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Influence of the addition of crushed glass on the physical and chemical properties of lead white oil paint

Lucy Cooper¹ⁱ, Alexandre Pierre^{2*}, Elisabeth Ravaud^{1,3}, Yannick Mélinge²ⁱⁱ, Odile Majérus³, Daniel Caurant³, Gilles Bastian¹, Myriam Eveno^{1,3}, Christine Andraud⁴, Aurélie Tournié⁴

¹ *Centre de Recherche et de Restauration de Musées de France, C2RMF, Paris, 14 Quai François Mitterrand, 75001 Paris*

² *CY Cergy Paris University, Laboratory of Mechanics and Materials of Civil Engineering L2MGC EA 4114), 5 mail Gay-Lussac – Neuville-sur-Oise, 95031 Cergy-Pontoise, France*

³ *Chimie ParisTech, PSL Research University, CNRS, Institut de Recherche de Chimie Paris (IRCP), 11 rue Pierre et Marie Curie, 75005 Paris, France*

⁴ *Centre de Recherche sur la Conservation (CRC), Muséum national d'Histoire naturelle, CNRS, Ministère de la Culture, 36 rue Geoffroy Saint Hilaire, 75005 Paris, France*

*Email: alexandre.pierre@cyu.fr

Abstract

Microscopic particles of transparent colourless silicate glass have been found in numerous oil paintings dating from the fifteenth and sixteenth centuries. The widespread occurrence of such powdered glass has been demonstrated in combination with various pigments and within different pictorial layers in works by artists belonging to the Italian, German, Netherlandish, French, Spanish and Portuguese schools. The aims of this paper are to evaluate the multiple current hypotheses for its use, which include modification of transparency, siccative effects and rheology, and through reconstruction experiments, to gain a better understanding of the modifications of the physical and chemical properties of the paint induced by the addition of glass powder. Experimental works have been carried out using lead white based oil paint mixtures, since this pigment is one of those most frequently mixed with crushed glass in Italian

ⁱ Present address: Bibliothèque nationale de France (BnF), laboratoire scientifique et technique, 14 avenue Gutenberg 77607 Bussy Saint-Georges, France.

ⁱⁱ Present address: Laboratoire de Recherche des Monuments Historiques (LRMH, CRC UAR 3224), 29 Rue de Paris, 77420 Champs sur Marne - France

paintings. Optical (reflectance and transmittance), rheological and Fourier transform infrared spectroscopy measurements were carried out on pure lead white paint as well as on paint mixtures containing varying amounts of crushed glass. These experiments indicated that the addition of crushed glass increases the transparency and siccative effect of paint films, without significantly altering rheological properties.

Keywords: Paint reconstructions, Lead white, Rheology, Glass inclusions, Oil paint

1. Introduction

The use of crushed glass in the context of oil painting is referred to in manuscripts dating between 15th and 17th centuries [1] [2] [1-2]. From the 1970s onwards, the observation of transparent particles has been mentioned anecdotally in studies of paintings and polychrome sculptures. However, the importance of this practice in European oil paintings from the 15th and 16th centuries only began to be appreciated over the past two decades.

It was first discovered in Italian works by Perugino and Raphael, and has since been found in pieces by other Italian artists such as Lorenzo Lotto and Leonardo da Vinci [3] [4] [5] [6] [7] [8]. The practice has also been reported in case studies for paintings belonging to Germanic, French, Portuguese and Spanish schools [9] [10] [11] [12]. Major surveys into the occurrence of crushed glass in paintings have been undertaken by Lutzenberger et al. [13] who focused on works by German and Dutch artists and by Spring [10] [14], who undertook an analytical assessment of the works in the National Gallery, London.

These studies have provided a better idea of the frequency and chronology of this painting practice, which coincides with the development of oil paint. The addition of powdered glass began in Northern Europe during the first half of the 15th century and c. 1430 in Netherlandish and Germanic paintings. It then spread to Italy in the second half of the 15th century.

