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Distorted oil paintings and wax-resin impregnation – A kinetic study of moisture sorption and tension in canvas



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ABSTRACT

Wax-resin impregnation and lining are former widely used conservation methods. It is well-known that these methods slow down moisture diffusion into the canvas and changes the corresponding development of tension. However, the rate at which these processes happen are not well characterized and it is therefore unclear how long treated paintings are protected from high moisture environments. In the present work, moisture sorption characteristics of wax-resin impregnated linen samples were measured using dynamic vapor sorption (DVS) and tensile tests. Samples of untreated linen, wax-resin impregnated linen and Berger's Ethyl Vinyl Alcohol (BEVA) treated linen as well as an aged wax-resin treated lining canvas from 1958 were measured. The samples were in equilibrium at 42% relative humidity at 23 °C in DVS and tensiometer when the relative humidity was stepped to 69% RH while monitoring the development of mass and tension respectively in the canvases. This showed that there is no or little delay from the time moisture is taken up by linen fibers until swelling and the possible tension build up sets in. Both wax-resin impregnated and non-impregnated samples took up moisture when the relative humidity was stepped up, but the wax-resin impregnated samples did so at a much slower pace than the non-impregnated ones. Tension built up in some canvas samples already at 69% relative humidity whereas others stayed unaffected until a relative humidity of 82% was reached. The findings confirmed that a fine weave canvas, tightly spun thread and the presence of wax-resin matrix in the voids between fibers all are factors that characterize a painting at risk of climate related shrinkage damage. It was also demonstrated that BEVA gel treatment had very little effect on the rate of moisture sorption as there was no penetration of the canvas. In the aged lining canvas, moisture was taken up at a rate that was intermediate between untreated and wax-resin impregnated linen, which was ascribed to cracks in the wax-resin coating.

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1. Introduction

A wax-resin mixture is virtually non-responsive to changes in relative humidity (RH) and was therefore previously thought of as a suitable material for impregnating or lining canvas paintings that would be exposed to humidity fluctuations. However, the adverse consequences were reported early on [1–4] and many western European conservation studios discontinued the use of the technique in the 1970s and 80s [5]. Apart from colour change, weave interference and flattening of impastos conservators have also seen bulging and delamination in wax-resin treated paintings as a result of fluctuating RH because of contraction in the canvas [6]. Thus, the

treatment that was supposed to help valuable paintings withstand poor climate conditions could in fact have an adverse effect. An example is given in Fig. 1 showing buckles in a painting from Master and Fellows of Trinity Hall, Cambridge that had been strip lined with wax-resin along the edges [7].

A large number of highly valued paintings in collections worldwide have received a wax-resin impregnation or lining and are at risk of suffering problems similar to those in Fig. 1 if not kept in strictly controlled environmental conditions.

Previous research has been carried out in order to try to understand the physics behind wax-resin impregnated canvas. Tassinari showed that an unrestrained wax-resin impregnated hemp canvas can contract at high RH [8]. It was later shown that restrained wax-resin lined canvas paintings sometimes respond to high RH by building up tension [9]. These forces, induced by moisture uptake, will increase the risk of distortion and delamination in wax-resin

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Fig. 1. Gerald Festus Kelly, Lord Chancellor F.H. Maugham PC (1866–1958), circa 1939. Detail on raking light (lit from left) before treatment. By permission of the Master and Fellows of Trinity Hall, Cambridge. ©The Hamilton Kerr Institute. The painting shows bulging as a result of a local wax-resin treatment. In areas without wax-resin there was no bulging.

lined paintings [10]. Whether a painting will be damaged depends on its general propensity to shrinkage as well as the mechanical properties of the wax-resin impregnated painting structure and on weave geometry of the canvas [11]. The reason why wax-resin treated canvas is more at risk of shrinking than untreated canvas is explained by the fact that the wax-resin matrix takes up space in the weave structure and thus enhances the effect of the swelling of the fibers when they adsorb moisture [9]. A study has furthermore shown that tension in wax-resin impregnated canvas over extended periods of time can lead to stress relaxation [12] which will further increase the risk of bulging. The purpose of wax-resin treatment was to protect the painting from the degrading factors such as moisture [6]. Although this was not fully achieved, the treatment will affect the kinetics of moisture sorption. Furthermore, the damage that the developed forces will do depend on the rate at which they are introduced. Forces that are introduced over a longer period of time, for example due to changes in the ambient climate, will often lead to distortion instead of failure in the painting structure [7]. Therefore, it becomes important to understand the kinetics of the processes involved.

