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Multiscale characterization of liquid and dry egg tempera paints based on ochre pigments

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ABSTRACT

Understanding the mechanical properties of paints is crucial for their preservation, as these properties determine how paints deform under climate-induced stress and, consequently, affect their durability. This study focuses on egg-tempera paints, whose mechanical characteristics have been minimally explored so far. Various formulations using two natural ochre pigments were investigated. Initially, the pigments were characterized to identify compositional and morphological differences. Rheological analysis was conducted to study the liquid properties of the formulations. Tensile tests and dynamic mechanical analysis were performed on unsupported dry paints to assess their mechanical properties. Additionally, single-sided NMR was used non-invasively to probe the network mobility before and after nine months of aging, providing insights into the network tightness. It was found that ochre-based paints display significant brittleness. The viscoelastic properties of tempera paints are predominantly influenced by the type of earth pigments used and the pigment-to-binder ratio. Importantly, the liquid properties were found to correlate with the solid-state behavior, emphasizing the critical role of formulation in the final performance of tempera paints.

1. Introduction

Paintings are valuable and vulnerable artefacts that can be subjected to various types and degrees of mechanical stress, arising from microclimate changes or from improper handling during transport [1,2]. Climate variations create physical stress in the paintings due to water sorption/desorption processes, particularly time-dependent moisturerelated deformation (swelling/shrinkage) of the decorative layer and the support. Such stress increases the risk of mechanical damage to the artworks, potentially leading to crack formation. Museums strive to maintain stable and controlled conditions for their preservation, often at great environmental and energy expense; the associated costs are likely to rise with increasing climate imbalance. In order to justify allowable ranges of climate fluctuations, 3D computer models are used to investigate the risk of mechanical damage upon relative humidity changes [3]. However, these models require the input of data specific to each layer of the painting, such as the wooden support, and the ground, paint, and varnish layers in the case of panel paintings. Therefore, mechanical properties specific for these components need to be fully understood in order to preserve these fragile materials. Many studies have explored the mechanical properties of paint layers as a function of temperature and humidity [4–10], as well as the effect of solvents in the context of cleaning and restoring artworks [11–13]. However, less attention has been paid to the effects of composition and pigment morphology [8], despite the fact that the resistance of these paints also depends on their initial formulation, including the nature of the binder, pigment

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morphology, binder-to-pigment ratio, and pigment-binder interactions [14].

Publications dealing with the mechanical properties of paints mainly focus on tensile tests on mock-ups with different binders: mainly oil paints [7,11,13,15–17], but also modern polymeric paints [4,6,8,12,18]. Very few studies have been devoted to tempera paints [10] despite their significance. Tempera painting, which refers to the use of an aqueous binder, was the predominant technique between the 13th and 15th centuries, particularly with egg yolk as a binder (egg-tempera paint). In modern and contemporary times, it has still been used by major artists such as Edvard Munch, Otto Dix and Mark Rothko. It may be applied to a large variety of rigid supports such as wood panels, walls, plaster, canvas or cardboard. Therefore, studying the mechanical properties of paints is crucial to estimate the risk of mechanical damage to the pictorial layer, particularly understanding the evolution of these properties from paint formulation, through drying, to aging.

Poznańska et al. [19] studied the mechanical properties of egg and rabbit skin glue tempera paints in the form of large specimens ($6 \times 6 \times 80 \text{ mm}^3$) with different pigments as a function of relative humidity (RH). Among the materials used in tempera paints, the yolk binder and earth-based pigments are highly sensitive to humidity, adsorbing more water as the RH increases, which makes them more prone to swelling. In Poznańska's work, tensile tests were performed on tempera paints and compared with those on preparatory layers composed of animal glue and ground gesso. The study found that egg-tempera paints are more brittle than gesso.

This study explores the relationship between the macroscopic and microscopic properties of egg-tempera paints by comparing two natural earth pigments. We aim to illustrate how the viscoelastic characteristics of both liquid and dry paints relate to the pigment microstructure and binder mobility within the film. Additionally, we investigate whether specific features of the final mechanical properties of the dry films can be traced back to the initial rheological properties of the paints.

This study expands on an earlier publication that explored the interactions and rheological properties of egg-tempera paints made with Sienna [20], a yellow ochre pigment. Notably used during the Middle Ages, Sienna was frequently employed for undercoats in skin tones. The previous work did not, however, examine the mechanical properties of the pigment. Here, we will compare two Italian natural earths — Sienna and Avana — which differ in mineralogy and microstructure, in order to examine the effect of pigment composition on both suspension and film properties.

Our approach uniquely integrates comprehensive characterization methods — including X-ray diffraction (XRD), Mössbauer spectroscopy, scanning and transmission electron microscopy (SEM and TEM), laser diffraction, and water vapor sorption — with rheological measurements, dynamic mechanical analysis (DMA), and single-sided NMR relaxometry. This combined methodology not only offers a detailed understanding of the textural properties and binder network strength but also provides novel insights into the effects of pigment composition and aging on paint performance.

2. Materials and methods

2.1. Materials

Sienna (#40400), Avana (#40200) and synthetic goethite (#48000) were purchased from Kremer Pigmente (Germany). Fresh organic hen eggs were bought from a local store. Paint preparation was done according to a previous study [20] by mixing tempera binder (75 wt% of egg yolk and 25 wt% of ultra-pure water) with the pigment powder (binder-to-pigment ratios are indicated further) with a glass muller and slab. For DMA measurements, 500 μ m (wet thickness) films were applied with an aperture film applicator on PET foil (Hostaphan® RN 75 Kremer Pigmente) sheets and gently peeled off with a spatula after drying. For NMR relaxometry, they were applied on glass slides. Both types of films

were covered with a lid during drying $(1-2 \text{ days at } 21 \text{ }^{\circ}\text{C} \text{ and } 40-60 \text{ \%} \text{ RH})$ to slow down the evaporation and avoid cracks. Once dried, the samples were kept at ambient conditions in transparent plastic boxes to avoid exposure to UV light.

