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Connecting rheological properties and molecular dynamics of egg-tempera paints based on egg yolk

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Abstract: Egg-*Tempera* painting is a pictorial technique widely used in the Middle Ages, although poorly studied in its physico-chemical aspects until now. Here we show how NMR relaxometry and rheology can be combined to probe egg-tempera paints and shed new light on their structure and behavior. Based on recipes of the 15th century, model formulations with egg yolk and green earth have been reproduced to characterize the physicochemical properties of this paint at the mesoscopic and macroscopic scales. The rheological measurements highlight a synergetic effect between green earth and egg yolk, induced by the interactions between them and the structural organisation of the system. ¹H NMR relaxometry emphasizes the presence and the structure of a network formed by the yolk and the pigment.

Egg-*tempera*, the painting medium based on egg-yolk, is one of the earliest - and most durable - to be used in Western art, and the preferred and most widely used painting medium on wood panels in Italy until the end of the 15th century when the advent of oil eventually largely replaced it. It has been employed by artists, on canvas as well as wood, because of its visual qualities and durability, and the way it combines with certain pigments which are difficult either to use or handle in oil - for instance green earth pigments.

In egg-*tempera* paint, pigments were ground in yolk as a binder^[1], with water as the diluent to make the paint fluid enough to be applied with a brush. Yolk is a complex biological medium composed of 51.0% of water, 30.7% of lipids, 16.0% of proteins, 1.7% of minerals and 0.6% of carbohydrate^[2]. The structure and composition of yolk has been studied in the agro-food industry but although it has been used in paint for centuries^[3], its structural organisation and properties have never been studied in any depth in paint.

Rare are the publications reporting on the physico-chemical properties of the egg-*tempera* medium. Most of them have focused on the identification of the binder. Among these publications, Higgitt et al. (2005) explore the use of egg and oil as binders in Italian paintings of the 15th and 16th centuries (mainly through chromatographic techniques)^[4]. A proteomic approach^[5] was also applied via sampling on proteinaceous binders in mid-18th century samples from paintings from South America. Other publications deal with the evolution/degradation of the egg-tempera paint medium. Indeed, infrared hyperspectral microimages were used to investigate the alteration of organic

binders in paint layers after artificial UV light ageing on painted mock-ups^[6]. Degradation via saponification has also been observed in paint layers consisting of lead-tin yellow type I and egg yolk binder in a panel painting from the 15th century^[7]. The swelling of egg-paint films subjected to cleaning (by water or an organic solvent)^[8] was monitored by NMR relaxometry^[9].

Other authors reported on the characterization of the paint surface (colour, reflectance, rugosity) depending on the *tempera* paint composition (nature of the pigment and binder, egg yolk or rabbit glue, and their proportions), using interferometric profilometry and hyperspectral imaging techniques^[10], and also Laser Induced Fluorescence^[11].

It is therefore surprising for a painting technique so central to the art of painting in Europe that the actual physico-chemical interactions involved in the rheological and paint-film forming characteristics of egg-yolk as a binder, and its interactions with different pigments, have not been the subject of any in-depth investigation.

Among the different pigments used in paint with egg *tempera* as the binder, green earth was chosen as the pigment to investigate, because of its ubiquitous use in medieval Italian panel paintings as an under-layer for flesh^[12], and its equally ubiquitous presence in 17th century landscape paintings in Italy, to the deterioration of which a number of PhD and research projects have been directed^[13] ^[14] ^[15]. Cennino Cennini^[1], who details 14-15th century practices in his treatise *Il libro dell'Arte*, (known in English as *The Craftsman's Handbook*), wrote that green earth "is good for use in faces, draperies, buildings, in fresco, in secco, on wall, on panel and wherever you wish." Not only its stability and low cost explain its wide use in Early Italian painting, but also its use for shadows, what would later in the 19th century be called a 'complementary' colour, to the pink hues of the flesh in the light. Moreover, its nature, non-swelling phyllosilicates, constitutes interesting properties. The main minerals are celadonite or glauconite, both are phyllosilicate of the mica's family, and mainly composed of silica, aluminium and iron. There are different deposits in Italy, Cyprus and Bohemia^[12].

