

## LOW MOLECULAR WEIGHT CELLULOSE ETHERS AS AEROSOLS FOR THE CONSOLIDATION OF COHESIVELY WEAK PAINT LAYERS

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### Abstract

*Due to Edvard Munch's (1863-1944) unconventional painting technique, choice of materials, and the unstable climate conditions of his studios, where the paintings were stored during his lifetime, many of his paintings, now housed at MUNCH, have cohesively weak and loose paint layers. As a result, consolidation and re-adhesion of these fragile paint layers are the most frequently performed conservation treatments on his paintings. A selection of low molecular weight (lmw) hydroxypropyl methylcellulose ethers (HPMC), new to the field of conservation, have been evaluated in comparison to methylcellulose (MC) A4C and sturgeon glue regarding their suitability for the consolidation of cohesively weak paint layers. The mock-ups used for these investigations were of a similar composition (pigment, binding medium and pigment-binding medium ratio) and porosity to a paint sample from the painting "Beach Landscape with Trees and Boats" from 1905-06 by Edvard Munch.*

*Viscosity and surface tension of aqueous solutions of the consolidants and their influence on the imbibition time and depth into porous paint layers were investigated. Fluorescence labelling was used to visualize the imbibition depth of an aqueous solution of the lmw HPMC E3 and MC A4C, applied as an aerosol. With this method it could be shown that the applied amount and the application method of the consolidant (with or without intermediate drying steps) can play a crucial role in the imbibition depth. To evaluate the consolidation effect of the tested polymers, the aerosols of their aqueous solutions were applied on the paint mock-ups in a reproducible and standardized way, using an automated two-axis-table. A customised abrasion test was developed to evaluate the comparative increase of the paint layer cohesion after consolidation. These preliminary investigations show lmw HPMC as promising alternatives to established consolidants. They allow for an ultrasonic nebulisation in higher concentrations and thus for the paint layer's consolidation in a lower number of applications.*

**Keywords:** Consolidation; Cohesively weak paint layers; Low molecular weight; Hydroxypropyl methylcellulose ethers; Imbibition; Viscosity; Surface tension; Fluorescence labelling

### Introduction

Paint layers with little or no binding medium are both porous and matt. They inherently are, or can become, cohesively weak. Cultural assets exhibiting cohesively weak paint layers

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(chalking, powdering and crumbling) have diverse geographic origins, belong to various epochs, and exhibit a wide range of material compositions.

They include ethnological and archaeological cultural assets; illuminated manuscripts; Netherlandish tuchlein [1]; Aboriginal bark paintings [2]; Egyptian sarcophagi [3]; wall paintings [4]; works on paper like wallpapers [5]; pastel [1, 6], charcoal, and chalk drawings [6]; painted historical interiors [7]; painted sculptures [8, 9]; and paintings by modern [10-13] as well as contemporary artists [6, 14-16].

The quest for a brighter, matt appearance of the painting surface, led artists such as Edvard Munch (1863-1944) to use paints with low proportions of binding medium, dilute the paint extensively, add chalk to the paint, or paint on highly absorbent supports [11, 12, 17, 18]. In such cases the available binding medium might not be sufficient to create a continuous pigment-binding film, resulting in porous paint layers with a low cohesion. The painting “Beach Landscape with Trees and Boats”, which has been used as a starting point for the creation of paint mock-ups in this study, is an example of E. Munch’s unconventional painting technique. He applied the liquid paint, prepared with a low amount of binding medium, directly onto an unprimed canvas.

The binder in porous paints has a higher surface contact with the environment, making it more susceptible to degradation. Environmental factors (i.e., temperature, relative humidity, light, pollutants) [19] mechanical stress (vibration and shock) [20, 21], the presence of certain additives or pigments [22] and conservation practices [23] (exposure to solvents, moisture, heat, pressure) can accelerate the degradation process of the binding medium.

One conservation strategy, when binder degradation leads to the risk of paint loss, is a consolidation treatment. In conservation literature the term consolidation is frequently used both for the strengthening of a cohesively weak material and the re-adhering of two recognisable surfaces of the same or two different materials (e.g., a paint layer fragment flaking off the ground layer) [24]. In the current study and based on the definition by Horie [25], consolidation is understood as the conversion of a cohesively weak substrate into a coherent whole by the incorporation of a material which creates or improves internal bonding.

To consolidate porous and cohesively weak paint layers, conservators apply a liquid consolidant (consisting of a polymer and a solvent) onto the surface of the paint layer with a brush, as a spray or as an aerosol, hoping that the introduced polymer will distribute and strengthen the material evenly, without compromising the surface’s optical properties. Practical consolidation treatments, however, are carried out without the possibility to assess the polymers imbibition and the final distribution and deposition after solvent evaporation.

Imbibition is defined as the displacement of the non-wetting phase (here air) by the wetting phase (here the aqueous polymer solution) in a porous medium by capillary forces [26]. In the context of consolidation, *imbibition* is therefore the more precise designation than the often-used term *penetration*.

Ultrasonic misters transform liquids into an aerosol and have been widely used for the consolidation of cohesively weak paint layers since the 1990’s [1, 14, 27-34]. The use of aerosols allows for a fine dosing and contact free application of consolidants, making this method particularly suitable for the consolidation of cohesively weak paint layers, which are often sensitive to mechanical stress.

Every polymer has its individual concentration maximum at which it can still be nebulised with an ultrasonic mister. Traditional consolidants such as gelatine, sturgeon glue, methylcellulose (MC), funori or JunFunori® can only be nebulised at low concentrations.<sup>2</sup> This can lead to the necessity of multiple aerosol applications to achieve the desired consolidation

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<sup>1</sup> SG 1.5%, Gelatine 1.5%, MC A4C 0.2%, Funori 0.2%, JunFunori® 0.1% using the AGS 2000 ultrasonic mister [6, 32].

effect [28, 32, 33, 35], resulting in long treatment durations and the paint layer's repetitive exposure to solvents. This observation prompted the investigation of hydroxypropyl methylcellulose ethers (HPMC), which are available in a wide range of average molecular weights, resulting in different viscosities in solution of the same concentration. Particularly the low molecular weight (lmw) HPMC were found to be interesting in the context of aerosol application of consolidants, as they can be nebulised in comparably high concentrations.

In this study, a selection of lmw HPMC (E3, E5, E15 and E50) with different average molecular weights were investigated in comparison to MC A4C and sturgeon glue (SG). Parameters such as their physicochemical properties – viscosity and surface tension, *maximal nebulisable concentration*, imbibition time, imbibition depth and consolidation effect were systematically compared.

The overall aim of this project was to contribute to the knowledge that supports conservators in their effort to choose and modify materials and techniques for consolidation in a more targeted way.

#### **Low molecular weight cellulose ethers**

The use of lmw cellulose ethers in conservation is not new [36-40] but no systematic study of their properties has been published.