2. Research aim

The research questions that are addressed in the present study concerns the interaction between humidity in air and painted canvas and the performance of moisture barrier conservation treatments aimed at stabilizing paintings towards fluctuating climate. The aim is to measure moisture sorption and tension build up in a range of differently treated canvas samples. A procedure for studying moisture sorption kinetic has been developed based on the time resolved mass response of a canvas sample to an instantaneous RH

change, using a DVS instrument. This allows the comparison of different moisture barrier conservation treatments, which is useful in the field of paintings conservation. A well-known problem for wax-resin lined paintings that have been exposed to severe climate fluctuations is the deformation of the impregnated paintings. This may be due to changing dimensions of the underlying canvas caused by moisture sorption and desorption over time. This question is explored by measuring tension in different canvas samples as a function of time after an instantaneous RH change.

3. Materials and methods

3.1. Samples

Three kinds of pure linen canvas were chosen for the experiment as shown in Fig. 2 these were open weave (CTS, Italy, piece No. 2297)¹, close weave (Ulster Weavers, quality 3151, piece No. Z4377)² and fine weave (Ulster Weavers, quality 1940)³. These were impregnated by first applying warm wax-resin mixture to the canvases and then melting the mixture into the fabric using a hot iron. Surplus wax-resin was scraped off from the back of the canvas with a spatula and the canvas was then ironed again on the back. The applied wax-resin mixtures were 70% by weight of bleached pure beeswax from Nidaros Handelshus and 30% by weight of dammar resin from Kremer Pigmente. For the fine canvas, mastic resin from Københavns Farvehandel was used since these early tests were initially done for a different test purpose.

For the Berger's Ethyl Vinyl Alcohol (BEVA) treated samples, three weight parts BEVA gel 371 Hot Sealing Adhesive from CTS 87030 from Kremer was thinned with four weight parts petroleum benzine (boiling point 80–110 °C). The solution was applied to the tensioned open weave canvas with a brush and the solution was ironed at 75 °C in order to smoothen it and allow the mixture to penetrate the canvas structure. The BEVA gel did not penetrate but was distributed as a discrete layer coating the canvas surface.

Two samples, referred to as Ma1 and Ma2, from an aged wax-resin impregnated lining canvas⁴ were taken in connection with a relining of a series of wax-resin lined paintings. The paintings selected from Bernstoff Castle, Denmark named "Scenes from the Park" were painted in 1765 by Johan Edvard Mandelberg.

The samples investigated are listed in Table 1. Canvas type, impregnation type and direction of tensiometer measurement is given together with a systematic name for each e.g. UnOpWe is an untreated, openweave canvas tested in the weft direction. This system is used throughout the present paper.

3.2. Instrumentation

Dynamic vapour sorption (DVS) measurements were carried out using an Aquadyne 2 DVS instrument from Quantachrome. Samples were placed on the balances and allowed to equilibrate for 5–15 days in the controlled climate of the DVS sample chamber at a constant 42% RH and 23 °C until constant mass was attained (40% RH and 21 °C in the case of UnCl smp2 and WaCl smp2). The humidity was then switched to 69% RH at 23 °C while logging of the sample mass was continued.

¹ Open weave: 9 warp threads pr cm (thickness: 0.5–0.7 mm); 11 weft threads pr cm (thickness: 0.4–0.6 mm). Cover Factor = 0.73

² Close weave: 19 warp threads per cm (thickness: 0.4–0.7 mm); 16 weft threads per cm (thickness: 0.5–0.7 mm). Cover Factor = 0.99

³ Fine weave: 26 warp threads per cm (thickness: 0.2–0.4 mm); 24 weft threads per cm (thickness: 0.2–0.3 mm). Cover Factor = 0.90

⁴ Lining canvas: 11 warp threads per cm (thickness: 0.5–0.8 mm); 8 weft threads per cm (thickness: 0.4–0.7 mm).