Extensive bibliographic study revealed that although crushed glass was most often detected in surface glaze layers, mixed with red lake pigments, glass particles have been detected with a variety of pigments and at different layers of the painting stratigraphy.

While in Germanic and Netherlandish paintings, glass was found almost exclusively with red lakes generally applied in the upper layers, this does not seem to have been the case for Italian paintings, where one of the pigments most frequently found mixed with glass particles was lead white [10]. The majority of the Italian works studied by Spring, 27 out of 45, ie. 60%, used glass particles in priming layers, very often in combination with lead white and lead-tin yellow [10]. Artists mostly from Umbria, Northern Italy, Tuscany, Venice and Rome and such as Pietro Perugino, Michelangelo and Raphael, were found to use this combination in priming layers. The practice of using crushed glass along with lead white in preparation layers was also found in subsequent studies of paintings by Lorenzo Lotto and Leonardo da Vinci [6] [7] [8]. The differences in location of the glass in Italian paintings, either in superficial or in deeper layers, must be underlined. It raises the question of the reasons of such a use of glass in oily lead white based grounds by the painter.

Elemental analysis of the transparent and colourless glass particles revealed the use of two types or families of colourless 'ash' glasses, differentiated by the flux used to melt the glass. The type of the glass used by the artist depends on the geographical location where the work was done, as well as the background or training of the artist. In Italy and around the Mediterranean, glass was made from the ashes of marine plants rich in sodium giving a soda type glass (>10 % weight Na_2O and 60-70 % weight SiO_2 approximately). While in Continental Europe, including the Netherlands and Germany, glass was made from the ashes of forest plants rich in potassium, producing the so-called potassic glass (>22 % weight $[\text{CaO} + \text{K}_2\text{O}]$ and 50 % weight SiO_2 approximately) [15] [16] [17] [18] [19]. Manganese oxide was also used as a raw material in these glasses, added as a decolorizer in order to offset the yellow green hue resulting from iron

oxide impurities [20]. This is of interest since manganese is known to have a siccative effect on oil paints with Mn^{2+} ions promoting surface drying during the curing of oil paint [21]. This ability for manganese to accelerate the drying of oils had been understood since the early 1800s and it is known to have been included as a drier in British artists' colormen's catalogues from the 1890s [22] [23].

Several hypotheses regarding the usefulness of crushed glass as an additive in oil paint, have been proposed both in ancient recipes and through recent publications [2] [13] [14]. Firstly, the addition of glass may increase the transparency of the paint layer by acting as a transparent filler [24]. Secondly, it has been suggested that the glass particles may change the texture of the mixture and thereby improve its workability during application. [14] [25] [26]. Finally, it has also been proposed both in historical manuscripts and in recent scientific studies that the powdered glass has a siccative action on the paint [2] [10] [14].

Whatever the reason, the addition of colourless glass to the paint would have needed to provide some rapid and tangible benefit for the artist. Reviewing the previously published scientific studies, mentioned above, allowed us to summarize the composition of the glass particles, as well as the associated types of pigments and pictorial layers found in the historical examples.

2. Research aim

To the best of our knowledge, the studies published into the use of crushed glass in paintings have been limited to a description of analytical findings with no previous exploration undertaken into possible modifications of the paint induced by the addition of the glass. This paper, which focusses on lead white pigment, is part of a larger research project aiming to evaluate these three principal hypotheses for several different pigments and glass compositions through reconstruction experiments [27] [28]. Lead white was chosen as the pigment in this

study since the scientific literature [6] [7] [8] [10] demonstrates the significant occurrence of powdered glass mixed in lead white in Italian works.

In order to study whether the addition of glass powder has any effect on the physical and chemical properties of lead white oil paint, paint samples were prepared with linseed oil as the binder, lead white as the pigment and with soda lime type glass powders. Optical, rheological and Fourier transform infrared spectroscopy measurements were undertaken on pure lead white paint as well as on paint mixtures containing varying amounts of crushed glass. Some conclusions, specific to the use of glass particles, are drawn and their influence of the physical and chemical properties on the painting is discussed.

