RESEARCH ARTICLE

Evolution of the viscoelastic properties of painting stratigraphies: a moisture weathering and nanoindentation approach

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Abstract

In this investigation on the mechanical behaviour of paint films, we use a new ferrule-top nanoindentation protocol developed for cultural heritage studies to examine the impact of repeated relative humidity variations on the viscoelastic behaviour of paint films and their mechanical properties in different paint stratigraphies through the changes in their storage and loss moduli. We show that the moisture weathering impact on the micromechanics varies for each of these pigment-oil systems. Data from the nanoindentation protocol provide new insights into the evolution of the viscoelastic properties dsue to the impact of moisture weathering on paint films.

Keywords: Nanoindentation, Mechanical behaviour, Viscoelastic properties, Dynamic mechanical analysis, Paint stratigraphy, Moisture variations, Environmental conditions

Introduction

Evolution of the mechanical properties of oil paints through drying, natural aging, or moisture and temperature variations can induce internal stresses and may lead to macroscopic alteration such as crack initiation and delamination [1–3]. Therefore, investigating the mechanical behaviour of oil paintings and their multi-layered structures is of major interest to understand their long-term stability. In this paper we focus on the impact of moisture leading to weathering, on a set of variant paint layer build-ups using three different pigments, as well as an exemple of a ground layer stratigraphy, the latter a reconstruction of an often used 17th-century method of canvas preparation. Previous research has quantified the mechanical properties of oil paints and evaluated the influence of some pigments and binding media on the layers' mechanical properties. They studied how chemical processes inherent to the material composition of the paint, as well as the cross-linking evolution due to natural drying results influence their mechanical behaviour evolution over time [1, 2, 4–7]. Thus, the fresh reconstructions we used in this study are expected to be softer than fully dried reconstructions and historical paintings [8].

Next to the natural aging processes of oil and pigment combinations, and inherent chemical changes, environmental conditions can also modify their mechanical behaviour [1, 4, 8–10]. Temperature and moisture content variations are both external parameters that may induce significant modification of the mechanical response of painting supports such as canvas or panel, as well as the various ground, paint and varnish layers, depending on their composition [11–14].

To evaluate and model the macroscopic behaviour of the whole painting stratigraphy under relatives humidity (RH) variations, Mecklenburg and colleagues [4] tested the behaviour of several oil paints and artist's materials individually, and at fixed RH levels. For instance, they showed how a RH increase results in the decrease of the elasticity modulus of various pigment-oil systems—such as Naples Yellow, Burnt Sienna or Flake White—and illustrated the impact of RH levels on their behaviour [4].

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Mecklenburg et al. then proposed Finite Element Modeling analysis to assess the response of paint build-ups.

Although the RH-dependence of the elastic modulus was considered, the influence of repeated cycles of RH has yet to be investigated. Building on this literature and to improve our insight on the behaviour's evolution over repeated cycles of relative humidity, this research focuses on both elastic and viscous properties of oil paints prepared with different pigments, and on the impact of repeated moisture cycles. Thus, we study the consequences of moisture weathering, a process by which the materials exposed to moisture and relative humidity variations may undergo changes and evolution in their properties, leading to potential degradation. For this study, the relative humidity varies from 30 % to 85 %.

To study the influence of repeated moisture adsorption-desorption cycles on the viscoelastic properties of different paints, we prepared fresh laboratory reconstructions. With these samples, we controlled all parameters, from the pigment to binding medium compositions, the layering and preparation of the build-up, as well as the testing conditions. As the age and mechanical properties of these samples differ from historical artworks, further research and modeling will be necessary to transpose our results to historical paintings; however, our measurements provide the first steps towards an evaluation of the impact of repeated moisture variations on paint build-ups. We considered three pigments mixed in linseed oil: lead white, a basic lead carbonate, $2PbCO_3.Pb(OH)_2$, ultramarine, a blue silicate mineral of the sodalite group $(Na, Ca)_8(AlSiO_4)_6(S, Cl, SO_4, OH)_2$, and an organic red lake pigment made of madder precipitated on a hydrated alumina substrate. To access the paint layer's sensitivity to moisture uptake and quantify the difference in terms of mechanical behaviour, induced by the layer position within the stratigraphy, we aim to study the properties of those layers that are located between other layers in the stratigraphy. Such an analysis requires local measurements of the material moduli.