2.2. XRD

X-ray diffraction (XRD) diagrams of earths were collected using a Bruker D8 diffractometer equipped with Co radiation ($\lambda = 1.78897$ Å) operated at 40 kV and 40 mA. Intensities were measured with a Vortex 60EX silicon drift detector (Hitachi High-Tech America) for 8 s per 0.026° 20 step over the 5–90° 20 Co K α angular range. Divergence slit, the two Soller slits, the antiscatter, and resolution slits were fixed at 0.3°, 2.3°, 0.3°, and 0.2°, respectively. Quantitative phase analysis was performed from the Rietveld refinement of XRD data using the Profex software [20,57]. Quantification of the sample amorphous content was also performed from the Rietveld refinement of XRD data after addition of an internal standard (~20 wt% of corundum — α -Al₂O₃) to the sample and careful mixing and homogenization.

2.3. Mössbauer spectroscopy

The Mössbauer spectra were recorded in the transmission mode using a commercial constant acceleration spectrometer and a homemade liquid nitrogen stationary cryostat. A Co/Rh (50 mCi) Mössbauer source was kept at room temperature. The spectra were leastsquare fitted using the Voigt-line-based method to describe a hyperfine magnetic field distribution (HFD) implemented in the RECOIL software [21]. The isomer shifts are referenced to metallic iron at room temperature.

2.4. Scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM/EDS)

Scanning electron microscopy (SEM) analyses were carried out using a Zeiss Sigma 300 microscope at a voltage of 20 kV. Quantitative analysis was performed with a Bruker AXS microanalysis system composed of SDD 6030 129 eV EDS detector along with Esprit v2.2 software, although the particle size was too small and the roughness did not allow for proper measurements. The powder was deposited on a pad covered with carbon tape. The samples were covered with a conductive carbon film (~30 nm thick). For the quantitative treatment, carbon was deconvoluted but not considered in the quantification.

2.5. Transmission electron microscopy (HR-TEM)

Transmission electron microscopy experiments were performed on a JEOL-JEM 2100Plus electron microscope operating at 200 keV (LaB_6 gun) with an Orius camera 4 K (Gatan). EDX spectra were acquired with a SDD 80 mm² detector (Oxford Aztec software). Preparation of the samples were done by ethanol suspension deposition onto copper grids coated with a carbon membrane.

2.6. Laser diffraction particle size analysis

Size measurements were performed with a Mastersizer 3000 laser diffraction particle size analyzer with Hydro EV accessory (Malvern Panalytical). Powders were dispersed in water. Measurements were repeated three times per sample and the results are reported as volume and number distributions.

2.7. Water vapor sorption

Water vapor sorption isotherms were measured gravimetrically with the use of a vacuum microbalance from CI Electronics, UK, in the full relative humidity (RH) range (5 to 90 %) at 25 °C. A sample of ~ 0.1 g

was weighed and outgassed prior to a measurement under a vacuum of a residual pressure of <10 Pa. The vacuum was maintained until a constant mass was obtained, then subsequent portions of water vapor were introduced. The moisture content in a sample exposed to a given RH eventually attained a constant level termed the equilibrium moisture content (EMC). EMC is expressed as the increase of the initial mass of the outgassed sample in percent. Samples were considered to have reached EMC when the mass changes were <5 μ g in 3 min, provided at least 30 min had elapsed. The measurements were repeated twice and an average isotherm was calculated. The Guggenheim-Anderson-de Boer (GAB) three-parameter equation was used to describe the sorption of water vapor on the investigated materials:

$$\text{EMC}(\text{RH}) = \frac{V_{\text{m}} \cdot \mathbf{c} \cdot \mathbf{k} \cdot \mathbf{RH} / 100}{\left(1 - \mathbf{k} \cdot \mathbf{RH} / 100\right) \cdot \left(1 + (\mathbf{c} - 1) \cdot \mathbf{k} \cdot \mathbf{RH} / 100\right)}$$
(1)

where EMC is the equilibrium moisture content in percent, RH — relative humidity in percent, Vm — the monolayer capacity in percent, c — an energy constant related to the difference of free enthalpy (standard chemical potential) of water molecules in the upper sorption layers and in the monolayer, and k — the third parameter, related in turn to the difference of free enthalpy of water molecules between the free liquid and the upper sorption layers and is smaller than 1 [22]. The GAB equation was fitted to experimental points in the range from 0 % to 80 % RH.

The specific surface area (SSA) of the sample can be calculated from the Vm determined [22]:

$$SSA = \frac{V_m \times N_A \times A}{w_w}$$
(2)

where V_m is the monolayer capacity from the GAB equation, N_A is Avogadro's number (6.02 \times $10^{23}~mol^{-1}$), A is the area of one water molecule (10.8 \times $10^{-20}~m^2$) and w_w the molecular weight of water (18 g/mol).

2.8. Digital microscope (DM)

Sample surfaces were analyzed using a high-resolution Hirox RX-100 optical microscope equipped with an HR-2500 lens with 20–5000 \times magnification.

2.9. Rheology

Rheological shear measurements were carried out using a Thermo Scientific HAAKE MARS 40 rheometer. A sandblasted titanium 35 mmdiameter and 2°-angle cone/plate geometry was used. Tests were performed at 25 °C using a plastic hood to avoid drying of the paint during measurements. The linear viscoelastic region (LVER) (0.01–1 %) was determined by preliminary strain-scanning measurements in the range 0.01–1000 % at a constant oscillation frequency of 1 Hz. Frequency sweep measurements were then carried out at constant strain $\gamma = 0.1$ % with decreasing frequency from 100 to 0.1 Hz.