To compare and correlate macroscopic with microscopic properties and molecular structure with dynamics in *tempera* paint, we report in this work a bi-technical approach to characterise this kind of paint by combining rheology and NMR relaxometry^[16]. While rheological measurements give access to the macroscopic *i.e.* viscoelastic properties (elastic modulus G' , loss modulus G'' and yield stress), NMR relaxation rates (R_1) measure the accessibility and the interaction of protons with the surfaces of the

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dispersed pigment on a shorter timescale. The decrease of the magnetization, *i.e.* the relaxation, is caused by the fluctuations of the interactions between spins, and is therefore a sensitive probe of the molecular dynamics of the spins on a timescale of the inverse of the Larmor frequency [17]. The rheological properties of the *tempera* paint are first compared to those of its constituents and the dynamics of ^1H within the samples are monitored by NMR relaxometry.

Recipes from Cennino Cennini [1] were used for the reconstructions of green earth *tempera* paints: mixtures of green earth and egg yolk were prepared and compared to green earth suspensions in water. When formulations of identical pigment mass fractions are compared, the consistency of the samples changes dramatically (Figure 1, at 30 %wt).

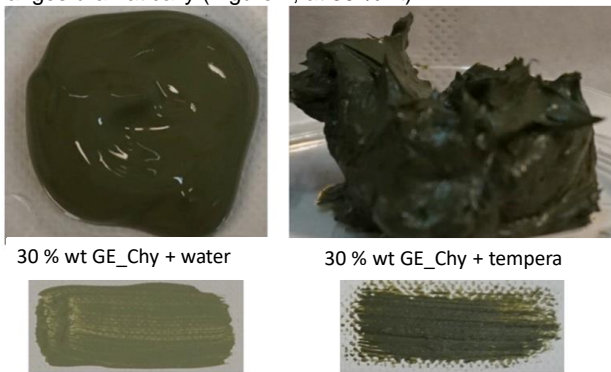


Figure 1: Visual comparison of formulations with 30 wt% of green earth, on the top left a suspension in water, on the bottom left the suspension applied on a canvas, on the top right an egg yolk tempera paint, on the bottom right the egg yolk tempera paint applied on a canvas.

Their rheological behaviour was then further investigated. All systems exhibit shear thinning behavior which is considered in the paint industry as beneficial for brushing. Comparing the aqueous suspension to the *tempera* paint, the latter exhibits far greater viscosities, shifted by a decade. This demonstrates an important synergistic effect between green earth and egg yolk in tempera paint: its consistency is considerably higher than that of a green earth water dispersion.

The dynamic properties of the systems confirm these observations. At low stress, the elastic modulus (G') is higher than the loss modulus (G''), and the moduli are constant (Figure 2): the paint is more elastic over the entire range of stress called the linear viscoelastic plateau. These higher elastic properties are the sign of considerable cohesion of the material. When the so-called yield stress is reached, the paint is destructured and flows ($G'' > G'$). By comparing the results on the tempera paint with the aqueous dispersion, we can see that the addition of egg yolk induces the enhancement of both the elastic and loss moduli as well as the yield stress (increased by a factor of three). This means that for the same amount of pigment, the painter must apply a stress ten times greater in order to spread his paint.

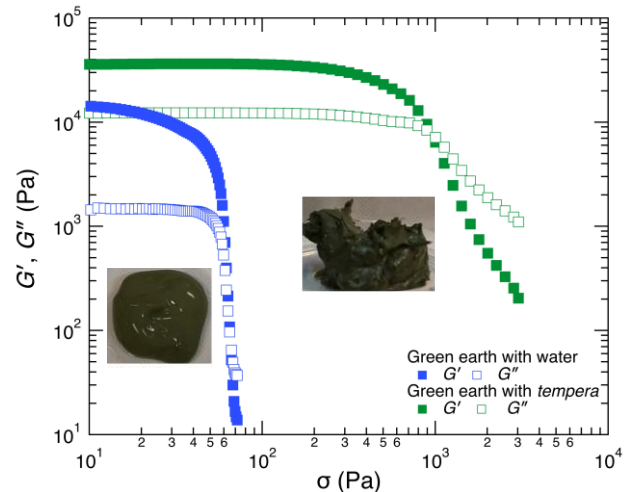


Figure 2: Oscillating stress-dependence of the storage modulus G' and the loss modulus G'' at 1 Hz and 25 °C for a model formulation of 30 wt% of green earth with water (blue) and egg tempera (green).