3. Materials and methods

3.1. Glass particles in painting

Based on previous studies [3-11], glass particles have been detected in mixtures with a variety of different pigments and colourants. The size of the glass particles present in paint samples has been shown to vary between 2 and 50 μm . [13]. However, since the thickness of a paint layer is generally less than 30 μm , particle sizes between 2 and 30 μm are most often detected. The concentration of glass within a pictorial layer appears to vary from less than 5% to around 20% of the surface area.

Glass was most commonly found in layers mainly containing red lakes, lead white and carbon black. For example, in the “Calvary” painted in France by Josse Lieferinxe (early 16th century, Louvre Museum), potassic glass particles are present in the priming and under layers. Figure 1 shows a glass particle mixed with lead white and red lake in a pink layer between two blue layers composed of azurite from a sample of the Virgin’s blue mantle.

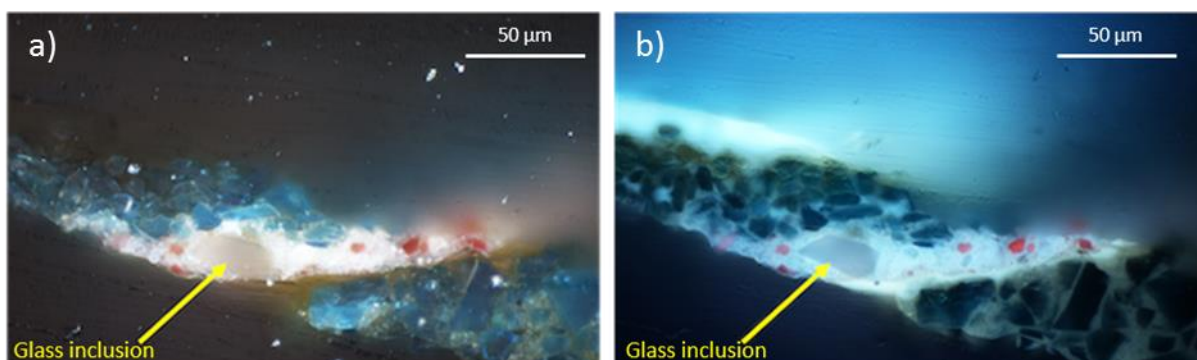


Figure 1. Cross-section from a sample of the Virgin blue mantle in “Calvary” by Josse Lieferinxe (1493 – 1508), Louvre Museum: a) under visible light b) under ultraviolet light.

Although both soda and potassic type glass particle have been found in 15th and 16th century oil paintings, we decided to focus our study on the soda type which was the formulation produced in Italy during the 15th-17th centuries and is the most common type found in Italian paintings and therefore also the type most often mixed with lead white pigment [10].

For the reconstruction experiments, we use a modern commercial colourless soda lime glass. Quantitative analysis of its composition was carried out for elementary analysis by PIXE (Particle-Induced X-ray Emission) and PIGE (Particle-Induced Gamma-Ray Emission) (AGLAE-C2RMF). The results are presented in **Table 1** and are compared with published historic soda glass compositions [29] [30] in Table 2. The modern glass is a relatively pure soda-lime type, with low iron and manganese impurities. It contains lower relative quantities/percentages of alkali metal oxides (Na₂O and K₂O) and higher quantities of CaO and SiO₂ than historic glasses. It was selected in this initial study in order to eliminate any possible siccative effect which could be caused by the manganese since one theory is that the manganese ions located on the surface of the glass grains leach into the paint mixture containing the pigment particles in suspension in the oil binder [10].

Table 1. PIGE and PIXE analysis of the modern commercial soda lime glass.

Modern soda lime glass	Oxide									
	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	CaO	MgO	Fe ₂ O ₃	MnO	SO ₃	TiO ₂
% weight	74.61 ± 0.07	1.57 ± 0.05	9.78 ± 0.04	0.80 ± 0.01	11.17 ± 0.09	1.66 ± 0.03	0.08 ± 0.003	<0.01	0.14 ± 0.02	0.04 ± 0.003

Table 2. Composition of the historic soda type glasses used during 15th-18th centuries [29] [30].