To evaluate the mechanical properties of the multi-layered paint samples, we adjusted a nanoindentation device and protocol. The complete methodology of the ferrule-top indentation proposed was described in Tiennot et al. [15]. The optomechanical device adapted to carry out the required measurements allows a depth-controlled indentation profile, and a precise analysis of both storage and loss moduli of the materials. As verified in previous research [15], the accuracy of the indentation localisation and of the Dynamic Mechanical Analysis (DMA) measurements allowed by this protocol, supports the investigation of the complete build-up structure of paintings, giving access to all layers without embedding the samples as cross-sections in polyester resin. Therefore, by using this indentation protocol, we investigate both elastic and viscous components of paint film's behaviour, their modification over eight cycles of relative humidity, and their evolution in terms of viscosity. We can study experimentally that repeated moisture variations induce different mechanical responses of paint layers, varying with the nature of the pigment as well as with the position within the stratigraphy. The discrepancies induced by these modifications of the paints' properties may be involved in the stress field created within the paint stratigraphy. This phenomenon and its influence on crack initiation and propagation in paintings, provide the rationale for our research.
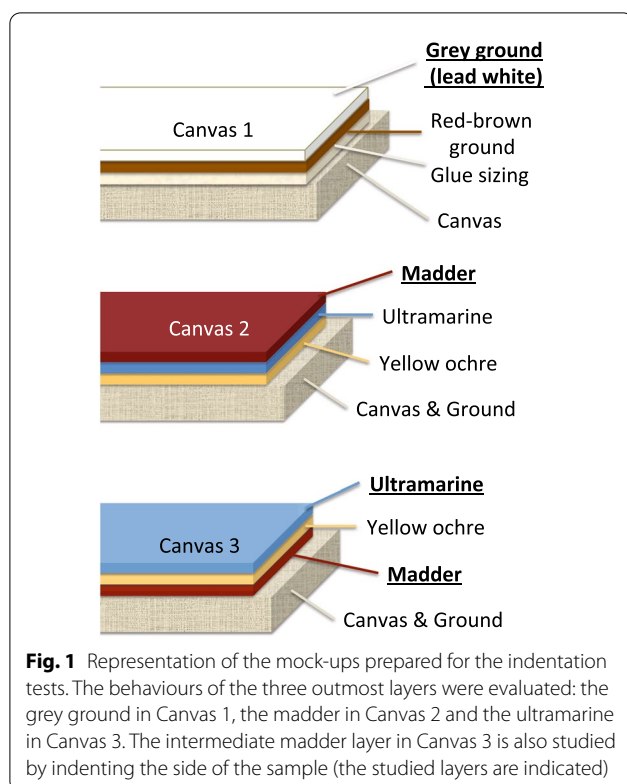
Thus, this paper aims at illustrating the evolution of the behaviour of paint layers under repeated RH variations in terms of elastic and viscous moduli. The investigation of moisture-induced chemical processes involved in these variations, are part of a broader, future research plan. Our nanoindentation-based research is one step towards the quantification of the viscoelastic moduli's evolution of pigment-oil systems, with respect to their nature and their position in the paint stratigraphy, and help to further improve our understanding of the micromechanics of paint layers.

Materials

For this research, we prepared a set of laboratory reconstructions. The paint layers were applied by brush and as homogeneously as possible on the canvas. Each resulting layer measured around 50–65 μm in thickness. The layers were applied on the center of the canvas, to avoid the potential heterogeneities related to the stretching of the canvas.

The first laboratory sample follows a typical build-up of a 17th-century Netherlandish canvas preparation stratigraphy, as an historically informed mock-up limited to the ground layers. It consists of a double ground applied on a stretched linen canvas prepared first with a size layer of rabbit skin glue in water (5 %). This preparation is followed by the application of a first ground layer consisting of a mixture of chalk (7.5 g) and red earth (1g) in boiled linseed oil (3.7 ml). The second ground is a grey ground layer, consisting of a mixture of lead white (18 g), chalk (4 g) and small amounts of yellow ochre (0.1 g), and ivory black (0.2 g) in boiled linseed oil (11.7 ml). This laboratory sample is designated as Canvas 1 (Fig. 1). The canvas was cured in an ultraviolet chamber for 24 h after the application of the first and second ground layer.

The other mock-ups studied were prepared on a primed canvas (commercially purchased) using three individual paint layers composed of yellow ochre, ultramarine and madder, in boiled linseed oil. Each pigment requires a different amount of oil to obtain the right

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Fig. 1 Representation of the mock-ups prepared for the indentation tests. The behaviours of the three outmost layers were evaluated: the grey ground in Canvas 1, the madder in Canvas 2 and the ultramarine in Canvas 3. The intermediate madder layer in Canvas 3 is also studied by indenting the side of the sample (the studied layers are indicated)

consistency for easy application. On this basis we determined the proportion of pigment to oil as follows: in 5 ml of linseed oil, we added respectively 8.3 g of ochre, 7.5 g of ultramarine and 3.6 g of madder to prepare the paint layers. Two alternative build-ups were prepared as follows: Canvas 2: Ochre-Ultramarine-Madder and Canvas 3: Madder-Ochre-Ultramarine (Fig. 1).

All layers applied were UV-cured using UV-A (around 1.5 mW/cm^2) for 24 h after its application. The next layer was applied by brush and cured under the same conditions.