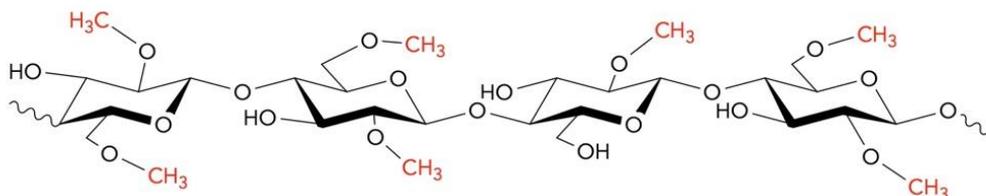
Low molecular weight cellulose ethers are produced through a controlled oxidative depolymerisation of higher molecular weight cellulose ethers [41]. Cellulose ethers are polydisperse, as it is technically complex to produce polymer molecules with uniform chain length [42]. The average molecular weight of a polymer reflects its average degree of polymerisation and has an important influence on the viscosity of its solution. Solutions of lower molecular weight cellulose ethers have comparatively lower viscosities [43]. Cellulose ethers are usually categorized into low, medium, and high viscosity types according to their viscosity at 2% (w/v) in aqueous solution at 20°C [43]. *T. Wüstenberg* [41] proposes the following differentiation for the methylated cellulose ethers MC and HPMC (Table 1).

**Table 1.** Definition of MC and HPMC designations in terms of viscosity [41]

Designation	Viscosity 2% (w/v) in H <sub>2</sub> O at 20°C (mPa·s)
Low viscous	6-100
Medium viscous	400-4,000
High viscous	15,000-250,000

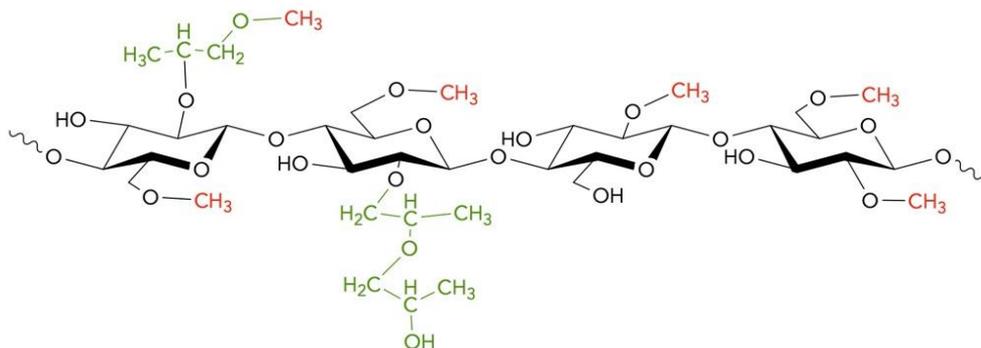
For the current research, where polymer solutions at different concentrations are compared, it is clearer to describe the evaluated materials in low, medium and high molecular weight categories.

Methylcellulose ethers are produced from native cellulose through the etherification of hydroxyl groups in the  $\beta$ -D-glucose units (AGU, anhydrous glucose unit) with methyl groups (-OCH<sub>3</sub>) (Fig. 1). The degree of substitution of the water-soluble MC varies between 1.3-2.6 methyl groups per AGU, making up a gravimetric content of 25-33% [41].



**Fig. 1.** Molecular structure of a methylcellulose. In total seven hydroxyl groups of the four AGU's have been substituted with methyl groups (red) resulting in an average degree of substitution (DS) of 1.75 (meaning that in average 1.75 of the 3 free hydroxyl groups per AGU have been substituted) [41]

HPMC are chemically related to MC. However, in HPMC the hydroxyl groups are not only substituted with methyl but additionally with hydroxypropyl groups ( $-\text{OCH}_2\text{CHOHCH}_3$ ) (Fig. 2). The degree of substitution varies between 1.5-2. HPMC have with 19-30% similar gravimetric content of methyl groups like the MC, but additionally contain 3-12% hydroxyl groups [41].



**Fig. 2.** Molecular structure of a hydroxypropyl methylcellulose. In total seven hydroxyl groups of the four AGU's have been substituted: two with hydroxypropyl groups (green) and five with methyl groups (red). In addition, two hydroxyl groups of the hydroxypropyl groups have been further substituted with one methyl (red) and one hydroxypropyl group (green). The presented molecule has an average degree of substitution (DS) of 1.75 but a differing molar substitution (MS) of 0.75 for the hydroxypropyl groups and 1.5 for the methyl groups [41]

Surprisingly HPMC have rarely been used in conservation, although Feller and Wilt reported in 1990 that „*Hydroxypropylmethylcellulose (HPMC) products that are largely of methylcellulose composition with only a modest percentage of hydroxypropyl substitution tend to possess high stability equal to or better than methylcellulose*” [43]. Only recently HPMC have been tested for their suitability in the contexts of paint layer consolidation [44], single-thread tear mending [45] and wood bonding [46].

## Experimental part

### Materials

#### Mock-ups

Mock-ups were prepared to mimic the materiality and porosity of a paint area in the painting “Beach Landscape with Trees and Boats” (Woll 637) from 1905-1906 by Edvard Munch. These were prepared with a 2:1 (w/w) mixture of synthetic ultramarine blue dark pigment (#45010, *Kremer Pigmente*) and casein (#7555.2, *Carl Roth*) 3% (w/w) in water on flax canvas. The preparation of the mock-ups is described in detail in C.N. Stahmann et al. [47].

#### Consolidants

In total six polymer products were investigated (Table 2). Namely the semi-synthetic cellulose ethers HPMC VIVAPHARM® E3, E5, E15, E50 from *JRS Pharma*, MC METHOCEL™ A4C from *Dow* (today *DuPont*) as well as the proteinaceous (collagen) sturgeon glue from *Störleim Manufaktur*. The sturgeon glue film, used for the preparation of the polymer solution, was prepared from dried sturgeon bladders. For this the sturgeon bladders were pre-swollen in deionised water for 1 hour at  $\sim 7^\circ\text{C}$  in the fridge and cut into small pieces; the pieces were returned into the same water and left to swell for another 12-16 hours in the fridge; the mixture was warmed up to  $50\text{-}55^\circ\text{C}$  for 1-1.5 hours and subsequently up to  $70^\circ\text{C}$  for 15 minutes; the warm mixture was filtered in two steps first using a kitchen sieve and then a washed, colourless nylon sock; the still warm and filtered solution was spread thinly on a Hostaphan RNT 36 foil, placed on an heatable low-pressure table; after two hours of pre-drying at room temperature the table was heated to  $30^\circ\text{C}$  for some hours and then turned off again to

let the film dry at room temperature for another day; the film was removed from the foil and stored in a glass jar; to allow for final drying the glass jars were just loosely closed [48-52]. The solutions were prepared with deionised water in different concentrations. The cellulose ethers were initially dispersed in 80°C hot water and stirred on a magnetic stirrer until a solution was formed during cooling to room temperature. Subsequently they were cooled down to ~7°C for at least 12 hours, to allow for complete hydration. The sturgeon glue film was dissolved in deionised water prior to use (30°C).