The molecular dynamics of ^1H is first monitored by NMR MOUSE at 19.6 MHz. Even though the strong gradient of the magnetic field leads to a small sensitive volume and thus lower sensitivity than measurements with large volumes in homogeneous fields, the advantage of this mobile NMR is to analyse the same samples as those used for rheology measurements. Only one ^1H population is observed due to the difficulty in measuring very high relaxation rates in these conditions. At this frequency, the relaxation rate R_1 of the dispersion of green earth, which contains paramagnetic species, increases with the pigment concentration (Figure 3). The presence of a paramagnetic center is indeed supposed to increase the relaxation and thus R_1 [19]. Conversely R_1 seems approximately constant for the tempera paint meaning that these protons are not directly in interaction with the mineral surface we can thus assign them to the lipoproteins of the yolk.

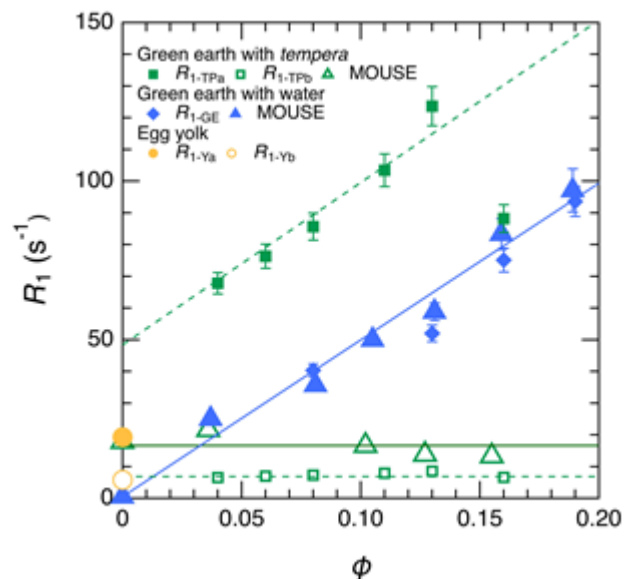


Figure 3: NMR relaxation rates vs volume fraction of green earth pigments in water (blue) and in tempera (green). Triangles correspond to data measured with the NMR MOUSE, squares and diamond with the Spinmaster FFC at 22 MHz. For comparison, relaxation rates of the egg yolk are plotted as yellow circles.

In order to go further in the assignment of the ^1H population, R_1 dispersion curves have been recorded on a wide frequency range using a Stellar Spinmaster Fast Field Cycling (FFC) relaxometer for the pigment aqueous dispersion R_{1-GE} , the egg yolk R_{1-EY} and tempera paint R_{1-TP} (Figure 4). Thanks to the wide range of Larmor frequencies, the attribution of the different proton populations can be refined. Indeed, two ^1H populations are observed in egg yolk (R_{1-EYa} and R_{1-EYb}) and in tempera paint (R_{1-TPa} and R_{1-TPb}). On the basis of Laghi et al. [20] analysis of ^1H relaxation in egg yolk, one can assign the fast relaxation rate R_{1-EYa} to water interacting with lipoprotein and the slowest R_{1-EYb} to lipoproteins themselves. This assignment is confirmed by the NMR spectrum recorded at 300 MHz (see SI). The protons of water molecules exhibit a faster relaxation than those of lipoproteins. Going further, the highest relaxation rate R_{1-TPa} in tempera paint can be attributed to water interacting with the pigment and the lowest R_{1-TPb} to dispersed lipoproteins. This is confirmed by the isotopic substitution of H_2O by D_2O that only affects the fast component of the relaxation (See SI).