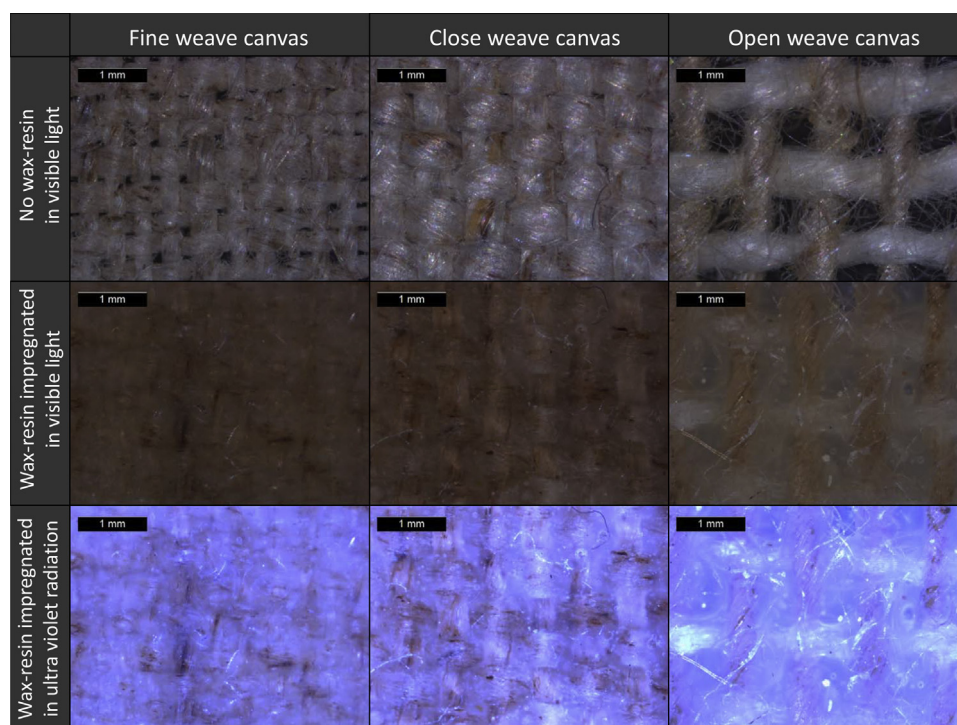


Fig. 2. The three linen canvases (fine weave, close weave and open weave) photographed under polarized light with a Leica DM4M microscope before impregnation with wax-resin and in polarized light and ultraviolet radiation after impregnation.

Table 1
Overview of sample material, names and tests conducted.

Sample treatment	Linen type (see Fig. 2)	DVS test	Direction of tensiometer test	Tensiometer test
Untreated (Un)	Open	UnOp	Weft	UnOpWe
	Close	UnCl	Weft	UnClWe
	Close	UnCl smp2	Warp	UnFiWa
	Fine		Weft	UnFiWe
Wax-resin impregnated (Wa)	Open	WaOp	Weft	WaOpWe
	Close	WaCl	Weft	WaClWe
	Close	WaCl smp2	Warp	WaFiWa
	Fine		Weft	WaFiWe
Beva gel (BG)	Fine	BGOp	Warp	BGFiWa
			Weft	BGFiWe
Wax-resin impr. Relined with Beva film + sailcloth (BfS)	Open	WaBfSOp	Weft	BfSWe
	Fine			
Mandelberg lining 1B (Ma1)		Ma1		
Mandelberg lining 12L (Ma2)		Ma2	Unknown	Ma2

DVS: dynamic vapor sorption.

Restrained force development analyses of samples were performed in custom built tensiometers designed and constructed by Marion F. Mecklenburg (described by [13]) in controlled environmental chambers at 23 °C. The humidity in the chamber was controlled with saturated salt solution in water; potassium carbonate (K_2CO_3) for 42% RH, potassium Iodide (KI) for 69% RH and potassium chloride (KCl) 83% RH. The specimens (10 × 150 mm) that had been kept at 42% RH two weeks prior to the test, were restrained to 2.3 N/cm in the grips of the tensiometer. The force was recorded by a strain indicator (strain indicator P-3500 + SB10 Switch & Balance unit from Measurements Group, Instruments division). The gauge length was 90 mm. The first 6 days the samples were left to stress relax and then the RH was stepped up to 69% by changing the saturated salt solution in the chamber, after three weeks the RH was stepped up to 83% for the samples that had

thus far been non-responsive. The tension was recorded at regular intervals throughout the experiment.