**Table 2.** Specific properties of tested polymers as stated in the manufacturers' data sheets, if not indicated differently

Product	VIVAPHARM®				METHOCEL™	Sturgeon glue
Manufacturer	JRS Pharma/J. Rettenmaier & Söhne				Dow (DuPont)	Störleim Manufaktur
Chemical class	Hydroxypropylmethylcellulose (HPMC)				Methylcellulose (MC)	Protein
Type	E3	E5	E15	E50	A4C	/
Date of manufacture	11/'17	7/'18	3/'18	6/'18	6/'18	'18
Max. loss on drying (%)	2.5	2.1	1.3	2.7	n.a.	n.a.
Hydroxypropyl-content (%)	8.8	9.8	9.1	9.9	/	/
Methoxyl-content (%)	29.9	29.3	29.4	29.8	30.4	/
pH value	2 % (w/w) in H <sub>2</sub> O, at					
	5.8	7.0	7.3	6.2	7.3	7.1
Viscosity	20°C					
(mPa·s)	3.3	5.3	15.7	58.5	365	1.7±0.1 <sup>3</sup>
Weight average molar mass (g/mol)	15,000 <sup>4</sup>	/	/	63,000 <sup>5</sup>	212,000 <sup>6</sup>	100,000-150,000 <sup>7</sup>

## Methods

### I Physicochemical properties

#### Viscosity

The dynamic viscosity ( $\eta$ ) of the aqueous consolidant solutions was measured with an oscillating-plate viscosimeter (SV-10, A&D). The viscosity was measured at the *max. nebulisable concentrations* for all the consolidant solutions. For HPMC and MC solutions, viscosity was additionally measured at 1%, 2% and 3% (w/w). Prior to the measurements, the liquids were stirred on a magnetic stirrer for 10 seconds at 100rpm to ensure homogenisation.

#### Surface Tension

The surface tension ( $\gamma$ ) of deionised water and the aqueous consolidant solutions were measured using the pendant drop method with an OCA Optical Contact Angle Meter and the SCA 20 software from *DataPhysics GmbH, Germany*. An Injekt-F syringe (*Braun*, 1mL) with a stainless-steel cannular with a straight tip (*Fisnar Europe*, outer diameter 1.275mm) was used with an integrated automated dosing system to disperse hanging drops of the same volume (14 $\mu$ L). The surface tension of the aqueous consolidant solutions were measured at their *max. nebulisable concentration* and HPMC and MC additionally at 1%, 2% and 3% (w/w). The measurements were replicated 10 times. Prior to the measurements, the liquids were homogenised on a magnetic stirrer for 10 seconds at 100rpm.

#### Imbibition Time

The time droplets of deionised water and aqueous consolidant solutions took to imbibe into the mock-up paint layer, was measured using the Optical Contact Angle Meter OCA from

<sup>3</sup> Own measurement at 2.2% at 20°C using a SV-10.

<sup>4</sup> Measurements were performed on a HPMC Methocel E3P (*DOW*) [49]

<sup>5</sup> Measurements were performed on a HPMC Metolose 60 SH-50 (*Shin Etsu*) [49].

<sup>6</sup> Measurements were performed on a MC A4C (*DOW*) [50].

<sup>7</sup> Soppa 2018 p. 43 [24] citing: [51] Haupt 2000, [52] Geißinger and Krekel 2007 p. 323

*DataPhysics*. The integrated dosing system with the same syringe and cannula as listed above were used. Drops of the same volume (5 $\mu$ L) were dispersed and set down onto the paint layer's surface. The process was recorded with a camera and the time that the drop needed from placement to complete imbibition measured. All solutions were tested at two concentrations namely at their *max. nebulisable concentration* and at 1% (w/w). The measurements were replicated 10 times. The relative humidity (RH) during measurements varied between 50-80%.

## II Nebulisation of liquid consolidants

### Settings

For the aerosol application of the consolidant solution, the ultrasonic mister Recolo 1000 (*pfm medical hico GmbH*) was used. For all experiments the ventilation and nebulizing intensity of the device were turned to their maximum (level 4 of 4), the water reservoir was filled with water (20°C and in the case of sturgeon glue solution 40°C) to the maximum filling height and the conical insert cup was filled with 15ml of consolidant solution. The water in the reservoir and the solution in the insert cup were changed every 10 minutes as the temperature of the ultrasonic mister, and with it the temperature of the inserted liquids, rise with operating time.

### Maximal nebulisable concentration

To allow for a comparison of the consolidation effect achieved with the different polymers, it was essential to apply the same volume of consolidant solution per surface area. This was a challenging task as the ultrasonic mister's aerosol output (volume or mass per time) depends on a combination of factors such as the liquid's viscosity and surface tension. It cannot be simply standardised by choosing the same concentration or viscosity of the polymer solutions or the same device settings.

The maximal concentration at which the solutions resulted in a uniform aerosol output, was determined by measuring the mass of consolidant solution that collected in a petri dish after 10 minutes of aerosol application. For the tests the settings were used as described above. The nozzle of the mister was placed in perpendicular position with 2cm distance to a petri dish placed on a precision balance (*Kern, max. 120g d = 0.001g*). The device was run for 1 minute before recording the mass increase every minute over 10 minutes. The determined concentrations were named *max. nebulisable concentrations*, they resulted in an aerosol stream that was considered still intense enough for the use in practice (0.14-0.24g/10 minutes) (Table 3). For all polymer solutions the mass increase per minute over 10 minutes is approximately proportional to the application time. For a detailed description see C.N. Stahmann, 2021 [53].

**Table 3.** Aerosol applied mass of polymer solutions at their *max. nebulisable concentration* collected in a petri dish after 10 minutes of aerosol application measured in grams on a precision balance (SD in brackets)

Polymer	MC A4C	HPMC E50	HPMC E15	HPMC E5	HPMC E3	SG
Aerosol applied mass after 10 minutes (g)	0.17 $\pm$ 0.2	0.18 $\pm$ 0.02	0.14 $\pm$ 0.03	0.17 $\pm$ 0.01	0.17 $\pm$ 0.02	0.24 $\pm$ 0.01
Concentration (% w/w)	0.6	1.2	2.4	3.75	4.9	2.2

## III Imbibition depth

### Fluorescent labelling of CE polymers

For the investigation of the imbibition depth HPMC E3 and MC A4C were labelled with the fluorescent marker 5-(4,6-Dichlorotriazinyl)-Aminofluorescein (5-DTAF D0532-100mg *Sigma Aldrich* >90% (HPLC), CAS 21811-74-5).

5-DTAF has an emission maximum of 516nm and an absorption maximum of 492nm. It binds covalently to the hydroxyl end groups of polysaccharides and has a molecular weight of 531,73g/mol. For a detailed description of the labelling procedure of MC A4C see *K. Soppa* 2018, pp.77-81 [24]. For the labelling of the HPMC the procedure was changed: The adhesive (1.0g) was dissolved in a sodium-bicarbonate buffer (0.01M, 6mL). The fluorochrome (5-

DTAF, 3mg per 1g adhesive), dissolved in DMSO (0.25mL), was added to the adhesive dropwise during 2 hours under constant stirring (~300rpm). The labelling reaction was carried out for four days at RT in the dark. The solution was then heated to about 100°C, the precipitated HPMC was then centrifuged at about 50°C (40,000R, 60sec) to eliminate the unreacted 5-DTAF. This was done three times. The E3 dissolves quickly when cooled down. The centrifuge could not be heated higher than ~50°C, therefore a high material loss can be assumed. Subsequently, the solution was cooled down, diluted to approx. 2% and DMSO as well as the buffer agent were removed by an aqueous dialysis (fresh distilled water) in a membrane (MWCO: 4000–6000). The progress of the dialysis was controlled via measurement of the pH levels. After three days of dialysis, the content of sodium ions was nearly the same as in the unmodified adhesive. After dialysis, the solution was dried. The yield was 65%.