2.10. Mechanical properties

The dynamic mechanical analysis and static tensile tests were performed using Dynamic Mechanical Analyzer Discovery DMA 850 (TA Instruments) in room conditions (25 °C, 50 %RH). For testing, samples were cut as rectangular strips from dry layers which, after drying, were about 0.2 mm thick (dimensions and densities of the samples are reported in Table 3). The samples used were unsupported free films with width 7–9 mm and length about 30 mm and were mounted in tension with measuring length 10 mm. Strain scans were performed using a sinusoidal strain amplitude in a range of 0.01–0.1 % at a constant frequency of 1 Hz to determine linear viscoelastic region (0.01–0.04 %). Based on this, frequency sweep measurements were performed at constant strain of 0.01 % with increasing frequency from 0.01 to 100 Hz. Static tensile tests were performed with 0.125 mm/min displacement rate. The tests were repeated twice and the trends were consistent.

2.11. NMR relaxometry

NMR relaxometry measurements were obtained with a 27.63 MHz Magritek PM2 NMR-MOUSE with a Kea2 console at ambient temperature and humidity (21 °C and 30–40 % RH). A CPMG excitation was applied during 2048 echoes for a total acquisition time of 79.3 ms with a pulse length of 2.3 μ s. A 50 μ m slice was probed within the film and the signal obtained corresponds to an average of 1000 scans with a recycle delay of 2 s. The data were processed with an in-house Python code allowing to perform a bi-exponential fitting corresponding to (Eq. 3). In order to simplify the figures, a low-pass filter was applied to the relaxation curves with a cutoff frequency corresponding to the inverse of the duration of one echo (i.e. 38.7 μ s).

$$y(t) = \sum K \times e^{-\frac{t}{T_{2K}}}$$
(3)

3. Results and discussion

3.1. Pigments characterization

3.1.1. Composition

Avana and Sienna are similar in appearance, as both are Italian earth pigments with an ochre hue derived from the iron oxide they contain. However, since these natural earths are sourced from different deposits, their compositions vary. X-ray diffraction (XRD) analysis (Table 1) shows that Sienna contains three times more goethite (FeOOH) than Avana. This aligns with the observation that the color of Sienna closely resembles that of synthetic goethite, while Avana appears slightly darker (Fig. S1). In addition, hematite was identified in Avana (3.3 %), contributing to its darker hue. In Sienna, two types of goethite are present, with a shift towards higher angles indicating a reduction in dspacing due to an aluminum-for-iron substitution of approximately 10-15 % [23-25]. Crystals are smaller in Al-goethite than in pure goethite: Rietveld refinement, and more especially line broadening analysis, revealed average coherent scattering domain sizes of approximately 15 nm and 80 nm, respectively (Fig. S2 and Fig. S3). Goethite in Sienna is mainly Al-substituted (17.1 % of substituted goethite for 6.4 %

Table 1

Mineralogical compositions of Sienna [20] and Avana determined from Rietveld refinements. For each pigment, first column corresponds to individual component proportions and second column to proportions of mineral families.

	Sienna		Avana	
	[%wt]	[%wt]	[%wt]	[%wt]
Goethite	23.5(4)	23.5	6.5(2)	6.5
Hematite	-	-	3.3(1)	3.3
Kaolinite	32.7(5)	44.8	12.7(5)	13.3
Smectite	12.1(5)		_	
Chlorite	_		0.6(2)	
Calcite	12.9(2)	13.6	31.6(5)	58.8
Gypsum	0.7(1)		24.6(4)	
Anhydrite	_		2.6(2)	
Quartz	1.6(1)	4.3	0.3(1)	0.3
Anatase	2.7(1)		_	
Amorphous	13.8(11)	13.8	17.9(12)	17.9

The proportions of the main minerals are shown in bold.

of pure one), whereas only pure goethite (6.5 %) is present in Avana with a coherent scattering domain size of \sim 75 nm. The clay content also differs between the two samples: there are three times more clay minerals in Sienna (44.8 % corresponding to kaolinite and smectite) than in Avana (13.3 % of kaolinite mainly). On the other hand, considerably more carbonates (more than twice as much calcite in Avana than in Sienna) and sulfates (27.2 % gypsum and anhydrite) are found in Avana. In the latter, more than half of the mass (58.8 %) consists of calcium minerals (carbonates and sulfates).

Mössbauer spectroscopy is a valuable tool for characterizing ironcontaining samples. It efficiently identifies iron oxides and hydroxides, common components of natural or synthetic ochre pigments [23]. Because the method is only sensitive to iron atoms, its detection limit is lower than that of X-ray diffraction's (XRD), especially since it also observes micro- and nanometer species affected by superparamagnetic fluctuations. In the superparamagnetic state, Fe^{3+} compounds give similar Mössbauer spectra to a doublet, which hinders the phase identification. The superparamagnetic fluctuations can be suppressed, at least partially, at low temperatures, exposing static magnetic properties that are distinctly different for goethite α -FeOOH and hematite α -Fe₂O₃ in the studied pigment samples. Therefore, the Mössbauer spectra were recorded at room temperature (RT) and 85 K for reliable phase identification.

Fig. 1 shows the Mössbauer spectra of Sienna and Avana. The fit parameters are summarized in Table S1. The spectra were fitted considering a hyperfine magnetic field distribution (HFD), which is the appropriate method for oxide samples with reduced crystallinity [24]. Both Sienna and Avana contain mostly goethite and hematite phases. The spectrum of the synthetic goethite pigment used as a reference is shown in Fig. S4.