The variation of R_1 measured using the NMR MOUSE versus pigment volume fraction ϕ shows very distinct behaviours for the sample without and with egg yolk (Figure 3). For aqueous dispersions of pigment, R_1 linearly increases as the concentration increases since the fraction of water close to the paramagnetic centers increases [21]. Indeed, celadonite minerals contains large amount of Fe^{III} [12], which paramagnetism strongly enhances NMR relaxation [22] via the electron- ^1H nucleus dipole-dipole interaction. The linear dependence demonstrates that the water is in fast exchange between the pigment surface and the interparticle space [22]. For the tempera paints, the absence of variation indicates that this ^1H population (corresponding to the R_{1-TPb} measured by FFC, i.e. to dispersed lipoproteins) are then far from the mineral surface since dipole-dipole interaction fluctuations scales as $1/r^6$. The other population R_{1-TPa} shows a parallel increase to R_{1-GE} and can be ascribed to water both in fast-exchange with mineral surfaces, and close to slow-moving proteins as evidenced earlier.

An interesting feature is the presence of the quadrupolar peaks on the R_{1-EYa} and R_{1-TPa} dispersion curves (Figure 4). The enhancement of the relaxation at very specific frequencies is referred to as the Quadrupole Relaxation Enhancement [23] and is due, here, to the presence of ^{14}N quadrupole nuclei. The quadrupole peaks, the position of which depends on the ^{14}N quadrupole parameters, appear when the dynamics are sufficiently slow [17]. Their presence on the R_{1-TPa} dispersion curve confirms the slow motion of these large lipoproteins in the vicinity of the pigment. The modelling of the R_{1-GE} dispersion curves has shown that the phyllosilicate basal surface is expressed at low field while the edge surface at higher field [24]. At low frequency, R_{1-TPa} dispersion curve is parallel to the R_{1-GE} one but shifted to higher values meaning that the relaxation due to the basal surface

is similar. Above 2 MHz, the R_{1-TPa} dispersion curve differs strongly from R_{1-GE} . A possible explanation is a preferential adsorption of the high-density lipoproteins on the edge surfaces of the phyllosilicate.

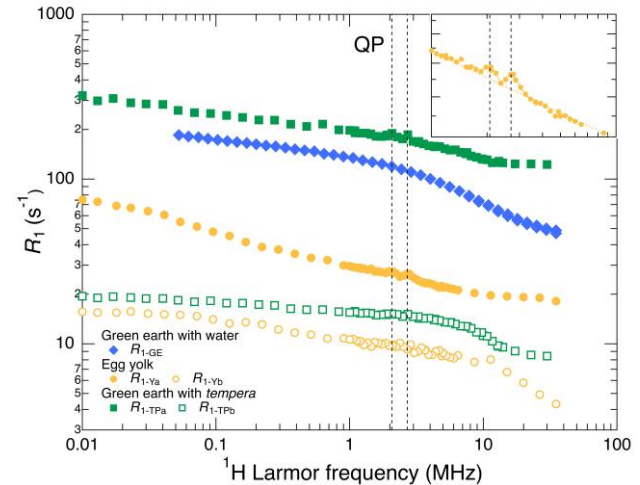


Figure 4: Dispersion of the NMR relaxation rates of ^1H with Larmor frequency for green earth dispersed in water (blue), egg yolk (yellow) and green earth dispersed in *tempera* (green) at about 30 wt% and 25 °C. One population is identified in aqueous dispersion while two populations can be distinguished in egg yolk and dispersion in *tempera* (see main text). Inset: quadrupolar peaks identified in R_{1-EYa} and R_{1-TPa} .

The correlation between the rheological properties and the mesoscopic dynamics is examined by plotting the elastic modulus G' versus the ^1H relaxation rate for tempera paints with increasing amount of green earth (Figure 5). On the one hand, no correlation can be seen between the slow component of the relaxation R_{1-TPb} and the elastic modulus G' . It indicates that a large part of the lipoproteins is still mobile in these dense mixtures, and that these do not contribute to the increase of the mechanical properties. On the other hand, R_{1-TPa} shows a significant correlation with G' and can be ascribed to water in the vicinity of both the pigment, as seen by the linear increase of the relaxation rate with ϕ , and adsorbed proteins as the presence of quadrupolar peaks show. From these observations, we can infer that these proteins are preferentially adsorbed on the reactive edges of the pigment platelets and that this adsorption is the origin of the strong change in the rheological properties and the observed synergetic effect.