For test samples, centimeter pieces were cut from the canvas, relieving the initial stresses, and were prepared and stored under the same laboratory controlled atmosphere for 1 month at fixed relative humidity RH= 50 % and temperature T = 20 °C.

For the present investigation on the moisture-weathering impact, we specifically studied the outer layers in the three mock-ups: grey ground, the ultramarine and madder layers, while the ochre layer was not considered in this investigation. First, we focused on the three outmost layers: (i) the grey ground containing lead white paint in Canvas 1, described as 'grey ground' in the following sections, (ii) the madder layer in Canvas 2 and (iii) the ultramarine paint in Canvas 3 (Fig. 1). To further investigate the influence of the paint film's position on the evolution of the mechanical behaviour and the damage

that may be induced by moisture variations, the madder layer on Canvas 3 was also investigated (Fig. 1). Section 3 describes the repeated environmental changes applied and the indentation protocol used to estimate the evolution of the pigment-oil systems through RH changes.

Methods

Exposure conditions: moisture cycles

We first evaluated the properties of the reference mock-ups prior to any RH variations, conditioned at T = 20 °C and relative humidity RH = 50 %, henceforth described as the initial state. Then, to study the sensitivity of the mechanical properties to moisture, some samples were exposed to several (1–8) cycles of RH variations, using a climate chamber. The selected range for the RH conditions is 30–85 %. After stabilization at RH = 30 % during 4 h, the samples were exposed to 8 successive cycles of RH variations under isothermal conditions at T = 23 °C. Each cycle consists of a humidification phase, reaching 85 % of RH and stabilized at that level during 24 h, and a drying phase, until stabilization of the RH at 30 % during 24 h. After the cycles 1-4-6-7-8, the tested samples were removed from the climate chamber, and stabilized again under laboratory conditions for at least one month to allow the equilibrium in moisture content (T = 20 °C and relative humidity RH = 50 %). Under each of these variant solicitations, the changes in mechanical properties of the grey ground, ultramarine, and madder paint layers due to repeated moisture variations were evaluated. Thus, the viscoelastic properties of the paint layers after 1-4-6-7-8 cycles of the defined RH variations were measured using the indentation protocol described in Sect. 3.2.

Nanoindentation protocol

The nanoindentation protocol performed for this research was designed to evaluate the mechanical properties of paint films at microscale through depth-controlled analysis. The detailed methodological approach is described in Tiennot et al. [15]. We set up the present experiment according to these guidelines. However, one important difference is that the indentation protocol is carried out on small samples cut from the mock-ups, and not on embedded cross-sections.

To prepare our ferrule-top probe, a borosilicate sphere up to 70 µm in diameter is attached to a micromachined glass cantilever, and an optical fiber monitors precisely the bending of the probe while in contact with the sample. This manufactured spherical probe, specifically designed for this research, results from numerous mechanobiological studies, successfully using this methodology [16, 20]. A camera placed on top of the equipment allows proper localisation of the measurement

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on the surface. The ferrule-top indenter, and the optical fiber interferometry used to monitor the cantilever bending, allow the accurate indentation depth—and the induced strain— control along the measurement. Thanks to this optomechanical device, we can perform accurate Dynamic Mechanical Analyses (DMA) to measure the storage E' and loss E'' moduli of the tested materials [17–20]. The storage modulus represents the ability of the material to store energy and relates to the elastic part of the behaviour, and the loss modulus represents the part of the energy dissipated and underlines the viscous properties of the material. These properties characterize the viscoelasticity of the paint layer. To prevent creep and its potential influence on the measurement of E' and E'', the dynamic indentation is performed after a relaxation period, allowing the paint to reach a mechanical equilibrium, at a constant indentation depth over time. Thus, a first approach phase at the speed of $v = 5 \mu m\,s^{-1}$ is followed by a 2 s loading after the first contact. When the indentation depth $d_{ia} = 2\mu m$ or $d_{ib} = 5\mu m$ is reached, and after a relaxation time of 20 s, DMA via small oscillations at an amplitude $A = 0.05\mu m$ is completed. The chosen frequency sweep of five frequencies ranging from $f_1 = 1$ Hz to $f_5 = 10$ Hz allows the evaluation at constant indentation depth of the viscoelastic properties of the sample and the quantification of its storage E' and loss E'' moduli, as well as the loss factor $tan\phi = \frac{E''}{E'}$ (Fig. 2). The indentation depths selected for this research are fixed at $d_{ia} = 2\mu m$ or $d_{ib} = 5\mu m$. As the layers measure at least $50\,\mu m$, the substrate is not likely to influence our ferrule-top measurements.