The impact of labelling on the viscosity and surface tension of polymer solution was assessed. Due to the low amount of available labelled polymers the viscosity of HPMC E3 could only be measured at 1% (w/w), the viscosity of MC A4C at 0.15% (w/w), using a rotational viscosimeter (*rotavisc lo vi IKA*). The surface tension of both solutions was measured at 1% (w/w).

#### *Consolidant application*

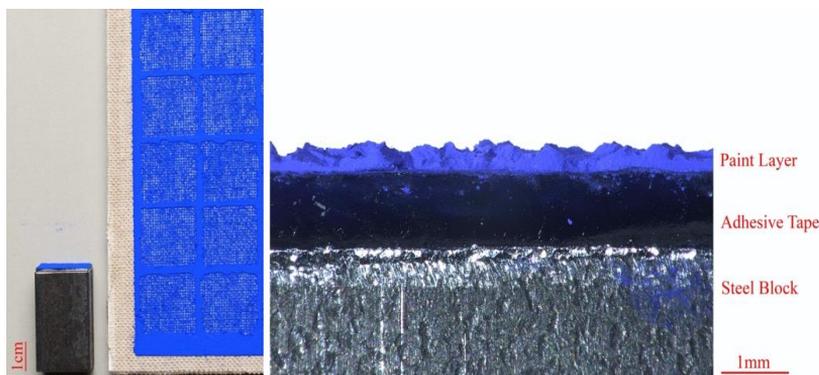
The fluorescent labelled polymer solutions HPMC E3 3.5% (w/w) and MC A4C 0.6% (w/w) were applied using the Recoilo 1000 in the settings described above. The aerosol stream was pointed onto the surface of the mock-up, in a fixed position, for different time intervals: 2 seconds, 6 seconds, and 3x2 seconds with intermediate drying of 7 minutes. The nozzle of the aerosol device was placed perpendicular with a 2cm distance to the mock-ups surface. The device was started one minute before each application, to generate a stable aerosol stream. During this time a petri dish was placed between aerosol stream and mock-up. Each application was repeated three times in three different areas, and two of the three test areas were subsequently sampled. The samples were embedded in Technovit 7100, and thin sections (25µm) were prepared with a rotary microtome (*Leitz*), following the detailed description by *K. Soppa 2018* [24]. The thin sections were secured with a transparent film (*Cloeren Technology*) and glued to microscope slides with the uncovered surface facing up with instant glue (*UHU "Blitzschnell Minis"*) and imaged using a Zeiss Axioscope 5 Fluorescent Microscope (*Colibri 3 blue LED excitation light 470nm, Zeiss 90 HE LED filter, EC Plan Neo Fluar 10x/0,3 objective, Axiocam 305 and 503 camera*).

#### *IV Consolidation effect*

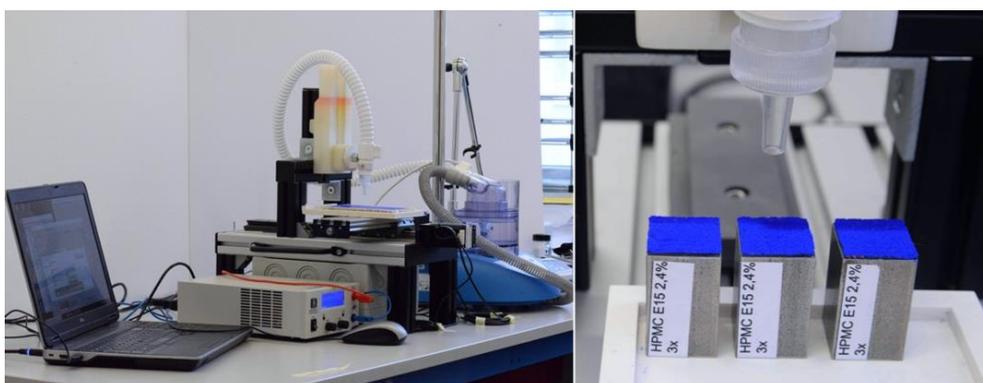
The consolidation effect was studied using a customized and standardized abrasion test. For this purpose, the original mock-ups had to be modified. The paint layer was adhered reversely onto steel blocks with double sided tape (*UHU transparent*) (Fig. 3). The steel blocks all had the same size and weight (2.0x2.0x3.2cm, 100.9±0.1g) and functioned as weights for the abrasion test. The surface of the modified mock-ups was uneven and rougher due to the canvas imprint, which after the modification was facing upwards.

The paint layers were consolidated with the consolidant solutions in their *max. nebulisable concentration* in 1 and 3 applications. The aerosol was applied using an automated two-axis-table (based on a *Proxxon KT70 CNC-ready module*) which moved the mock-ups in a defined speed (5.681mm/s) and direction (lines with a 50% overlap) underneath the running aerosol stream. The mock-ups were placed on a 3D printed tray, fixated to the two axes. Each axis was driven by a NEMA 17 stepper motor, in combination with a stepper motor driver (*Top Direct, TB6600*) and a microcontroller (*National Instruments, MyRIO-1900*). The movement sequence of the two axes were controlled through a custom software written in LabView and executed through the MyRIO-1900 controller. The nozzle of the ultrasonic mister was fixed with a 3D printed holder in a perpendicular position and with a 2cm distance to the paint layer (Fig. 4). With a nozzle diameter of 5mm and the mock-ups linear movement with a speed of 5.681mm/s an area of ~5x5.7mm is consolidated per second. With a 50% overlap, each surface

area was exposed to the aerosol stream for 2 seconds during a single application and for 6 seconds after three applications.