The Sienna spectrum changes strongly with temperature. At RT, it is dominated by a doublet characteristic of Fe³⁺ (59 % of the spectral intensity) and a sextet with asymmetrically broadened lines assigned to goethite (36 %). The spectrum also includes a weak sextet (5 %), unambiguously indicating hematite thanks to its characteristic hyperfine magnetic field (B_{hf} = 50 T) and quadrupole interaction shift (ε = -0.1 mm/s). In the spectrum run at 86 K, the hematite contribution remained unchanged (5 %), and B_{hf} typically increased. However, unlike bulk hematite, the Morin transition manifested in the sign change and absolute value doubling of the quadrupole shift ε was not observed. The suppression of the Morin transition can be caused by the nanocrystalline character of the hematite phase or by isomorphous Al-for-Fe substitution

[3]. The effect of Al substitution and/or reduced crystallinity is also apparent for the goethite phase. At 86 K, the goethite component meaningfully grew to a total of 89 % at the expense of the doublet. Moreover, the goethite contribution is distinctly differentiated between pure (p-) and Al-substituted goethite, which is reflected in the existence of two spectral components, Sextet 2 and 3, respectively, in Table 1. They essentially differ both in $\langle B_{hf} \rangle$ and ΔB_{hf} : the p-goethite component has the parameters of the well-crystalized and stoichiometric compound – a high $\langle B_{hf} \rangle$ with a narrow distribution width – whereas the Al-goethite component exhibits values typical for aluminum substitution and/or reduced crystallinity [25]. These features of Al-goethite contribute to the value of the hyperfine magnetic field, measured at a given low temperature, typically 80 K, according to the formula [25]:

$$\begin{split} B_{p} & (80 \text{ K}) = 50.55 - 10.8 \times \text{Al} - 20.8 \times \text{MCD}^{-1} \\ & \text{or} \\ & (B_{hf}) & (80 \text{ K}) = 51.00 - 26.3 \times \text{Al} - 0.0228 \times \text{SSA}, \end{split}$$

where B_p is the most probable B_{hf} value of HFD, Al is the aluminum substitution, MCD is the mean crystallite dimension (in nm) obtained from the broadening of the diffraction line, and SSA is the specific surface area (in m²/g). For an aluminum substitution of 0.15 and a crystallite size of 15 nm from the Rietveld analysis, we obtain $B_p = 47.5$ T, in good agreement with the 47.8 T value from Mössbauer analysis (Fig. S5). The specific surface area (SSA) of goethite phase in Sienna can be estimated from the above equation knowing $\langle B_{hf} \rangle$ and the aluminum content as SSA = 112 m²/g, consistent with a pedogenic origin [26].

The spectral components of the Avana spectrum are similar to those in Sienna. However, their relative contributions are distinctly different. First, the Fe³⁺ doublet that dominates in the RT Sienna spectrum is the weakest in the RT Avana spectrum, in which magnetic sextets dominate. It indicates better crystallinity and/or lower Al substitution of goethite, consistent with XRD results. The goethite sextet is not very different from the reference synthetic goethite (Fig. S4 and Table S1), with only slightly lower B_{hf} (31.2 T compared to 35.6 T). The relative contribution of hematite (34 %) is considerably higher in Avana than in Sienna, consistent with relative proportions of goethite and hematite obtained from XRD. The relatively high content of hematite in Avana is responsible for its darker color. The low-temperature Avana spectrum presents narrow sextet lines and well-defined hyperfine parameters for both goethite and hematite. The most probable Bhf value of HFD for the goethite component (Fig. S5), $B_p = 50.1$ T, is only slightly lower than that for pure and well-crystalline goethite. Obviously, both phases



Fig. 1. Mössbauer spectra of Sienna (a, b) and Avana (c, d) measured at RT and 86 K (upper and bottom row, respectively). Color code: yellow — goethite, yellowish — Al-goethite, red — hematite, gray — Fe^{3+} doublet. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

contain no or very few Al-for-Fe substitutions, and superparamagnetic relaxation arising from nano-crystallinity is effectively blocked at 86 K. The lack of the Morin transition in Avana, similar to Sienna, is caused by the small crystallite size.

Finally, the residual minor doublet component observed for both samples at 86 K can be explained as coming from paramagnetic Fe^{3+} ions in clay minerals, e.g. in kaolinite [27].

3.1.2. Microscopic characterization

Fig. 2 shows SEM images of Sienna and Avana. Both samples feature large particles ranging from a few microns to several tens of microns, surrounded by small, needle-like particles approximately 1 μ m in length, which are characteristic of goethite (see SEM images of synthetic goethite in Fig. S6). Laser diffraction analysis confirms the presence of small particles, most under 1 μ m in size (Fig. S7). EDX analysis shows that both samples contain calcite aggregates, while Avana also includes gypsum (Ca/S ratio = 1). In Sienna, there are also clay particles smaller than 1 μ m identified as kaolinite (Si/Al ratio = 1) and smectite (Si/Al ratio = 2). SEM images suggest that Avana has a greater abundance of goethite needles compared to Sienna, but EDX analysis reveals a higher iron content in Sienna, which is consistent with the composition determined by XRD. Smaller or differently shaped goethite particles may also coexist with the needle-like structures.

TEM images of both earths are shown in Fig. 3; additional information is provided by elemental maps (Fig. S8). Avana includes ironcontaining needle-like particles (<1 μ m) that are assigned to goethite not or weakly Al-substituted (Al/Fe < 0.1). Fe-rich round nanoparticles with a higher Al content (Al/Fe > 0.1) are also found. Platelet particles attributed to kaolinite (Si/Al ratio = 1) as well as larger ones corresponding to gypsum (Ca/S ratio = 1) and calcite (Ca-rich large particles $\sim 5 \ \mu$ m) account for the remaining material. In Sienna, two types of platelet particles are observed, the Si/Al ratio of which allows them to be labelled as smectite (Si/Al ratio = 2) and kaolinite (Si/Al ratio = 1). Ca-rich large particles about 5 μ m in size are attributed to calcite. Fe-rich particles are also found; they include pure or weakly Al-substituted (Al/Fe < 0.1) needle-like particles and highly Al-substituted (Al/Fe > 0.3) round nanoparticles, which is close to the maximal substitution [28].

The difference in morphology observed is consistent with the literature, where a smaller aspect ratio of goethite particles corresponds to increased Al-substitution, which indicates that Al-substitution inhibits crystal growth [29–31]. This difference can be linked to the geological context of their natural formation [28]. In addition, the nanometric size of Al-substituted goethite can explain the high value of SSA calculated with Mössbauer (see previous Section 3.1.1).