As less damage and more valid deformation fields are expected with this ferrule-top device and protocol, we can collect the elastic or viscoelastic properties and evaluate the nonlinearity of paint layers more precisely. Moreover, this methodology supports the study of the overall structure of a painting stratigraphy, allowing the measurements on the surface or the side of a cross-section, as presented in Tiennot et al. [15]. This previous research on the influence of the indent location on the sample showed that there is no difference between the measurements made on the surface and the side of the build-up. These results strengthen the advantages of the ferrule-top indentation and the defined protocol. Thus, the properties of the outmost layers, on C1: grey ground, on C2: madder layer, and on C3: ultramarine layer, are measured by performing the indentation protocol on the surface of the samples. The DMA testing on the covered madder layer is performed on the side of the Canvas 3. This measurement is illustrated in Fig. 3. We performed several measurements on random locations on the surface or the side of the layers. The average values and the standard deviation results from 3 to 7 indentation analyses. The indentation measurements were performed in a room under controlled conditions at fixed temperature T = 20 °C and fixed relative humidity RH = 50%.

Results

Properties of the paint films at the initial state

The values of the storage E' and loss E'' moduli measured by indentation at the first frequency of the of the dynamic analysis $f_1 = 1$ Hz and at the penetration depth of 2 μm are summarized in Table 1. The average values and the standard deviation (under brackets) are obtained from 3 to 7 measurements randomly performed on the paint layer. The mechanical properties at the initial state are measured via indentation, before any RH variations.
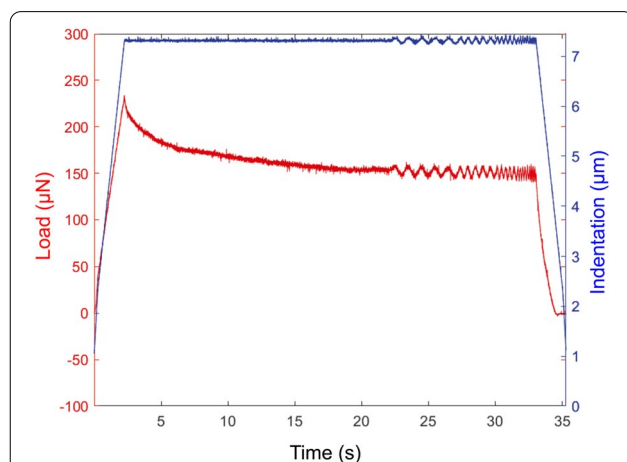

Fig. 2 Depth-controlled indentation profile (in blue) at 5 μm and load recorded (in red) for the ultramarine layer during the dynamic analysis
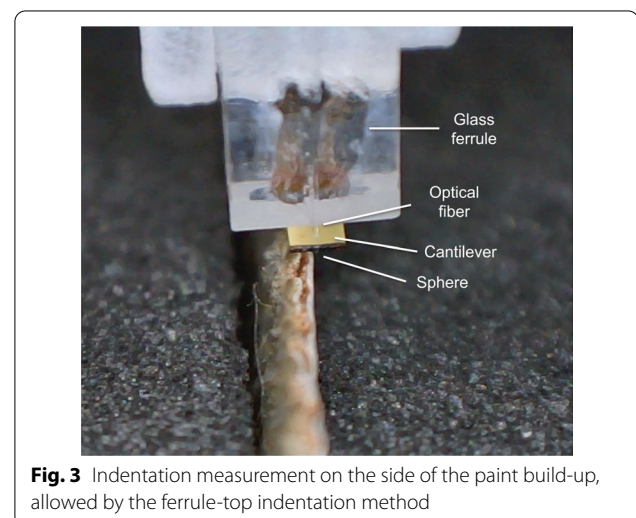

Fig. 3 Indentation measurement on the side of the paint build-up, allowed by the ferrule-top indentation method

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These properties are considered as references for this research.
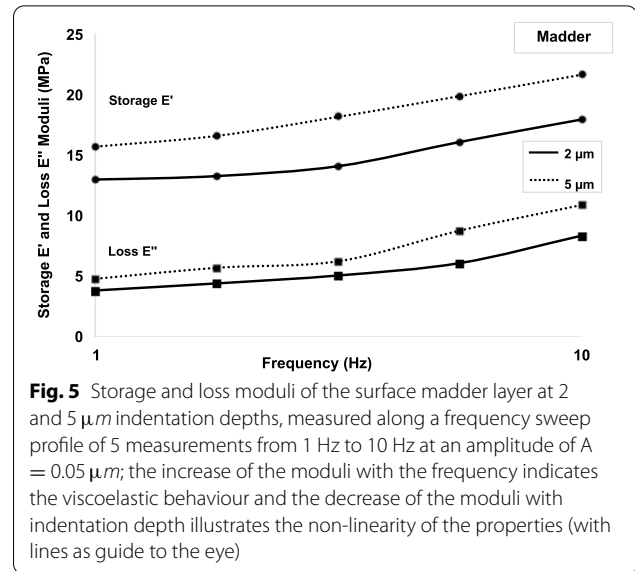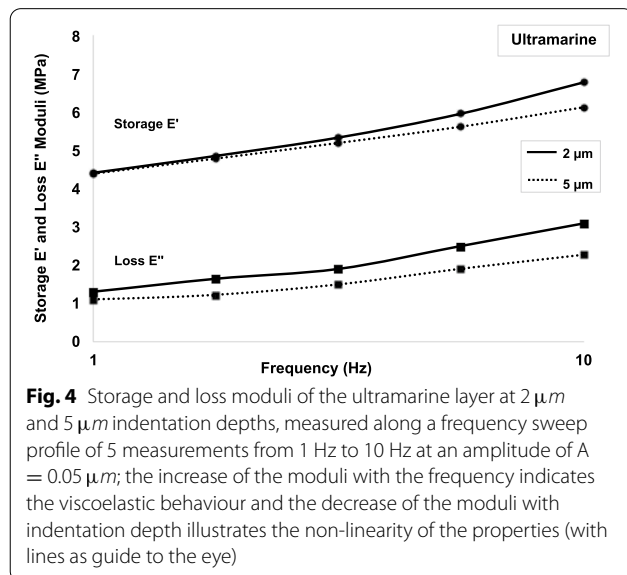
Grey ground