4. Results and discussion

The moisture sorption kinetics was measured using a DVS instrument on a series of canvas samples. The results are plotted as % mass change as a function of time in Fig. 3. All samples took up moisture when RH was stepped up from 42% to 69% as seen by the increasing sample weights, some gained more (e.g., UnOp) than others (e.g., WaOp), some reached equilibrium quickly (e.g., UnOp) while others took longer (e.g., WaOp). This difference was a result of sample type and treatment; untreated linen adsorbed moisture quickly (Fig. 3. UnCl, UnOp and UnCl smp2) whereas linen

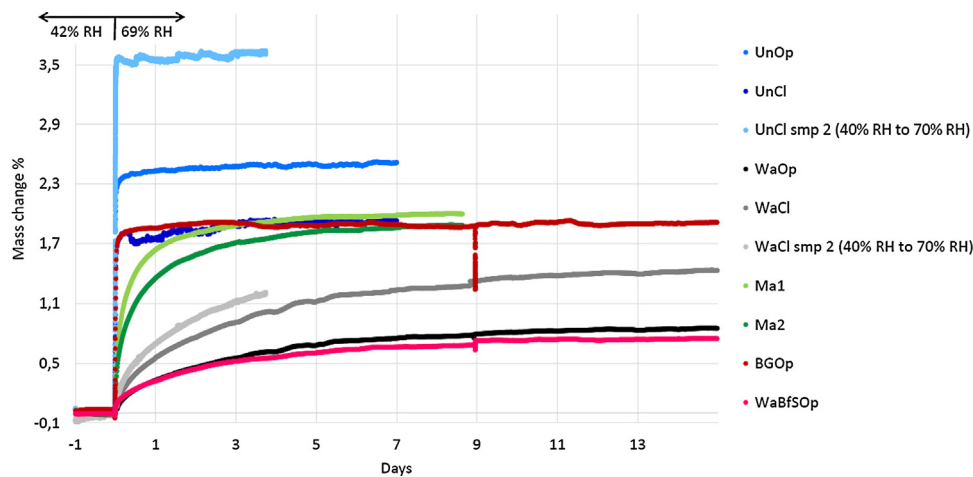


Fig. 3. Dynamic vapor sorption (DVS) measurements of 10 different samples of canvas. The change in mass of the sample in percent of the initial mass at equilibrium at 42% relative humidity (RH) (at day 0) is plotted as a function of time in days. At day 0 the RH is stepped up from 42% RH to 69% RH at 23 °C (40% RH to 70% RH at 21 °C for UnCl smp2 and WaCl smp2).

that had been impregnated with wax-resin reacted much slower (Fig. 3. WaOp, WaCl and WaCl smp2). As expected the wax-resin coating on the linen fibers acted as a moisture barrier thus retarding the uptake of water by the fibers.

The wax-resin matrix does not adsorb moisture itself, which was verified in a DVS measurement on the wax-resin alone. Changing the RH from 42% RH to 69% and even down to 10% RH did not affect the mass (data not shown).

Another result that can be read from Fig. 3 is that the different types of untreated linen (UnCl, UnOp, UnCl smp 2) adsorb moisture to different extents. Close weave linen (UnCl) took up 2% moisture and open weave (UnOp) linen 2.5% when stepping the RH from 42% RH to 69% RH at 23 °C. The second close weaved sample (UnCl smp 2) took up 3.5% but under slightly different experimental conditions (40% RH to 70% RH at 21 °C). Thus, different types and batches of linen adsorb moisture to different extents.