3.1.3. Moisture susceptibility

In order to compare the surface area of the earths and their affinity for water, measurements of water vapor sorption isotherms were carried out. This section follows a previous study on Avana and other pigments (azurite, lead white), and on tempera binders including egg yolk [10]. Here, we focus on a single type of pigment (ochre), and study the impact of its composition on its behavior in relation to humidity. Water sorption isotherms of pigments (Fig. 4) show a similar shape which indicates multilayer physisorption, with a layer thickness that increases with relative humidity (RH). Both earths have considerable hygroscopic capacity, that of Sienna being higher than that of Avana. As an example, at a RH of 50 %, the equilibrium moisture contents (EMC) are 3.5 % for



Fig. 2. SEM photos of Avana (top) and Sienna (bottom) pigments.



Fig. 3. TEM photos and EDX analysis on Avana (top) and Sienna (bottom) pigments.



Fig. 4. Water vapor sorption isotherm of Avana [10] and Sienna, and for comparison, synthetic goethite isotherm, fitted by GAB model.

Table 2

GAB constants obtained from the fit of water vapor sorption isotherms to the experimental data.

Pigment	Vm (%)	с	k	SSA (m ² /g)
Avana [10]	0.70(0.04)	16.2(3.4)	0.81(0.03)	25
Sienna	2.44(0.07)	17.7(1.5)	0.72(0.02)	88
Goethite	0.234(0.004)	55.9(5.4)	0.69(0.01)	8

Sienna and 1.1 % for Avana. Due to their micron particle size (see previous section), calcite in Sienna and gypsum in Avana present negligible specific surface areas (SSA) [32]. Pure goethite exhibits weak vapor sorption (Fig. 4) due to its low SSA (Table 2), which is a result of its large particle size, as measured by SEM (Fig. S6). In Sienna and Avana, the needle-like goethite particles are similar in size and shape to those of pure goethite (Fig. 2), suggesting they contribute little to moisture sorption. Therefore, the water adsorption of ochres is mainly due to the smectites they contain, which have a high SSA (over $100 \text{ m}^2/\text{g}$) because of their smaller particle sizes. Indeed, smectites, which are only present in Sienna, have a much higher water content because their interlayer spaces are hydrated, unlike kaolinite, where hydration occurs only on the outer surfaces. This is why the EMC of Sienna is three times greater than that of Avana across the whole RH range, Sienna containing about three times more clay than Avana. The presence of fine-grained Al-

Table 3	
Paint sample characteristics.	

-					
Sample name	Binder-to- pigment (B/P) mass ratio	Dry pain	Dry paint samples		
		PVC* [%]	Thickness [µm]	Density [g/ cm ³]	
Egg yolk film	-	0	130	1.09	
Avana 1.0	1	44	200	1.61	
Avana 1.25	1.25	39	200	1.52	
Avana 1.5	1.5	34	220	1.39	
Sienna 1.25	1.25	38	200	1.33	
Sienna 1.375	1.375	35	220	1.21	
Sienna 1.5	1.5	33	220	1.22	

 * Pigment volume concentration (PVC) when films are dry, calculated from pigment bulk densities and dry egg yolk film density.

substituted goethite in Sienna may also contribute to its high water sorption as compared to Avana.

To gain a better understanding of the interactions between earth pigments and water vapor, isotherms can be fitted using the GAB model (see Section 2.7), particularly suitable for mixtures rich in swelling clays. The values obtained for the three parameters V_m, c and k are listed in Table 2 and are consistent with those measured on other mixtures like soils [33]. They are significantly different from other pigments such as lead white (V $_m \sim 0.3$ %, c ~ 8 and k ~ 0.7) [10]. Determination of the pigments SSA from the GAB model is possible using Eq. 2. The parameter V_m is proportional to the SSA of the mixtures because it corresponds to one physical monolayer of water molecules. Sienna and Avana have SSA around 90 and 30 m²/g, respectively (Table 2). It can be noticed that the higher value obtained here in comparison to the one obtained with N₂ adsorption ($\sim 50 \text{ m}^2/\text{g}$) [20] is due to the smectites. Indeed, moisture adsorption occurs on the external surfaces and in the interlayer spaces of smectites, whereas $N_{\rm 2}$ allows mainly to probe only the external surfaces of minerals [34]. The parameter c expresses how strongly water binds to the primary sorption sites. It is slightly higher for Sienna, showing that the affinity for water is slightly higher than for Avana. Parameter k characterize the sorption state of the molecule in the upper sorption layers. It is closer to 1 in Avana as observed in kaolinite-rich soil, whereas the lower k of Sienna would reflect the presence of smectite [22,33].

Poznańska et al. showed that for tempera paints, the water vapor adsorbed by the dry paints can be estimated as the sum of the amounts sorbed by both the binder and the pigment. Dried egg yolk binder significantly adsorbs water (e.g. ~ 5 % at RH 50 %), much more than azurite and lead white, but in amounts comparable to ochre. As a result, ochre-based tempera paints are highly sensitive to high relative humidity [15,35], due to the significant water vapor sorption properties of both the pigment and the egg binder. Poznańska et al. also observed the swelling of paints with moisture adsorption. Indeed, smectite is highly swellable and kaolinite is a non-swelling clay [19]. Therefore, Sienna-



Fig. 5. Formulation of paints: water, binder (75 % egg yolk (EY) and 25 % water), and pigment theorical weight content before and after drying.

based paints are expected to be more sensitive to moisture changes compared to Avana-based ones.

3.2. Ochre-based egg-tempera paints characterization

3.2.1. Paint formulation

Six Sienna and Avana-based paints were formulated with different binder-to-pigment ratios (Fig. 5) to obtain a paint that could both be applied to a PET substrate and removed from it after drying in order to prepare unsupported films for mechanical testing. For each pigment, the preparation with the lowest binder-to-pigment ratio corresponds to the minimum amount of binder that needs to be added to each pigment in order to obtain a paint; this can also be characterized by the Critical Pigment Volume Concentration (CPVC), frequently mentioned in the litterature. With a pigment content above the CPVC, the amount of binder is insufficient to effectively mix the pigment, pores are present in the material after drying and the layer is not continuous. Conversely, adding too much binder causes the paint to crack as it dries, due to shrinkage during water evaporation. The binder demand is greater for Sienna than for Avana, likely because Sienna has a much higher smectite content, which increases its capacity to absorb water. Moreover, the binder demand is known to increase with decreasing pigment particle size [36] resulting in a higher specific surface area (SSA). The formulations selected in this study allow the formation of homogeneous films, without apparent bubbles or cracks (Fig. S9).