**Fig. 3.** Modification of mock-ups, using a steel block and double-sided tape to fixate the reversely exposed the paint layer



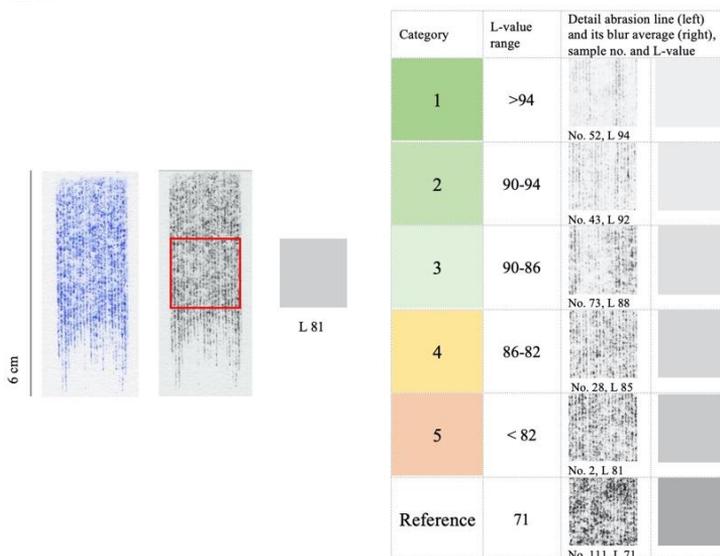
**Fig. 4.** Set-up during consolidation process with the two-axis table and ultrasonic mister (left) and three sample blocks during consolidation on a tray which moved the samples in x- and y-axis underneath the running aerosol stream (right)

Before testing the achieved consolidation effect, the paint layers were left to dry for 21 days (at 20-22 and 50-55% RH). For testing the consolidation effect a customized abrasion test was developed, based on DIN ISO 4628-7:2006-07. The steel blocks, with the consolidated paint layer facing down, were slid in a defined speed (10mm/s) for 6cm over a white Whatman® chromatography paper, using an automated film applicator.

For the image processing the paper sheets with the abrasion lines were scanned (1200dpi) and digitally processed using *Adobe Photoshop* (Fig. 5). The digital processing, based on DIN EN ISO 21227-1:2003, included: 1. grey scaling 2. setting the contrast to 100%, 3. cropping an area from the centre of the abrasion line to a defined size (18x18mm), 4. creating an average blur, 5. quantifying by measuring and documenting the L-value of the L\*a\*b colour space, which stands for the luminance or brightness component of grey values ranging from 0 (black) to 100 (white).

Five categories were defined according to the L-values (Fig. 5). The categories are ranging from **1.** L-value >94, **2.** L-value 90-94, **3.** L-value 90-86, **4.** L-value 86-82 to **5.** L-value <82. The test of non-consolidated references produced a L-value of 71. A manual abrasion test with a fine brush (with Toray white synthetic fibres, *Leonhardy, Size 0*) running over the mock-up's entire length for 3 times under the microscope showed that already category **3.** did not

show any pigment pick up upon mechanical action and thus, resulted in a *sufficient consolidation* effect.



**Fig. 5.** Abrasion test procedure, with an abrasion line on Whatman-Paper and the steps towards its quantification, including the greyscaling, cropping, creation of an average blur and measurement of the L-value (left) the categorization of the reached consolidation effects based on the L-value (right)

## Results and discussion

The results presented are valid only for the paint systems tested (synthetic ultramarine blue and 3% casein 2:1 (w/w)). Paint layers prepared with other pigments, having diverging surface energies, particle size distributions and grades of porosity might lead to different results [30].

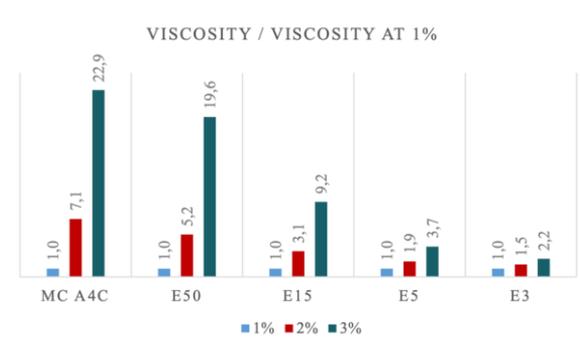
### *I Physicochemical properties*

#### *Physicochemical properties - Viscosity*

The viscosity measurements of the cellulose ether solutions at 1%, 2% and 3% (w/w) show as expected, that the viscosity is rising with increasing concentration (Fig. 6 and Table 4) [41]. When doubling the concentration from 1% to 2% (w/w) the viscosity of the low molecular weight HPMC E3 increases only 1.5 times (from 2.0 to 3.0mPa·s), whereas the viscosity of the medium molecular weight MC A4C increases 7.1 times (from 33.6 to 239.0mPa·s) (Fig. 6). The larger and more branched the involved macromolecules, the stronger the intermolecular interaction and the higher the proportion of molecules per volume unit (concentration), the higher is this internal friction and thus the viscosity [54, 55]. Sturgeon glue (1%, w/w) at 30°C has the lowest viscosity of the tested polymer solutions.

**Table 4.** Viscosity of the polymer’s aqueous solutions at 1.0, 2.0 and 3.0% (w/w) measured with an oscillating plate viscosimeter (SD in brackets)

Polymer	T (°C)	Viscosity (mPa·s)		
		1.0	2.0	3.0
MC A4C	20	33.6±0.1	239.0±11.3	769.0
HPMC E50	20	9.8±0.6	50.7±1.5	192.0
HPMC E15	20	4.2±0.3	13.2±0.8	38.5
HPMC E5	20	2.4±0.1	4.5±0.3	8.9
HPMC E3	20	2.0±0.1	3.0±0.2	4.4
SG	30	1.4	/	/



**Fig. 6.** Viscosity increase factor as a function of concentration of MC A4C and HPMC E50, E15, E5 and E3 (viscosity/viscosity at 1% (w/w))

*Physicochemical properties – surface tension*

Measurements of the surface tension show, not surprisingly, that in all cases the addition of polymers to demineralised water (71.0mN/m) produces solutions with decreased surface tension (Table 5). The addition of 1% (w/w) MC A4C or 1% (w/w) of sturgeon glue reduce the surface tension to about 61mN/m. The surface tensions of HPMC E3, E5, E15 and E50 at 1% (w/w) are all in the range of 46±1mN/m. The results show that the here tested HPMC reduce the surface tension of water more efficiently than MC A4C, which is in accordance with literature [41].

An increase in concentration of MC or HPMC only has minor additional effects in reducing the surface tension. The slight increase in surface tension of MC with rising concentration is probably caused by the high and increasing viscosity of the solutions, which make it difficult to reach equilibrium in pendant drop measurements. The high viscosities make it difficult to reach equilibrium in pendant drop measurements which can lead to higher values of the surface tension. In addition, a higher standard deviation of the results was established ±5.5mN/m (MC A4C 3% (w/w)) compared to ±0.5mN/m (HPMC E50 3% (w/w)).

**Table 5.** Surface tension of the polymer’s aqueous solutions at 1.0, 2.0 and 3.0% (w/w), all measurements were repeated 10 times if not indicated differently (SD in brackets)

Polymer	Solution T (°C)	Room T (°C)	Surface Tension (mN/m)		
			1.0	2.0	3.0
Deion. H <sub>2</sub> O	21.5	21.5	71.0 (0.1)		
<b>Concentration (% w/w)</b>			1.0	2.0	3.0
MC A4C	21.5	21.5	61.6±2.0	62.9±2.3	66.5±5.5
SG	30.0	27.0	61.5±0.8	60.7±1.0	/
HPMC E50	21.5	21.5	46.9±0.4	46.2±0.2	45.2±0.5
HPMC E15	21.5	21.5	46.0±0.1	45.6±0.2	44.7±0.2
HPMC E5	21.5	21.5	45.8±0.1	45.9±0.1	45.1±0.1
HPMC E3	21.5	21.5	45.7±0.3	/	/

*Physicochemical properties*

*Viscosity and surface tension of consolidant solutions at max. nebulisable concentration*

The viscosities of the polymer solutions in their *max. nebulisable concentrations* vary significantly. This shows that there is no uniform viscosity limit at which polymer solutions can no longer be nebulised with an ultrasonic mister. Sturgeon glue 2.2% (w/w) (30°C) has the lowest viscosity with only 1.7mPa·s and HPMC E15 2.4% (w/w) (21.5°C) the highest viscosity of 20.8mPa·s. The values of the remaining polymer solutions are distributed between the two extremes (Table 6).