BEVA gel impregnation did not lower the rate of moisture uptake by the linens (see Fig. 3, BGOp) due to the fact that there was free access to the canvas from the back since the BEVA gel had not penetrated the structure. Slow moisture sorption kinetics was observed for the canvas relined with BEVA film and sailcloth (WaBfSOp), however, this linen had been wax-resin impregnated prior to the BEVA treatment. Two samples of lining canvas from a Mandelberg painting were analyzed (Ma1 and Ma2) as shown in Fig. 3. These samples reacted to moisture changes at a rate that was intermediate between untreated linen and linen recently impregnated with wax-resin. The lining samples had extensive cracks in the wax-resin material. Cracks provide access for moisture to the linen through the impregnation and it therefore makes sense that the rate of moisture uptake was higher in these cracked samples than for recently wax-resin treated linen and lower than for untreated linen.

These differences in kinetics are summarized in Table 2 where equilibrium values of the mass change seen in Fig. 3 are listed along with the number of days it took the % mass change to reach 75% of its equilibrium value (this term is referred to as $t_{75\%}$). $t_{75\%}$ was 0.010–0.021 days for untreated linen and ca. 4.3 days for wax-resin impregnated linen. For the Mandelberg paintings $t_{75\%}$ was 0.7–1.2 days. A similar interpretation of tensiometer data is listed in the table as well, which will be discussed below.

The same samples of impregnated and untreated linen respectively, that was measured using DVS in Fig. 3, were also measured using a tensiometer as shown in Fig. 4. The force is given in Newton per centimeter (sample with) and plotted as a function of time in days. At day 0 the humidity is stepped from up from 42% RH to

Table 2
Kinetic parameters.

DVS		
	Equilibrium mass change(%)	$t_{75\%}$ (days)
UnOp	2.5	0.010
UnCl	1.9	0.021
BGOp	1.9	0.021
Ma1	2.0	0.66
Ma2	1.9	1.2
WaOp	0.86	4.3
WaCl	1.4	4.3
WaBfSOp	0.76	4.2
Tensiometer		
	Tension increase ^a (N/cm)	$t_{75\%}$ (days)
WaFiWe	1.4	4.5
UnFiWe	0.53	0.14
BGFiWe	0.30	0.23

DVS: dynamic vapor sorption; RH: relative humidity.

^a Samples are mounted with a certain initial tension in the tensiometer, the RH-induced tension increase adds to this initial tension and $t_{75\%}$ is the time it takes to reach 75% of the tension added.

69% RH. In most samples the tension is unaffected by this change in humidity except in three finely woven samples in the weft direction (WaFiWe, BGFiWe, UnFiWe) where the tension increase as a result of the RH change. The warp direction behaves much differently and this difference in weft and warp is confirmed by previous results [9].

The untreated sample of the finely woven canvas (UnFiWe) and the BEVA gel treated sample (BGFiWe) reached their equilibrium tension fast and the wax-resin impregnated linen (WaFiWe) took longer, as expected from the DVS results in Fig. 3. The tension in the wax-resin impregnated, finely woven sample (WaFiWe) grew considerably larger than for the untreated and BEVA-treated samples with the same canvas. This could be due to the wax-resin matrix filling the voids as discussed above, but it seems that only on the finely woven canvas did the wax-resin mixture have this pronounced effect.

In the warp direction the untreated finely woven canvas (UnFiWe) started to build up tension when the RH was stepped up to 69% but quickly turned back to the tension it had at 42% RH. Open and close weave as well as the Mandelberg sample (Ma2We, WaClWe and WaOpWe) did not build up stable tension at 69% RH.