Tempera paints contain water both from the yolk, which is about 50 % water, and from additional water added as a diluent (Fig. 5). In contrast to oil paints, where curing and hardening involve chemical reactions, tempera paints primarily dry through the evaporation of water. This leads to differences in the paint composition before and after drying. The density of an egg yolk film is around 1.1, while the pigment densities are approximately 2.9 for Sienna and 2.8 for Avana, as measured by pycnometry. As expected, the film density decreases with an increasing binder-to-pigment (B/P) ratio. Despite the similar densities of the pigments, the overall density of the dry films is higher for Avana than for Sienna. The calculated porosities are about 30 % for Avana paints and 40 % for Sienna paints. This difference could be due to air being incorporated during mixing or to the higher clay content in Sienna, which swells with water and creates porosity as the water evaporates. This is supported by microscope images of the dry samples (Fig. 6), where Sienna paint shows pores on the surface, whereas Avanabased paints appear more uniform and form a continuous layer.

3.2.2. Bulk rheological properties

Rheological properties characterize the consistency of the paint and its behavior under the brush, which affect the final appearance of the decorative layer. They reflect the interactions of the investigated systems: the stronger the interactions, the more viscous and solid-like the mixed material. Traditionally, tempera is used in a very liquid form and applied in thin layers with short brushstrokes [37]. Flow and dynamic properties of Sienna-based egg-tempera paints have been characterized previously [20]: they show a shear-thinning behavior conferred by the egg yolk, consistent with results obtained from egg-tempera paints based on green earths [38]. Moreover, dynamic strain sweep measurements of earth-based tempera paints indicated storage moduli G' varying from 10¹ Pa for high water contents [20] to 10⁵ Pa for pigment-rich compositions [38]. The painter can adjust the formulation at a later stage to achieve the desired texture.

Here, we compare the viscoelastic properties of egg-tempera paints based on Sienna and Avana pigments in order to eventually link them to their mechanical properties in the next section. Dynamic oscillatory frequency sweep measurements in the 0.1–50 Hz range of pigmented and unpigmented paints are displayed in Fig. 7. The yolk binder exhibits a liquid-like behavior, with the loss modulus (G["]) greater than the storage modulus (G[']). Tempera paints exhibit a solid-like behavior (G['] – G["]) except for formulation Avana 1.5 with a high binder-to-pigment (B[']).



Fig. 6. Microscope images of surface of paint samples Sienna 1.5 (a) and Avana 1.5 (b) with a zoom of \times 30.



Fig. 7. Frequency sweep measurements at a strain of 0.1 % of egg yolk binder and Sienna and Avana tempera paints. Full points correspond to G' and empty points to G.

P) ratio, which exhibits a liquid-like behavior similarly to the binder. For all investigated systems, both moduli increase with the frequency. Overall, the lower the B/P ratio, the weaker the frequency dependence of G' and G", indicating a stronger solid character due to stabilization by pigment-binder interactions. This is also illustrated by the ratio tan $\delta = G''/G'$ that expresses the viscous response relative to the elastic response and increases linearly with the B/P ratio (Fig. S10). For the same B/P ratios (1.25 and 1.5), moduli are much higher with Sienna than with Avana pigment and all Sienna paints exhibit a solid-like behavior. This behavior is consistent with a higher content of clay, which adsorbs liquids, though it can also be linked to the shape of the particles and to the pigments that are very similar from the painter's point of view underline the strong influence of even minimal formulation differences on application properties and final rendering.

3.2.3. Properties of freshly dried and naturally aged paints

The mechanical response of freshly dried paint films has been investigated using dynamic mechanical analysis (DMA) and tensile testing, which are complementary techniques allowing the behavior under dynamic (small, non-destructive strain) and static conditions (large, destructive strain) to be studied, respectively.

The viscoelastic properties of liquid paints, previously assessed using



Fig. 8. DMA measurements of freshly dried egg yolk binder and Avana and Sienna tempera paints: frequency sweep measurements at a strain of 0.01 %. Error bars show standard deviation for two measurements. Full points correspond to E' and empty points to E.

rheology, are compared here with those of solid paints measured through dynamic mechanical analysis (DMA) [39]. While rheology evaluates properties under shear and DMA under tension (in this specific case), both methods provide insights into the viscoelastic response of the material. Analysis is performed at low strains and is therefore not destructive. A photograph of the setup can be seen in Supplementary Information section (Fig. S11). Frequency sweeps of egg yolk and tempera paints are displayed in Fig. 8. All storage moduli E' are larger than loss moduli E" and are in a range of 0.4–1.1 GPa. Moduli increase slightly with the frequency, which indicates that the mechanical response of dry egg-tempera paints varies insignificantly within the investigated range of deformation rates, similarly to glue-based ground [40]. The moduli of egg yolk are an order of magnitude lower than those of the paints, indicating that the paints are approximately 10 times stiffer than the binder film without pigment. This is in line with the modulus reinforcing theory, indicating that the addition of fillers (in this case pigment particles) generally increases the modulus [41]. Also, the paints are stiffer when the pigment volume concentration (PVC) is increased since pigment has a reinforcing effect [41,42] as pigmentbinder and pigment-pigment interactions increase [43].