**Table 6.** *Max. nebulisable concentration* of the tested polymers with ultrasonic mister Recolo 1000 and the solutions' viscosity and surface tension (SD in brackets)

Product	VIVAPHARM®				METHOCEL™	Sturgeon glue
Manufacturer	JRS Pharma/ J. Rettenmaier & Söhne				Dow (DuPont)	Störleim Manufaktur
Derivate	Hydroxypropylmethylcellulose (HPMC)				Methylcellulose (MC) A4C	
Type	E3	E5	E15	E50		
Max. nebulisable concentration (% w/w)	4.9	3.75	2.4	1.2	0.6	2.2
Viscosity (mPa·s)	9.6±0.2	13.6	20.8±0	15.2±0.5	9.7	1.7±0.1
Surface tension (mN/m)	46.8±0.4	44.8±0.1	44.9±0.2	45.9±0.3	61.6±1.4	60.7±1.0

The fluorescent labelled HPMC E3 could not be nebulised at the previously determined *max. nebulisable concentration* and therefore had to be reduced from 4.9 to 3.5%. This is likely due to the increased viscosity and/or decreased surface tension (Table 7) of HPMC E3 as a result of labelling with 5-DTAF. The MC A4C in contrast shows a slight drop in viscosity and rise in surface tension after labelling and can be nebulised at 0.6%.

**Table 7.** Viscosity and surface tension of HPMC E3 and MC A4C pure and labelled with 5-DTAF (SD in brackets)

Polymer	Viscosity (mPa·s) at 20°C and concentration (% w/w)		Surface tension (mN/m) at 21.5°C and concentration (% w/w)	
HPMC E3	<b>1.84</b>	1.0	45.7±0,3	1.0
HPMC E3 + 5-DTAF labelling	<b>2.28</b>	1.0	42.8±0,2	1.0
MC A4C	<b>1.98</b>	0.15	61.6±2.0	1.0
MC A4C + 5-DTAF labelling	<b>1.96</b>	0.15	66.3±6.2	1.0

### Imbibition Time

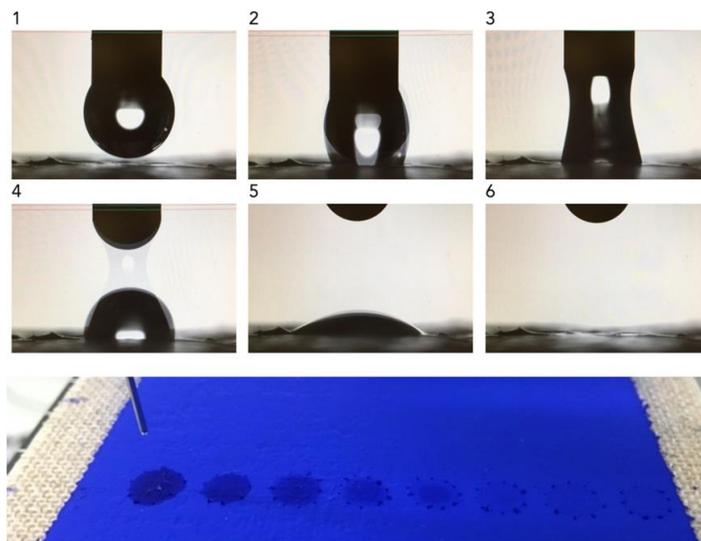
All polymer solutions spread on the paint layer. This is relevant as wetting is a precondition for capillary-driven flow and thus for the spontaneous imbibition of a liquid into a porous substrate under capillary pressure [56]. Wetting is the result of the systems tendency to minimize its free energy. For wetting to occur, the surface tension of the liquid must therefore be lower than the free surface energy of the solid [54, 57]. The successful wetting in the experiments thus indicates that the free surface energy of the paint layer, consisting of inorganic pigment with a low amount of organic binding medium, is higher than the surface tension of all tested aqueous polymer solutions (ranging from 45.1-71mN/m).

The videos of the drop application (Fig. 7) show that spreading and imbibition happen simultaneously, confirming what has been described in literature [58].

In Table 8 imbibition times and wetting fronts are listed for all substances at 1% (w/w) concentration and compared with the viscosities and surface tensions of the same solutions. The wetting front of the droplets show only minor differences, indicating a similar lateral imbibition of the liquids.

**Table 8.** Aqueous solutions at 1% (w/w) and deion. water listed according to decreasing imbibition times with viscosity, surface tension and wetting front when applied on the mock-ups surface (SD in brackets).

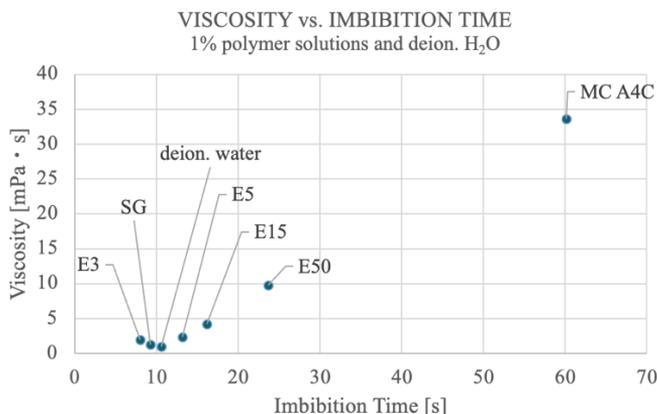
Polymer at 1% (w/w)	Solution T (°C)	Room T (°C)	Viscosity (SV) (mPa·s)	Surface tension (mN/m)	Imbibition time (s)	Wetting front ø (mm)
A4C	21-22	21.5	<b>33.6±0.1</b>	61.6±2.0	<b>60.1±6.4</b>	5.6±0.4
E50	21-22	21.5	<b>9.8±0.6</b>	46.9±0.4	<b>23.7±2.1</b>	5.6±0.4
E 15	21-22	21.5	<b>4.2±0.3</b>	46.0±0.1	<b>16.2±1.0</b>	5.6±0.5
E5	21-22	21.5	<b>2.4±0.1</b>	45.8±0.1	<b>13.2±1.7</b>	6.0±0.2
Deion. water	21-22	21.5	<b>1.0</b>	71.0±0.1	<b>10.6±1.1</b>	6.2±0.2
SG	30	27	<b>1.3±0.1</b>	61.5±0.8	<b>9.3±0.8</b>	6.0±0.0
E3	21-22	21.5	<b>2.0±0.1</b>	45.7±0.3	<b>8.0±0.9</b>	6.0±0.3



**Fig. 7.** Time stamps of video recording of drop application on the mock-up's paint layer using an OCA set-up. 1. drop approaching the surface (5 $\mu$ l), 2. drop placed on the surface, 3. and 4. setting down of drop, 5. spreading and imbibition of drop, 6. after complete imbibition of drop (top figure). Paint layer with a row of drop applications. On the right of the row, some of the drops have already dried completely, the outlines were marked with a probe (bottom figure)

Looking only at deionised water, E5, E15, E50 and A4C, a positive correlation between viscosity and imbibition time can be established, with viscosity rise leading to an increase in imbibition time (Fig. 8).