The dynamic analysis response of the grey ground at 2 μm and 5 μm was already published in [15]: both storage and loss moduli are frequency-dependent, increasing with frequency. Moreover, the slight decrease of the properties with indentation depth illustrates the non-linearity of the lead white film's behaviour. At the 2 μm indentation depth and 1 Hz indentation frequency, under the initial conditions, the depth-controlled indentation profile characterized the storage modulus at $E' = 34$ MPa and loss modulus at $E'' = 9.4$ MPa, and thus a loss factor at $tan\phi_{GreyGround-init} = 0.27$.

Ultramarine

Figure 4 presents the results of the depth-controlled indentation profile on the ultramarine paint film. Its viscoelastic behaviour is illustrated by the stiffening effect with the frequency. The evolution of the elastic and viscous moduli with indentation depth is the same as the one observed in the grey ground: they both decrease when the applied deformation increases. The initial reference moduli of the ultramarine paint at 2 μm and 1 Hz are $E' = 4.4$ MPa and $E'' = 1.3$ MPa, and the loss factor at $tan\phi_{Ultramarine-init} = 0.29$. These results indicate that the ultramarine paint prepared is softer than the grey ground.

Madder

Figure 5 presents the results for the behaviour of the madder layer applied as a top layer. Like the grey ground

Fig. 5 Storage and loss moduli of the surface madder layer at 2 and 5 μm indentation depths, measured along a frequency sweep profile of 5 measurements from 1 Hz to 10 Hz at an amplitude of A = 0.05 μm; the increase of the moduli with the frequency indicates the viscoelastic behaviour and the decrease of the moduli with indentation depth illustrates the non-linearity of the properties (with lines as guide to the eye)

and ultramarine films, storage and loss moduli of the surface madder layer increase with frequency, illustrating a viscoelastic behaviour. However, this layer exhibits an increase of the moduli when the applied deformation increases from 2 μm to 5 μm. At 2 μm and 1 HZ, $E' = 13$ MPa and $E'' = 3.8$ MPa, and the loss factor is $tan\phi_{Madder-surface-init} = 0.29$.

The indentation protocol performed on the cross-section's side also allows the characterization of the red layer as the first layer applied on the canvas and covered by the ochre and ultramarine paint layers. At the 2 μm depth, this red layer presents a lower storage modulus, with $E' = 5.2$ MPa and $E'' = 0.65$ MPa. This intermediate layer in the stratigraphy was expected to show lower moduli, as it dries less quickly because it does not interact directly with the atmosphere.

Moreover, it should be noted that the two madder layers' viscoelastic behaviour differ, as illustrated by the difference in loss factors. Indeed, at the initial state, the madder layer applied on the surface shows a loss factor at $tan\phi_{Madder-surface-init} = 0.29$, whereas the loss factor of the intermediate madder layer is measured at $tan\phi_{Madder-covered-init} = 0.21$. Therefore, before any RH variations, the outmost surface madder layer (i) presents lower storage and loss moduli and (ii) is more viscous than the intermediate madder layer. This result is of major interest for the study of the macroscopic behaviour of oil paint stratigraphies.