In this range of frequencies, the formulations have fairly similar moduli, in particular all Sienna-based paints have the same E' modulus of around 0.7 GPa irrespective of B/P ratio, which indicates a predominant pigment effect. Indeed, it seems that these formulations are close to the critical volume pigment concentration (CPVC) since the dry paints, even those with the highest B/P ratio, have a rougher surface than Avana (Fig. 6). The presence of more small clay particles in Sienna generally results in a larger specific surface area, which may explain the fact that the binder is better distributed between the pigment particles and that pigment-binder and pigment-pigment interactions are more numerous. Furthermore, the presence of platelet-shaped particles, as well as those of goethite needle-like particles, increases the stiffness of paints due to the particle morphology. Indeed, as has been shown for kaolin-based polymeric paints [8], the higher the aspect ratio of the fillers, the higher the modulus of the paint. The tensile moduli ratio tan $\delta = E''/E'$ is much below 1, which indicates almost no damping and is consistent with the mechanical behaviors observed. Unlike the rheology results, DMA does not reveal a clear variation in tan δ as a function of the B/P ratio (Fig. S12), which could be expected due to the solid character of the dry samples, and the limited formulation range studied that results in similar tan δ values. Still, two groups of paints can be distinguished as the tan δ values at F = 1 Hz are ca. 0.15 for Avana 1.25 and Avana 1.5, and ca. 0.1 for the other paints — tan δ of dry egg yolk is about 0.2.

As tan δ are small (indicating $E'' \ll E'$), E' modulus can be approximated to Young's modulus E. The range of values obtained for paint films (0.4–1.1 GPa) is lower than that determined for tempera in the form of large specimens ($6 \times 6 \times 80 \text{ mm}^3$ bars) (0.75–4.2 GPa) [10]. Differences may result from the sample preparation method and amount of pigment. The PVC estimates for the Avana films were 30–45 %, while those for the bulk samples were 75 %. As these are the first DMA measurements on unsupported tempera paint films, no comparison can be found in the literature. Regarding oil and polymeric paint films, de Polo et al. (2021) underlined the diversity of results obtained: lower moduli (mainly in the range 0.01–0.1 GPa) were obtained for fresh films ([12] and references therein), but they are highly dependent on the age and curing state of the paints since after a few months the moduli range broadens to 0.001–10 GPa [8,11,12,14,17,18]. Direct comparison is not



Fig. 9. Exemplary stress-strain curves of unpigmented and pigmented paints with different ratio B/P, showing that the films are very fragile. These tests are only illustrative as variation occurs but highlight the main trends. Blue area represents values of strain at break (at 50 % RH) for tempera bar samples [10] and vertical red line for gesso [45]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

possible, as results may vary according to the selected solicitation rate [44]. Only taking into account Young's modulus E, materials classification charts (E vs density) would indicate that tempera paints properties correspond to those of a polymer-like material. However, this is only true for very small sollicitations, as dry tempera paint films break much earlier than polymers. Actually, tempera paints should rather be compared to composite materials as the pigment particles are dispersed in the binder matrix. Generally, paints can be described as effectively filled polymer systems [16].

In addition to dynamic tests, static tensile tests were performed with a strain-controlled ramp. The obtained stress-strain curves are displayed in Fig. 9 and show stress (force per cross-section) as a function of strain (sample elongation). At low strain, in the linear zone, samples undergo elastic deformation. Beyond this point, deformation is irreversible. In the case of artworks, stresses, which can be caused by variations in environmental conditions or improper handling, should be avoided as they will result in permanent alterations of the artwork. Egg yolk film has the highest elongation at break (\sim 3 %) and the lowest stiffness; it is therefore the most flexible [39]. As for the investigated paints, estimated stresses at break are in the range of 0.9-2.3 MPa and elongations at break are in the range of 0.1–1.3 % which indicates that tempera films are very brittle. These values are close to measurements performed on tempera bars at ambient RH that display strengths between 0.5 and 1.5 MPa [10]. Between the support and the paint layer, preparation gesso layers (composed of animal glue and ground layers) are also very brittle and have a low strain at break [40,45], even smaller than those of paints studied here. In this particular case, the paints would be more resistant to cracking than the glue-based ground.

Two groups of paints can be distinguished here: stiff paints (Avana paints with low B/P ratio and all Sienna paints) which break at low strain (below 0.5 %) on the one hand, and on the other hand Avana paints with high B/P ratio (Avana 1.25 and Avana 1.5) which break at strains higher than 1 %. These two groups also correspond, from a rheological point of view, to viscoelastic and liquid-like paint groups, respectively. Thus, it seems that differences in the viscoelastic behavior of liquid paints are reflected in the mechanical properties of dry paints.

Single-sided NMR experiments were performed to measure the relative proton (¹H) density and the proton mobility in dry paint films. NMR relaxation signals in tempera paint films and in a film of unpigmented yolk binder are plotted on Fig. 10 (left) and Fig. S13, respectively. To extract relaxation times (linked to the ¹H mobility) and ¹H densities, magnetization curves are modeled by a sum of decreasing exponentials (Eq. 3); the resulting parameters are displayed on Fig. 10 and Fig. S13 (right). The signal of egg yolk film is fitted by a triexponential function, whereas only two exponentials are necessary to fit the signal of pigmented films. Indeed, because pigments speed up relaxation, the fastest relaxation component might be too fast to be detectable by the NMR MOUSE setup, which is limited to detecting components with T_2 times greater than approximately 1 ms due to its use of echo-based detection methods. The longest relaxation time T_2 of egg yolk alone is about 10 times longer than those of the paints. Two main factors may explain this drop of the NMR relaxation times. Firstly, the presence of pigments may lead to a decrease in the mobility of the binder ¹H. Secondly, paramagnetic species (Fe³⁺) present in the pigment considerably decrease the relaxation time and act as relaxation sinks. It can be suspected here that the NMR relaxation enhancement mainly originates from the Fe(III) contained in the pigments. When films are freshly dried, relaxation is faster with Avana than with Sienna (Fig. 10). This cannot be explained solely by the concentration of Fe(III) in the two pigments as the latter is higher in Sienna than Avana. The spatial organization of Fe(III) inside the minerals is also crucial. Indeed, when Fe (III) ions are close to each other, their magnetic moments are aligned within domains and if the particle size is small enough for them to be single-domain, all these aligned moments generate a supermoment [46,47]. The particle becomes superparamagnetic, leading to a much greater increase in NMR relaxation compared to an equivalent amount