Deionised water, sturgeon glue 1% (w/w) and E3 1% (w/w) have comparable low viscosities but strongly varying surface tensions. Nevertheless, the differences in imbibition times are marginal, when considering the standard deviation (Figs. 8 and 9).



**Fig. 8.** Viscosity versus imbibition time of deion. water and the polymer solutions at 1% (w/w)

On the first look, this seems to be contradictory to the equation of the Penetration Coefficient (PC, Eq. 1), which is derived from the Lucas-Washburn Equation [59-61] and describes the distance, which a fluid penetrates a capillary tube per unit time when flowing under its own capillary pressure.

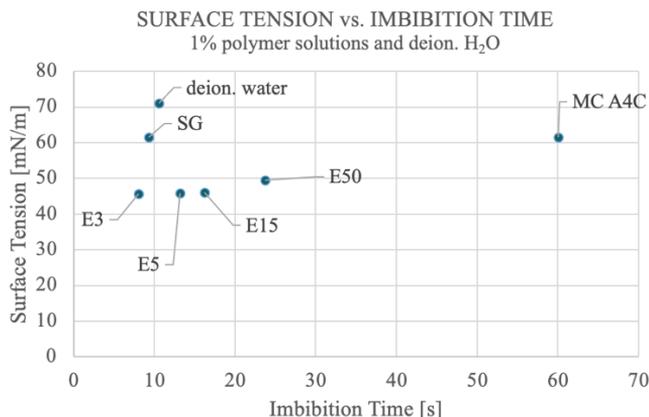


Fig. 9. Surface tension versus imbibition time of deion. water and the polymer solutions at 1% (w/w)

$$PC = \frac{\gamma \cdot \cos\theta}{\eta \cdot 2} \qquad \begin{matrix} \gamma = \text{surface tension} \\ \eta = \text{viscosity} \\ \theta = \text{contact angle} \end{matrix} \qquad [1]$$

The equation suggests that, once in a cylindrical capillary, the high surface tension of a liquid should promote its penetration rate. However, the high surface tension will also impact the wetting process, resulting in a higher contact angle  $\theta$ , and thus a reduction of  $\cos\theta$ , resulting in a lower penetration rate.

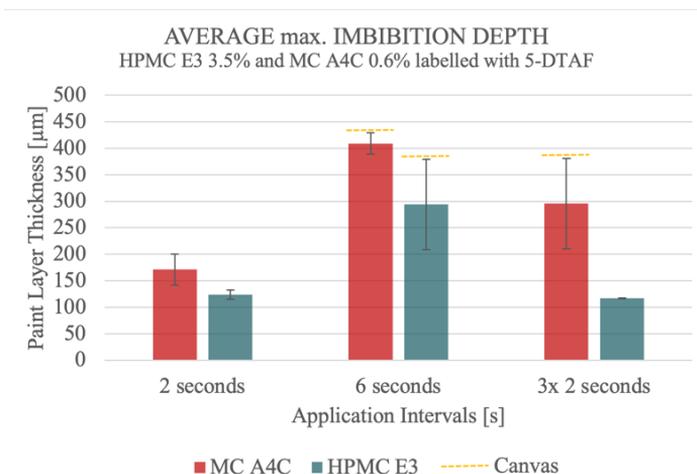
It was not possible to measure the static contact angle of the polymer solutions on the mock-up's paint layer as the applied drops immediately started imbibing the porous layer after application. The imbibition behaviour of deionised water, sturgeon glue 1% (w/w) and E3 1% (w/w) show that the contact angle has an important impact and cannot be neglected.

It needs to be considered that the Lucas-Washburn Equation and its modified forms, such as the Penetration Coefficient (PC), simplify the complex pore structure of porous media to a bundle of parallel capillaries with the same radii, to allow for predictions on capillary-driven flow in porous media [56]. In contrast, the pore structure in paint layers and most other porous media, is more complex and relevant factors, such as effective porosity, pore connectivity, tortuosity, pore radii and pore geometry are not considered.

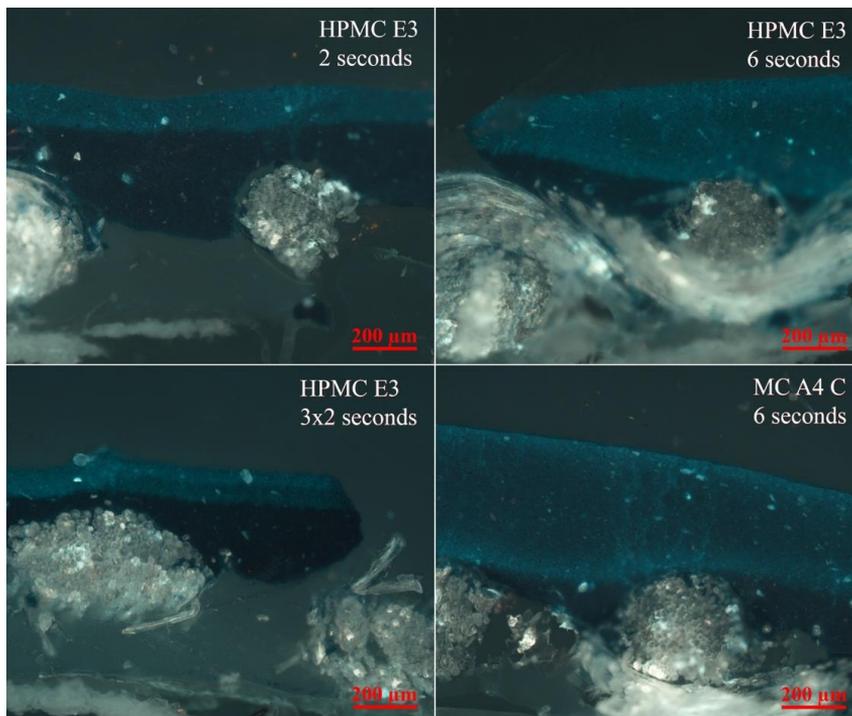
*Imbibition depth*

For each application interval two samples were investigated. The max. imbibition depth was measured and the average calculated (Figs. 10 and 11). The trends which have been observed were **1.)** The imbibition depth increases with the volume of applied consolidant. Both MC A4C and HPMC E3 double their imbibition depth when the application time is increased from 2 seconds to 6 seconds. **2.)** The application method (with or without intermediate steps) has an impact on imbibition depth. In the case of HPMC E3 the application of the same volume applied with intermediate drying steps (3x2 seconds) in comparison to a continuous application (6 seconds) shows that intermediate drying steps decrease the imbibition depth significantly, as has been previously shown by *E. Hummert et al.* [34]. In the case of the application of MC A4C solution, this effect is less clear. Both the single 6 second and the 3x2 seconds application reach a significant imbibition depth (Table 9). A reason for this different behaviour could be the higher aerosol output or the lower solid content of MC A4C. The higher volume of applied consolidant solution possibly has as a consequence that after the intermediate drying, liquid from previous applications will still be available in the pores and contribute to a deeper imbibition of the overall applied liquid.