Fig. 4 Storage and loss moduli of the ultramarine layer at 2 μm and 5 μm indentation depths, measured along a frequency sweep profile of 5 measurements from 1 Hz to 10 Hz at an amplitude of A = 0.05 μm; the increase of the moduli with the frequency indicates the viscoelastic behaviour and the decrease of the moduli with indentation depth illustrates the non-linearity of the properties (with lines as guide to the eye)

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Table 1 Values of the storage E' and loss E'' moduli (in MPa) measured by indentation at the first frequency of the of the dynamic analysis $f_1 = 1$ Hz and at the penetration depth of 2 μm; the average values are obtained from 3 to 7 measurements randomly performed on the paint layer, and the standard deviation is specified under brackets

	E'	E''
Grey ground		
Cycle		
0	34 (7.4)	9.4 (3.4)
1	11 (1.9)	3.6 (0.50)
4	7.5 (1.4)	2.4 (0.19)
6	6.3 (0.62)	2.2 (0.32)
7	7.5 (0.49)	2.3 (0.84)
8	8.0 (1.0)	2.1 (0.17)
Ultramarine		
Cycle		
0	4.4 (0.95)	1.3 (0.2)
1	2.2 (0.63)	0.61 (0.09)
4	2.9 (0.13)	0.83 (0.11)
6	4.0 (0.06)	1.2 (0.11)
7	4.1 (0.57)	1.4 (0.10)
8	8.0 (0.67)	2.6 (0.15)
Madder on surface		
Cycle		
0	3.1 (1.3)	0.7 (0.20)
1	6.4 (3.5)	1.6 (0.73)
4	7.2 (0.72)	1.5 (0.51)
6	6.0 (3.4)	2.0 (1.4)
7	5.8 (4.6)	2.8 (1.7)
8	5.8 (2.7)	2.4 (1.4)
Madder covered		
Cycle		
0	3.1 (1.3)	0.65 (0.2)
1	5.2 (3.8)	1.6 (0.21)
4	7.2 (0.72)	1.5 (0.81)
6	6.0 (3.4)	2.0 (0.51)
7	5.8 (4.6)	2.8 (1.4)
8	5.8 (2.7)	2.4 (1.4)

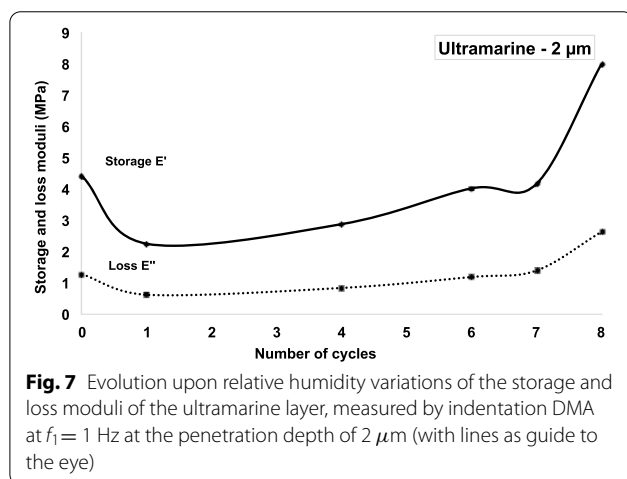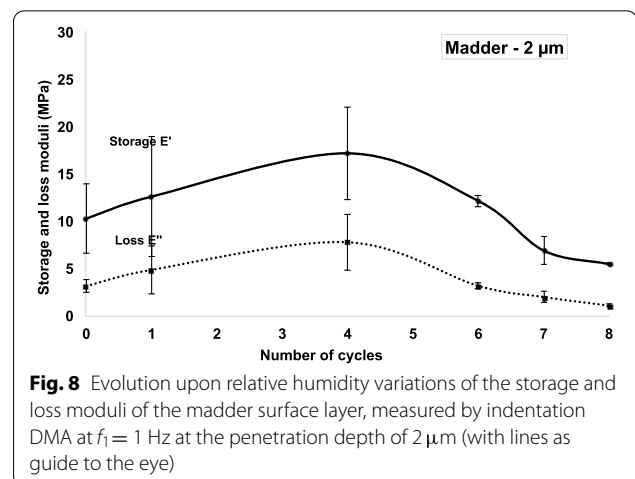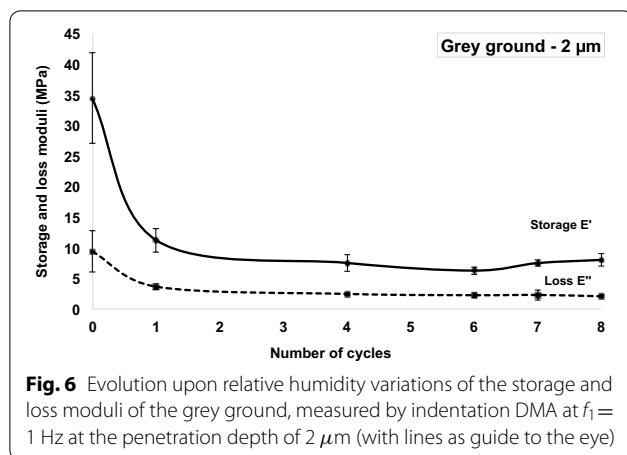## Evolution of the properties of the paint films under moisture cycles

Grey ground

Figure 6 shows the evolution of the grey ground's storage and loss moduli upon RH variations. The first cycle of relative humidity variations induces a significant decrease of both moduli, then followed by a slighter decrease during the following cycles. Based on these depth-controlled indentation profiles, the micromechanical behaviour of the grey ground is sensitive to moisture. Repeated RH variations induce a decrease of the storage and loss moduli of this layer. Under the assumption that the same swelling strains result from the RH variations during all the cycles, lower stresses are likely to develop in this grey ground after moisture weathering. This is a valuable information for the comprehension of the long-term stability upon generation of hygric stress. The exact evaluation of these moisture-related stresses is part of further research.