Fig. 10. Filtered NMR relaxation curves before (top left) and after aging (top right) in a 50- μ m slice of tempera paint films. Parameters extracted from biexponential fitting; pre-exponential factors (middle) and T₂ relaxation times (bottom) before (solid lines) and after (dashed lines) aging.

of isolated Fe(III). Many studies have been devoted to superparamagnetic particles and the relation of their magnetic properties and NMR relaxivity to their chemical, structural, and morphological characteristics [48,49]. It appears that hematite has a greater relaxivity than goethite. The greater relaxation in the Avana is consistent with the fact that Mössbauer detected much more hematite in Avana than in Sienna (Fig. 1). It can be also noted that in Sienna, some of the Fe³⁺ is substituted by Al³⁺ that is not a paramagnetic species, which could reduce the effect of the goethite [20]. In addition, the presence of many other components in Sienna can reduce the surface area of the binder interacting with goethite.

Bi-exponential fitting allows differentiating two proton populations: T_{2-fast} and T_{2-slow} . The T_{2-fast} population is present in higher proportions (50 % and 70 % in Sienna and Avana paints respectively, regardless of B/P ratio) and may correspond to high-density lipoproteins that are less mobile. This attribution is in line with the NMR relaxometry results on green earth tempera [50]. The T_{2-slow} population would then be associated to mobile lipids and low-density lipoproteins. As expected, the signal amplitude at the very beginning of the magnetization curve increases with the B/P ratio, as it is directly linked to the ¹H density (Fig. S14). Furthermore, T_{2-fast} and T_{2-slow} increase with the B/P ratio, as has been observed in oil paints [51]. In addition to the decrease of the paramagnetic species concentration, the decreased pigment amount in paint yields a more flexible film, as demonstrated with the tensile tests

(Section 3.2.3). NMR relaxometry therefore provides information on pigment-binder organization and network tension, which are linked to the initial B/P ratio.

The effect of aging at 21 °C under ambient RH conditions has been also explored. Strong differences are observed between the three films (Avana paint, Sienna paint, egg volk film). The aging leads to a decrease of the NMR relaxation times of Sienna paints (Fig. 10) and egg yolk film (Fig. S13). The proportion of the more mobile population (T_{2-slow}) , attributed to lipids, decreases significantly, from around 50 % to 30 %. Such a time decrease can be explained by the oxidation of lipids and lipoproteins followed by cross-linking [52,53]. An increase of the network tightness with aging has already been observed in oilcontaining paints by NMR techniques [54,55]. Furthermore, the signal amplitude at the very beginning of the magnetization curve decreases with aging for egg yolk film and both paints (Fig. 10 and Fig. S14). To a small extent, it may stem from a ¹H loss due the evaporation of volatile lipids arising from chain breakages. However, the main cause of NMR signal loss is due to the cross-links that reduce the mobility, as has been observed on waterborne and solvent-borne polymeric paints [56]. As the network hardens with age, egg tempera paints become stiffer, being less likely to resist external changes and more prone to cracking. Surprisingly, the magnetization curves for Avana films almost remain unchanged upon aging (Fig. 10 and Fig. S15). The high relaxivity of hematite may hide the effect of aging. This interesting question deserves further specific investigations.

4. Conclusion

Sienna and Avana are natural earths with distinct compositions and particle morphologies. These mineralogical differences influence the rheological properties of liquid paints. In particular, the clay content plays a crucial role, as it largely dictates binder absorption through the high affinity of swelling clays for water and strong pigment-binder interactions, which, in turn, impose the minimum binder-to-pigment ratio. In comparison to the previous work by Poznańska et al., the mechanical properties of tempera were measured on unsupported paint films mimicking historical paint layers. Generally, the tempera paints investigated in this study are very brittle, with moduli (E) ranging from 0.4 to 1.1 GPa. For the same binder-to-pigment mass ratio, Sienna-based paints exhibit a higher modulus (E) than Avana-based paints. The mechanical properties observed in liquid paints are reflected in their dry state. Notably, when the loss modulus (G'') of a liquid paint is higher than its elastic modulus (G'), the resulting dry paint tends to be significantly more flexible, as demonstrated in stress-strain tests. These intrinsic material properties change over time. With aging, the network crosslinks, which should result in a stiffer material that is less resistant to variations in external conditions. This study contributes to a better understanding of the aging of egg tempera paints, a mechanism less well understood than that of oil paints. Further research using dynamic mechanical analysis (DMA) could help quantify the changes in mechanical properties as tempera paint ages.

This pilot study enhances our understanding of the mechanical properties of the relatively understudied egg-tempera paints. Expanding this research by applying the same experimental protocol to different pigments with varying mineralogy and morphology would provide greater insights. Furthermore, as historical tempera paintings consist of several layers, including the paint, the preparatory layers and the wooden support, future studies should consider supported paint films to investigate paint/substrate interactions.

CRediT authorship contribution statement

Floriane Gerony: Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation. Katarzyna Poznańska: Writing – review & editing, Writing – original draft, Visualization, Investigation, Formal analysis, Data curation. Sonia Bujok: Writing – review & editing, Supervision. Laurence de Viguerie: Writing – review & editing, Methodology. Laurent Michot: Conceptualization. Bruno Lanson: Writing – review & editing, Investigation, Formal analysis. Sandra Casale: Writing – review & editing, Investigation. Fabrice Gaslain: Investigation. Józef Korecki: Writing – original draft, Visualization, Investigation, Formal analysis. Kinga Freindl: Visualization, Investigation, Formal analysis. Nika Spiridis: Investigation, Formal analysis. Côme Thillaye du Boullay: Visualization, Methodology. Anne-Laure Rollet: Writing – review & editing, Visualization, Conceptualization. Guillaume Mériguet: Writing – review & editing, Supervision, Funding acquisition, Supervision, Funding acquisition, Conceptualization. Maguy Jaber: Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

We declare no conflicts of interest associated with this publication.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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