applications. The peel test suggests the desirable adhesive and cohesive properties of the ULV-HPMC material, and MOBS 6P4 outperformed A4C. Other benefits include inertness and chemical stability, low molecular weight, good film-forming properties, suitable pH range, and good wetting properties. $\Delta E^{*}{}_{76}$ HPMC is soluble in water, ethanol, iso-propanol, and solutions remain stable under a broad pH range. The new materials are resistant to enzymatic and microbiological activity and in thermal aging testing, HPMC appears to be of similar stability as A4C, as noted earlier by Feller [5]. MOBS 6P4 outperformed A4C by a small margin ($\Delta E^{*}{}_{76}$: 6P4: 0.3 vs. A4C: 1.25).

While the increase of consolidant concentration from 0.1–0.25 wt% (traditional misting treatments using A4C) to 3.5 wt% (Edvard Munch treatment) or to 6 wt% (top MOBS 6P4 concentration using AGS-2000) may appear a small improvement, the major breakthrough is that the paint could be stabilized in 1–2 misting applications instead of 10 or more repeated applications, which typically are required when using high viscosity materials [10,13,14,49]. The decrease of water exposure could reach 400–900% (1–2 applications vs. 10), which is can be considered a significant improvement when treating water-sensitive surfaces. Further research is needed to assess the benefits of ULV cellulose ether materials in detail, expanding the range of tested cultural heritage materials, substrates, and testing methods. Additional information on adhesive properties and consolidation effectiveness could be obtained by micro-scratch testing. UV microscopy and tagging can be used to trace the penetration and distribution of the consolidation media into the substrates. Furthermore, a portable nuclear magnetic resonance NMR system (NMR Mouse) allows one to assess the consolidation effectiveness non-invasively, based on the proton density and chemical environment in a material [50,51]. Using NMR Mouse is feasible to assess mock-ups over 50 μm [52]. Furthermore, testing using UV labelling coupled with cross-section and fluorescence microscopy would allow one to investigate the penetration and distribution of the novel adhesive in the paint matrix. Since shock and vibration are among the major threats to the underbound paint during handling and transportation, the consolidated samples could be exposed to typical vibration frequencies and intensities so as to measure the mass loss and correlate it to concentration and type of consolidation medium and the method of application.

This pilot investigation was a first step in the introduction of two new ultra-low viscosity HPMC (MOBS 6P4 and 3P4) materials for the consolidation of sensitive unstable porous and powdery media. They appear worthy of further study and testing, as do other identified ULV materials such as Aquazol-5 (5 mPa·s), Shin-Etsu Metolose SM4 Methylcellulose (4 mPa·s), as well as low molecular weight Methocel HPMC grades, such as Methocel E3 Premium LV, E5 Premium LV. These all present the potential to supply conservators with novel ULV consolidants for stabilisation treatments. ULV is an important factor in the effectiveness and safety of consolidation treatment and the avoidance of undesirable physical and optical changes to sensitive media. While the new ULV-HPMC materials investigated in this pilot study present new opportunities for conservators, as with any other materials or method, it cannot be expected that they will be suitable for every situation. The range of applicability needs to be established by future testing and validation in in bench practice, which is a work in progress.

6. Conclusions

The climate crisis and unsustainable living increasingly threaten tangible cultural heritage worldwide. Many unstable sensitive materials cannot tolerate brush-applied liquid-phase consolidation materials, waters and organic solvents. Conservators, equipped with only traditional materials and methods, increasingly encounter sensitive surfaces which cannot be stabilized without unacceptable physical and optical changes. Developing non-contact aerosol-based methods which employ green and sustainable materials presents new opportunities to conservators. This study introduced new ecologically sustainable HPMC materials to stabilize sensitive porous media in a non-contact and minimally invasive way. New ULV-HPMC materials have potential application in conservation of paintings, paper, objects, and modern and contemporary materials. Novel ULV-HPMC materials can be nebulized at higher concentrations and tend to diffuse better than the available high viscosity consolidants. ULV materials reduce the treatment risks related to repeated exposure of sensitive substrate to water and liquids, which is an outcome of multiple re-applications of diluted high viscosity consolidants. The peel test showed desirable cohesive properties, and other benefits include low molecular weight, inertness, good film-forming properties, suitable pH range, and good wetting properties. ULV-HPMC is soluble in water, and greener solvents, such as ethanol, isopropanol. ULV-HPMC solutions remain stable under a broad pH range, and ULV-HPMC is resistant to enzymatic and microbiological activity. In the hygro-thermal accelerated aging, ULV-HPMC MOBS 6P4 marginally outperformed Methocel A4C, considered to be one of the most stable biopolymers in conservation. Notably, novel ULV-HPMC biopolymers are relatively low-cost, safe for conservator's health and the environment, and derive from renewable and sustainable sources. All of which resonates with the ICOM-CC's Melbourne 2014 declaration, European Green Deal, and the UN's Sustainable Development Goals, emphasizing the need of technological innovation in treatment materials and methods as a driver for greener and more sustainable cultural heritage conservation.

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