In general, due to the low number of repeated measurements, the imbibition depth results present large deviations and should be interpreted with care. During application it has been observed that the aerosol output of the MC A4C solution was higher than that of the HPMC solution, making a direct comparison of results not viable.



**Fig. 10.** Max. imbibition depth of HPMC E3 3.5% (w/w) and MC A4C 0.6% (w/w) fluorescent labelled with 5-DTAF shown in a bar diagram with large standard deviations



**Fig. 11.** Microscope images of thin sections (blue excitation light, 6.3x magnification) of paint layer on canvas, aerosol consolidated with fluorescent labelled HPMC E3 in 3.5% aqueous solution (w/w) after 2 seconds, 6 seconds and 3x2 seconds application intervals and labelled MC A4C in 0.6% aqueous solutions (w/w) applied for 6 seconds

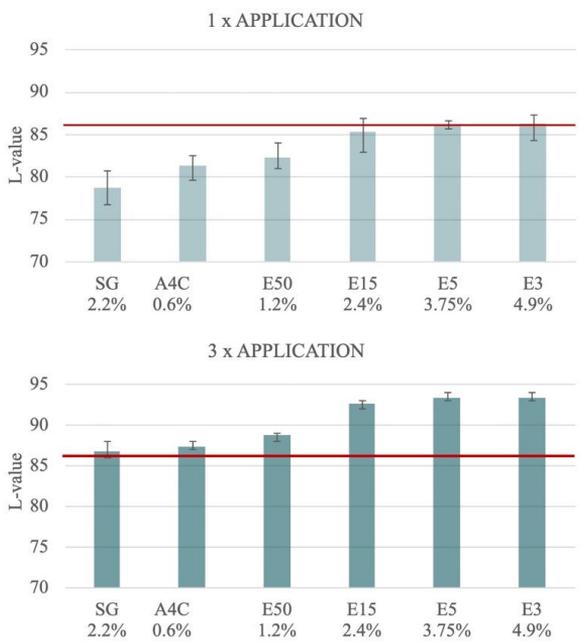
**Table 9.** Imbibition depths of aerosol applied and fluorescent labelled MC A4C and HPMC E3. Sample 1, sample 2 and average max. imbibition depths.

Polymers	MC A4C			HPMC E3		
	Average max. Imbibition depth	Sample 1 max. imbibition depth	Sample 2 max. imbibition depth	Average max. Imbibition depth	Sample 1 max. imbibition depth	Sample 2 max. imbibition depth
2 seconds	171	142	200	124	115	133
6 seconds	409	389*	429	294	209	379*
3 x 2 seconds	295.5	210	389*	117	116	117

\* Complete imbibition of paint layer

*Consolidation effect*

The paint layer that has been consolidated most efficiently shows the least abrasion and hence has the highest L-value. Test areas with a L-value higher than 86 show a *sufficient consolidation* effect. Only HPMC E3 (4.9% (w/w)), E5 (3.75% (w/w)) and nearly HPMC E15 (2.4% (w/w)), result in a *sufficient consolidation* after a single application (2 seconds). After three applications (6 seconds) all consolidants show a *sufficient consolidation* (Fig. 12).



**Fig. 12.** L-values of the abrasion lines of the consolidated mock-up paint layers. The red line indicates L-value 86, above which the paint layer shows a sufficient consolidation

**Conclusions**

In some cases, a consolidation treatment is required to prevent cumulative material loss and to preserve the physical integrity of the artwork. For planning and performing long-lasting, controllable, and targeted consolidation treatments conservators need knowledge on factors influencing the imbibition depth and distribution of consolidants in porous paint layers. The research here presented is a contribution towards this endeavour. In the following paragraphs the main conclusions are presented and discussed.

According to the Penetration Coefficient, the imbibition rate of liquids in cylindrical capillaries of the same radii depends on the liquid’s viscosity, surface tension and wetting capacity. Within the set of consolidant solutions tested on a porous paint layer, viscosity has the

most significant inversely related impact on their imbibition rate (the higher the viscosity, the lower the imbibition rate).

Imbibition depth increases with applied amount of liquid. The imbibition depth might be reduced when the same volume of liquid consolidant is applied with intermediate drying steps (here 7 minutes) instead of being applied continuously. This was the case for the higher concentrated HPMC E3 solution (3.5% (w/w)), however not for the MC A4C solution (0.6%, w/w).

The viscosities of the polymer solutions in their *max. nebulisable concentrations* vary significantly. This shows that viscosity is not the only determining property in nebulisation process. The here indicated *max. nebulisable concentrations* should not be interpreted as recommended value. The polymer and its required concentration must be chosen on case-by-case basis and with the aim of introducing as little new material as possible to the original artwork.

The tested low molecular weight cellulose ethers can be applied as aerosols in higher concentrations which allows for a sufficient consolidation effect after a single application. This will reduce the paint layer's moisture exposure and treatment durations. The amount of newly introduced material into an artwork should always be as low as possible. HPMC E15 (2.4%, w/w) and HPMC E5 (3.75%, w/w) should therefore be preferred to HPMC E3 (4.9%, w/w), all leading to a sufficient or nearly sufficient consolidation effect after one application. With MC A4C (0.6%, w/w) a similar consolidation effect can be reached after three applications. MC has proven its long-term stability in the context of conservation and should be prioritized until the long-term stability of low molecular weight HPMC ethers has been evaluated.

The target imbibition depth needs to be individually determined, based on the condition and thickness of the paint layer. Until now there is no method to evaluate the imbibition depth of a consolidant during a treatment of an original artwork. Further research is required.

### Authors contribution

This publication entails parts of the investigations performed in the context of Charlotte N. Stahmann's master's thesis, which was submitted in February 2021 at the Cologne Institute of Conservation Sciences at the Cologne University of Applied Sciences. The master's thesis was supervised by Prof. Dr. E. S. B. Ferreira and Dipl. Rest. Petra Demuth, both contributed to the development and design of the project. E.S.B. Ferreira further contributed to the drafting and writing of the manuscript. The measurements of the physicochemical properties and imbibition time were supervised by Prof. Dr. Birgit Glösen and Roxanne Engstler. Prof. Dr. Karolina Soppa performed the fluorescent labelling and consulted on their use. Eva Storevik Tveit participated in the selection of the case study "Beach Landscape with Trees and Boats". Andreas Käkel together with his students Kevin Inden, Dominik Roth and Marius Hasenbach developed and programmed the two-axis-table for the use in the context of this project. All co-authors read and made editorial comments to the paper.

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