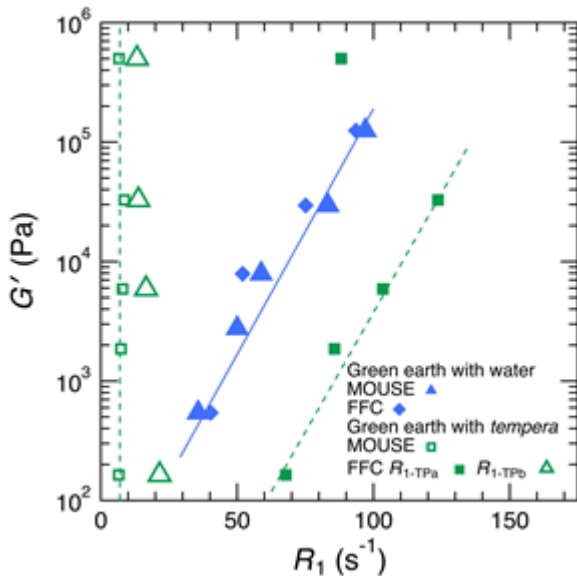


Figure 5: Evolution of the elastic modulus (G') as a function of the NMR relaxation rate (R_1) for series of green earth suspensions (blue) and tempera paints (green) of varied volume fractions (0.03 to 0.16). Triangles correspond to data measured with the NMR MOUSE, squares and diamond with the Spinmaster FFC at 22 MHz.

All in all, the tempera paint is on a macroscopic scale a viscoelastic material with a yield stress. Its elastic properties increase with pigment concentration, as does its yield stress. Under flow, it is shear-thinning which is an advantage for the painter. The addition of yolk as a binder increases the elasticity.

Relaxometry experiments confirm the dynamics of two proton populations, lipoproteins dispersed in the matrix and water close to the surface of the phyllosilicates and absorbed proteins, the interactions between proteins of the yolk and green earth are identified thanks to the quadrupolar coupling of ^{14}N observed in relaxometry.

The comparison of water dispersion of green earth, where water is only adsorbed on the mineral surface, and the (egg yolk) tempera paint, where both the lipoproteic binder and water interact with the surface (observed by relaxometry), has shown the synergetic effect observed in an egg-tempera paint from a rheological point of view. This explains also the importance of identifying two proton populations in the paint. One can infer the presence of a network between the edges/surface of the phyllosilicates connected by a part of egg yolk proteins giving rise to strong rheological changes, whereas the other part of lipoproteins appears to be unaffected.

This study does not claim to solve or answer all questions with regard to the importance of the binder type on the ability of the paint to be applied to a surface, rather it shows the great interest of combining those two techniques, applied to artistic paint materials, to give new insights in the network binder-pigment and put oneself in the painter's shoes.

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Keywords: tempera paints, green earth, rheology, relaxometry, yolk

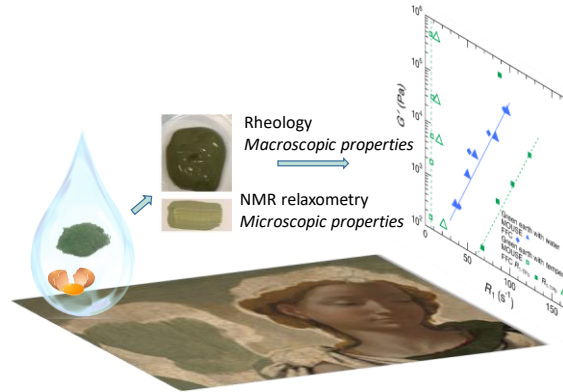
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COMMUNICATION

Crack the code of egg-tempera paints

The macroscopic and microscopic properties of egg-tempera paint prepared with green earth are highlighted via rheology and NMR relaxometry



Agathe Fanost, Laurence de Viguerie, Guylaine Ducouret, Guillaume Mériquet, Philippe Walter, Helen Glanville, Anne-Laure Rollet, Maguy Jaber*

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