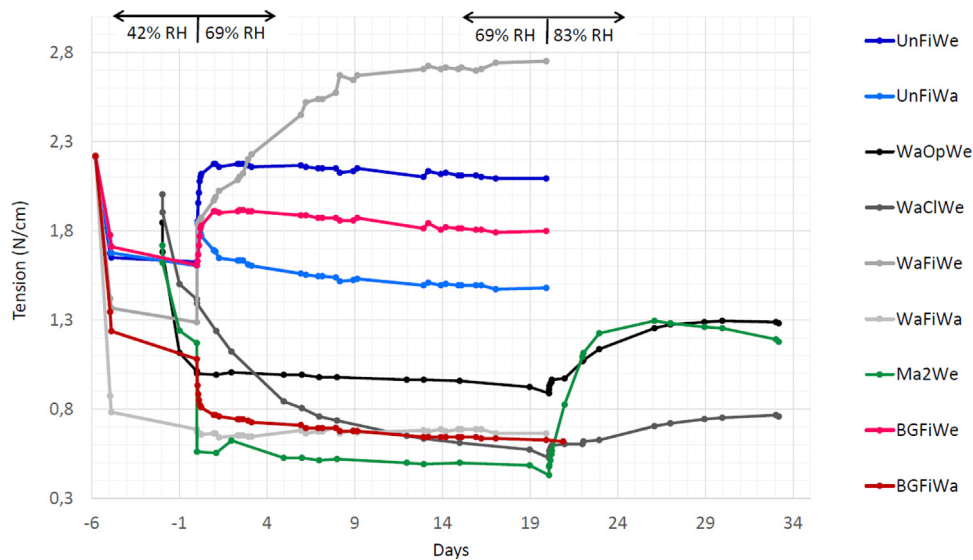


Fig. 4. Tensiometer measurements of 9 different canvas samples. The change in tension of the sample in Newton per cm with of the sample (N/cm) is plotted as a function of time in days. The samples are mounted in the instrument with the uniaxial force in the weave direction specified. The humidity is 42% relative humidity (RH) from day –6 to day 0, 69% RH from day 0 to day 20 and 83% RH from day 20 to day 33, the temperature was 23 °C.

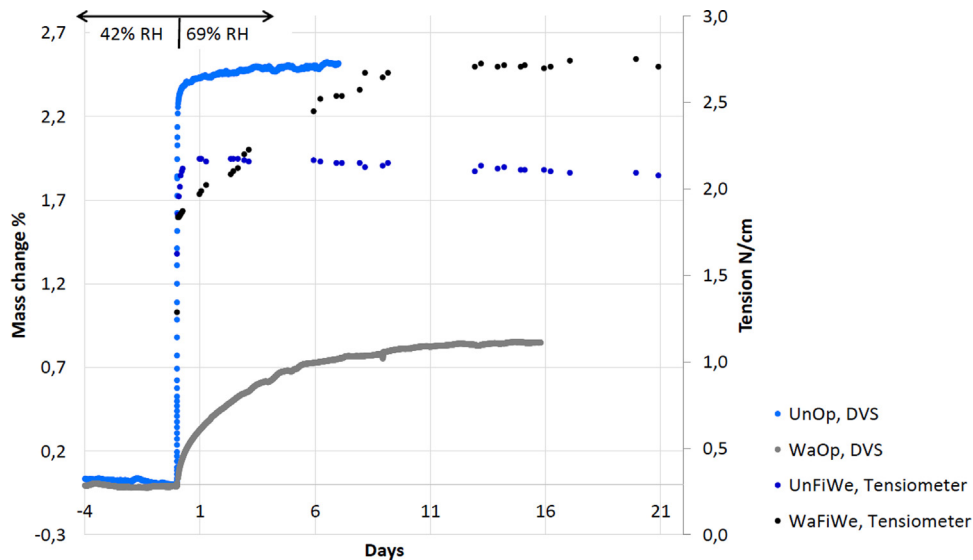


Fig. 5. Tensiometer and dynamic vapor sorption (DVS) measurements of untreated linen (dark blue: UnFiWe; light blue: UnOp) and wax-resin impregnated linen (black: WaFiWe; grey: WaOp). The climate was 42% relative humidity (RH) up to day 0 after which the RH was stepped up to 69% RH at 23 °C.

The reason for this does not relate to weave direction since both directions were represented among the samples that did not build up tension at 69% RH. The difference is rather the weave geometry, which governs the shrinkage effect of fiber swelling.

Many samples did not increase tension when RH was shifted from 42% RH to 69% RH, some even lost tension over time (WaClWe) due to continued stress relaxation, a tendency that has been previously reported elsewhere in wax-resin linings [12]. In order to provoke swelling and subsequent tension buildup the RH was shifted to 83% in three cases which lead to a tension increase for all of them (WaOpWe, Ma2We, WaClWe) even though the effect was still relatively moderate. It is interesting to see however, that the aged, wax-resin treated canvas sample (Ma2We) showed a sudden rise in force at this high RH level.