Ultramarine

The repeated moisture variations affect the ultramarine paint in a different manner. Figure 7 illustrates that the first cycles of moisture variations cause a slight decrease

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Fig. 6 Evolution upon relative humidity variations of the storage and loss moduli of the grey ground, measured by indentation DMA at $f_1 =$ 1 Hz at the penetration depth of 2 μm (with lines as guide to the eye)

Fig. 8 Evolution upon relative humidity variations of the storage and loss moduli of the madder surface layer, measured by indentation DMA at $f_1 =$ 1 Hz at the penetration depth of 2 μm (with lines as guide to the eye)

Fig. 7 Evolution upon relative humidity variations of the storage and loss moduli of the ultramarine layer, measured by indentation DMA at $f_1 =$ 1 Hz at the penetration depth of 2 μm (with lines as guide to the eye)

of both moduli. However, after 6 cycles of RH, the properties recover back to the initial state behaviour, and the last two cycles induce an increase of both moduli, with a storage modulus twice higher than before any moisture cycle (Fig. 7). This phenomenon may be the consequence of complex parameters that may be enhanced by moisture content variations, like inherent chemical processes, interactions created between oil and ultramarine, or curing and drying modification of oil [21].

Madder
Figure 8 shows that storage and loss moduli of the surface madder layer increase with the four first cycles of RH variations. However, from the 6th cycle, the moduli drop significantly and reach values lower than the ones recorded in the initial state. After 8 repeated cycles, the elastic modulus of the surface madder decreases significantly, as well as the viscous modulus.

Figure 9 illustrates that the moduli's evolution of the paint with the exact same composition but covered by

other layers is analogous. They both slightly increase before falling after 6 cycles of repeated sollicitations. As expected, the moduli's variations are lower for the intermediate red layer, less exposed to moisture than the layer in direct external contact with the RH variations in the enclosure. After the 8 cycles of RH variations, the values of E' and E'' get closer. Another noticeable result is the fact that after repeated RH cycles, however, the viscous modulus E'' of the intermediate madder layer is more affected by the repeated RH variations. This intermediate layer turns into a more viscous paint film after the 8 cycles of moisture weathering, with a loss factor of 0.41. These results illustrate that the intrinsic elastic and viscous properties of paint layers and their evolution depend on the position within the stratigraphy.

Discussion
In this research, we studied the storage E' and loss E'' moduli of oil paint build-ups. Before any RH variations, we found that the grey ground, mostly made of the fast-drying pigment lead white, presents the highest measured stiffness and the outmost ultramarine paint film shows the lowest elastic modulus. Our nanoindentation protocol also allows testing on the side of the canvas samples taken from the mock-ups and thus allows the investigation on the mechanical behaviour of layers in different position in the paint build-up. Based on our measurements, the covered madder layer shows lower elastic and viscous moduli than the madder layer located at the surface. These differences may be the consequence of the drying process that varies with respect to the position of the paint film in the layer build-up, and may also be the result of various interactions with the substrate and with the neighboring layers.

As exposure to environmental variations is identified as a primary source of alteration for paintings, we
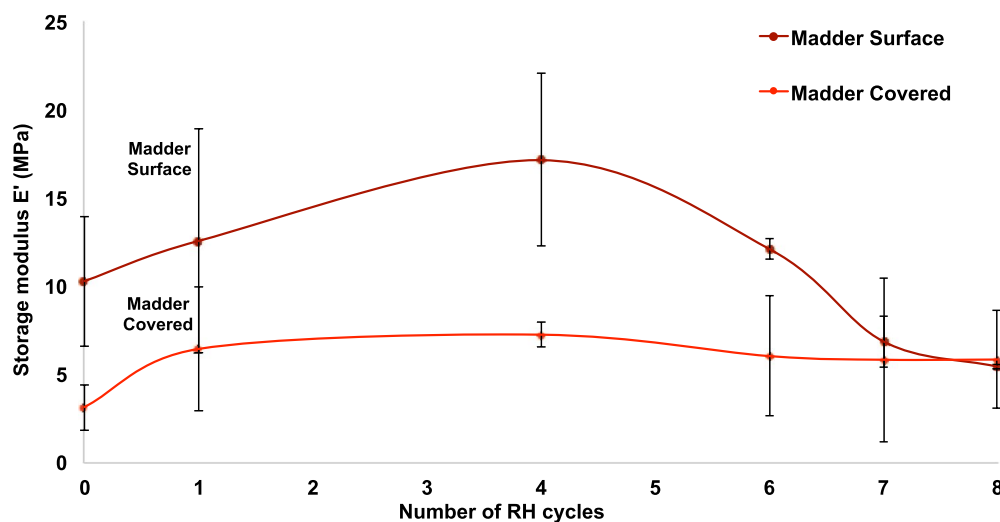
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Fig. 9 Evolution upon relative humidity variations of the storage modulus of the madder applied on the surface and covered layer, measured by indentation DMA at $f_1 = 1$ Hz at the penetration depth of 2 μm (with lines as guide to the eye)