Historic soda type glass compositions (oxide. % weight)												
Classification	Century	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	CaO	MgO	Fe ₂ O ₃	MnO	SO ₃	Cl	P ₂ O ₅
Cristallo	16-18	67.8 - 72.7	0.5 - 2.1	14.1 - 18.7	2.5 - 5.3	3.5 - 5.6	1.2 - 2.2	0.2 - 0.4	0.2 - 0.7	0.1 - 0.4	0.5 - 1.1	0.1 - 0.3
Vitrium blanchum	16-18	64.9 - 68.8	0.7 - 2.1	11.8 - 15.7	1.8 - 4.2	8.4 - 11.2	2.3 - 4.1	0.2 - 0.7	0.2 - 1.1	0.2 - 0.5	0.6 - 1.0	0.1 - 0.5
Façon-de-Vénice	16-17	61.8 - 66.0	1.3 - 1.6	13.1 - 15.9	4.3 - 6.8	8.6 - 10.6	2.4 - 3.3	0.3 - 0.5	0.2 - 0.5	0.1 - 0.2	0.6 - 0.8	0.3 - 0.4

3.2. Glass powder preparation

Two particle sizes of crushed glass were prepared in order to study the effect of specific surface area. These grain sizes were selected as a representation of the previously reported minimum and maximum ranges of particles detected in pictorial layers of works from the 15th to the 17th century. The first particle range is $\leq 10 \mu\text{m}$ and the second range is around 25-30 μm .

The protocol used for preparing the glass powders by grinding and sieving is based on the method published in [31] [32]. After grinding the glass and sieving the raw powder using a vibrating sieve shaker with stainless steel sieve of mesh size 80 μm , the fractions obtained with particle sizes up to 80 μm were washed with ethanol under ultrasound, to remove fine glass particles agglomerated on the surface of the grains. Sedimentation of the fine powder fraction $\leq 80 \mu\text{m}$ was then performed in ethanol in order to obtain particle size fractions of lower amplitude: $\geq 10 \mu\text{m}$ and $\leq 10 \mu\text{m}$. Ethanol washes were repeated several times until a clear supernatant was obtained. At the end of the decantation process, both powder fractions were dried in an oven at 50 °C for 24 hours. Finally, the vibrating sieve shaker with stainless steel sieves of mesh sizes 50, 32 and 25 μm was re-used on the fraction containing particles with sizes between 10 and 80 μm , in order to obtain a powder with particle sizes ranging between 25 and 32 μm . The homogeneity of the size of the grains of prepared powders was verified on representative samples using a scanning electronic microscope (SEM).

3.3. Paint sample preparation

Additive free ‘boiled’ linseed oil was used as the binder for the paint formulations. The lead white used (Kremer[®]) contains 90.34 % weight hydrocerusite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) and 9.66 % weight cerussite PbCO_3 , as determined by X-ray powder diffraction and Rietveld refinement.

For each of the two particle size fractions (≤ 10 and $25\text{--}32\ \mu\text{m}$), oil and lead white pigment mixtures, integrating three different glass addition concentrations (5, 20 and 50% by weight relative to the white lead pigment), were used to highlight the effect of the size and concentration of the glass inclusions. The composition of the mixture of lead white and oil was chosen to give a consistency which provided a good workability to the paint. From this reference mixture, glass powder was substituted for corresponding weights of lead white to preserve the weight ratio of solid fraction to oil. As a control, a sample of the pigment and oil was also prepared without the addition of crushed glass. Figure 2 illustrates the preparation of the painting and a summary of the parameters relating to the preparation of these paint film samples is given in the Table 3.