All flax fibers swell when RH is increased. Tension builds up in restrained samples when there is no more play between the swelling fibers. There is less play between fibers if wax-resin fills up the voids and if the voids are small to begin with e.g. in a finely

woven canvas with tightly spun threads. Thus, a wax-resin impregnated finely woven sample meets all of the criteria for tension build up. It is still unclear why the weft direction was more affected by the wax-resin treatment when it comes to building up tension, than the warp direction. However, a hypothesis could be that the higher tension in the weft direction is related to the fact that weft yarns are usually already straight, whereas warp yarns have more crimp, which has to be straightened out before additional force can be detected in tensile tests.

Both tensiometry and DVS yield information about moisture sorption kinetics; tension buildup for the tensiometer and mass gain for DVS. It is seen in Table 2 that the development of tension in three samples approximately follow the same kinetics as that derived from mass gain. The time it took for wax-resin impregnated samples to reach 75% of the equilibrium value ($t_{75\%}$) is 4.5 days in tensiometer (WaFiWe) and 4.3 days in DVS (WaCl and WaOp). For untreated canvas, it took 0.14 days ($t_{75\%}$) in tensiometer (UnFiWe) and $t_{75\%}$ was approximately 0.2 days in DVS (UnCl and

UnOp). For BGFWe the difference was somewhat larger between the tensiometer based $t_{75\%}$ of 0.23 days and the DVS based $t_{75\%}$ of 0.021 days (BGOp), but the tensiometers were only checked every hour on the first day, which means that some of the finer details of the initial RH response are not recorded. It seems that there is no, or little, delay from the time where water is taken up by the linen fiber to the time where swelling and contraction sets in, the two techniques yield similar kinetic data for samples that build up tension.

A comparison is made in Fig. 5 between wax-resin impregnated and untreated linen by DVS and tensiometer measurements in the weft direction. It is seen that the wax-resin impregnated samples have the same approximate time dependency of mass in DVS and tension in the tensiometer graphs, which is also the case for the untreated linen sample. The graphs illustrate that kinetics provided by tensiometer and DVS are similar for samples with tension build up, which was also concluded in the discussion of Table 2.

5. Conclusions

The fact that moisture is taken up by linen despite of a wax-resin barrier was confirmed in the present experiments where samples of impregnated and un-impregnated linen were measured in DVS at 42%RH and 69%RH. The wax-resin impregnated samples absorbed water vapor at a much slower rate than the un-impregnated ones, but the aged wax-resin impregnated canvases had a faster response than the newly made samples. This may be due to cracks in the wax-resin coating.

This moisture response in wax-resin impregnated samples is in contrast to the original intention of impregnating paintings with wax-resin, which was to seal the canvas from the surrounding atmosphere. It was also demonstrated that BEVA gel had very little effect on the access of moisture to canvas because the BEVA gel did not penetrate the linen sample thus permitting access of moisture from the back. The BEVA-treated samples adsorbed moisture almost as fast and to the same extent as the untreated linen.

Force development was measured as well and it was demonstrated that the samples that build up tension when the humidity was stepped up did so at a rate that was similar to the rate deduced from DVS measurements of the same sample. This suggested that there is no, or little, delay from the time when water is taken up by the linen fiber to the time when swelling and contraction sets in, the two techniques yield similar kinetic data for the samples that build up tension.

Some samples built up tension when RH was increased and others did not. All samples where tension increased were of the fine weaved canvas measured in the weft direction and this canvas also had a higher tendency for shrinkage when not in tension. All linens took up moisture to some extent and as a result all fibers were swelling. Tension builds up when there is no more play between the swelling fibers and this depends on the canvas geometry. There is less play in between fibers if wax-resin fills up the voids and if the voids are small to begin with e.g., in a finely woven canvas with tightly spun threads. Thus, canvases may build up tension

eventually if the RH is raised enough no matter if they are impregnated or not. The impregnation affects the rate at which tension increases and the RH level for the onset of shrinkage – or tension in the case of the restrained samples.

Thus, some wax-resin treated paintings will respond to increased RH whereas others will not. The result of the tension buildup, which may occur repeatedly depending on the ambient climate, can be distortions and delamination. The factors that affect whether this will happen to a painting include the time of exposure to raised RH and the degree of cracking in the wax-resin matrix, which may be increased with time due to oxidation in the resin and repeated swelling of the canvas threads. However, the main factor seems to be the canvas, its weave geometry and the weave direction.

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