investigated the impact of moisture weathering on the mechanical response of these oil paint films. Our results illustrate that paint layers are sensitive to moisture and that the impact of repeated RH cycles on the paint's micromechanics significantly depends on the nature of the pigment. Our indentation results show that the grey ground presents a strong decrease of both storage and loss moduli with the induced moisture weathering. However, upon 8 cycles of RH variations, the ultramarine paint tends to stiffen. This phenomenon may depend on various parameters. Each pigment requires a different amount of oil to form a paint film with a proper consistency for application. Such differences may impact the drying processes, the mechanical behaviour, the adsorption ability and thus the sensitivity to moisture of the pigment-oil systems.

Moreover, the differences in the viscoelastic moduli of the two madder films illustrate the influence of the position within the stratigraphy for the elastic and viscous behaviour of paint films. The covered madder layer is less affected by the moisture variations than the surface layer regarding the evolution of the bulk material properties. After the RH cycles, its viscoelasticity is affected, and its ability to recover from a deformation is reduced. The covered madder layer becomes more viscous after 8 cycles of RH variations than the surface madder. This phenomenon may impact the long-term behaviour of the overall paint build-up.

With these results we observe and quantify the differences in the evolution of the elastic and viscous properties of pigment-oil films with respect to their position in the paint stratigraphy. The intrinsic behaviour of a layer

upon moisture exposure depends on the interaction created with the other paint films of the build-up. This result is of major interest as it shows that one need to evaluate the intrinsic behaviour of a layer not only as an individual monolayer, but as part of a complex structure. The interaction involved between the different layers need to be considered in the study of the macroscopic mechanical behaviour of a painting.

Thus, pigment and oil systems show various sensitivity to moisture and to moisture weathering, depending on their nature. Such a difference in behaviour seems to be in close correlation with the own changes in viscoelastic properties upon repeated environmental variations, and with their position in the build-up. The enhanced discrepancies in elastic and viscous moduli of the different materials and layers may lead to the creation of stress fields, and potential macroscopic crack initiation. As a consequence, moisture-induced moduli's evolution impacts the local as well as macroscopic stress response. The exact evaluation of the stress field and the quantification of the hygric stresses generated in each layer and at macroscale are part of further research.

Conclusion

With this research using indentation, we evaluated the moisture weathering impact on the viscoelastic properties of a lead white-based ground, ultramarine, and madder paint film. This investigation uses the advantages of a specific ferrule-top nanoindentation protocol developed for cultural heritage studies to evaluate the storage and loss moduli of paint stratigraphies via DMA. Thanks to this approach, the mechanical properties of oil paint

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reconstructions and especially the moisture-induced evolution of their elastic E' and viscous E'' moduli are quantified. We determined experimentally the differences in the evolution of the elastic and viscous properties of paint layers and their variations depending on the exposure to moisture cycles. Based on our results, the composition of the paint layer and its position in the stratigraphy, also when considering layers with a similar pigment-binding medium composition, play a major role in the mechanical behaviour of a paint layer build-up. The nanoindentation results illustrate the evolution of viscoelastic behaviour of paint layers and underline that changes in elastic and viscous moduli within a layer evolve (i) upon repeated RH variation with respect (ii) to the pigment-oil combinations intrinsic sensitivity to moisture and iii) to the layer position within the stratigraphy.

Material list

Available information for the materials used to prepare the reconstructions.

> Animal skin glue: Verfmolen de Kat
> Red earth: Kremer Pigmente (ref: 4043)
> Lead white: Haagsch Schilderkundig genootschap Stichting Arti et Gaudia
> Madder: Madder Lake, genuine; Kremer Pigmente (ref: 37202) − PVC = 33%
> Ultramarine: Ultramarine Blue, light; Kremer Pigmente (ref: 45080) − PVC = 39%
> Boiled linseed oil: Royal Talens

Author's contributions
MT, EH and DI conceived the research. MT designed the research. DI and EH oversaw the study. MT performed the experiments and analyzed the data. All the authors contributed to the manuscript preparation and writing, and approved the final version. All authors read and approved the final manuscript.

Availability of data and materials
The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests
D.I. is co-founder and shareholder of Optics11. Rest of the authors do not have any competing interest.

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