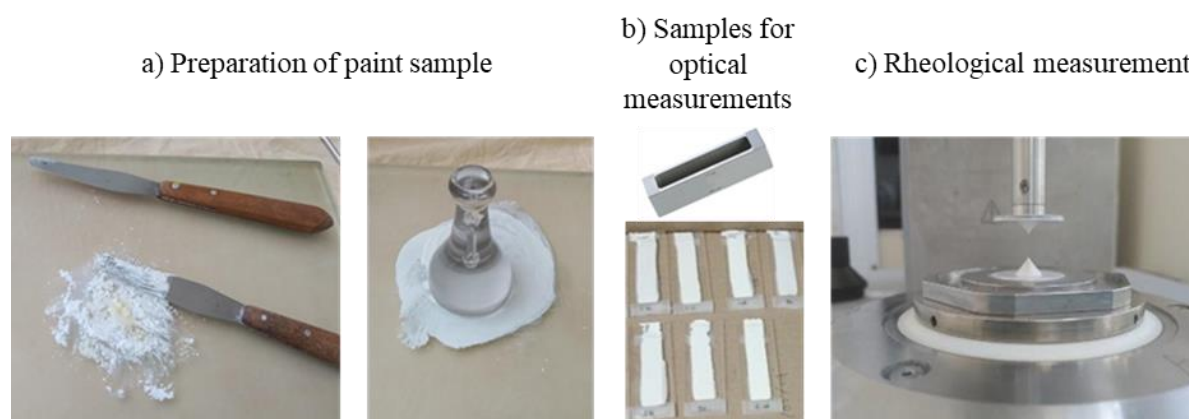


Figure 2. Images showing the preparation of lead white oil paint samples for measurements: a) Paint sample preparation with knife and grinding b) Film applicator and paints film for optical measurements c) Paint sample during a rheological test.

For the rheological measurements, paint mixtures were used in their fresh state and applied directly to the rheometer. For the other measurements, mixtures of fresh paint were applied as thin films on to microscope slides (see **Figure 2** b) with the help of a 4-sided film applicator which enabled films of 30 and $90\ \mu\text{m}$ to be deposited. For the Fourier Transform infrared measurements, the films were applied at a thickness of $120\ \mu\text{m}$.

For the optical measurements, films were prepared at 2 thicknesses (30 and $90\ \mu\text{m}$) and the films were left to dry before measurements were carried out. It should be noted that the

applicator was used manually and film thicknesses for both the wet and dry films were not verified by another method.

Table 3. Mix-design of the paintings tested in this study.

Mixture	Glass concentration (% weight in relation to lead white pigment)	Particle size (μm)	Paint formulation
1	Without glass	-	4 g lead white + 1030 μl linseed oil
2	5	≤ 10	3.8 g lead white + 0.2 g glass powder + 1030 μl linseed oil
3		25 – 32	
4	20	≤ 10	3.2 g lead white + 0.8 g glass powder + 1030 μl linseed oil
5		25 – 32	
6	50	≤ 10	2.0 g lead white + 2.0 g glass powder + 1030 μl linseed oil
7		25 – 32	

3.4. Fourier Transform Infrared (FTIR) measurements

The FTIR (Fourier Transform Infrared Spectrometry) analyses were carried out on a Frontier spectrometer coupled with a Spotlight 400 Imager (Perkin-Elmer), using attenuated total internal reflection (ATR) imaging mode with a germanium crystal controlled by Spectrum IMAGETM software. The Spotlight Imager microscope is equipped with an MCT detector to allow the creation of hyperspectral maps of the samples.

Measurements were undertaken on the samples by focusing on maps of 100 x 100 μm (pixel size 1.56 μm) between 4000 and 750 cm^{-1} . The drying of the paint films was monitored under laboratory conditions at room temperature. Once the fresh paint film had been spread on its support (microscope slide), an IR mapping was recorded every hour during the first 8 hours and then at 24 and 48 hours and at 3.5 months using the same acquisition parameters.

3.5. Spectrophotometry measurements

A Cary 5000 UV-VIS-NIR (Agilent) spectrophotometer was used. This model is coupled with an integrating sphere with a diameter of 110 mm, covered with a very fine powder coating of polytetrafluoroethylene (PTFE). The measurements were carried out over a visible spectral

range, from 380 to 780 nm, with a measurement time of 100 s and a baseline correction. First, a "reference blank" was acquired in order to establish a reference characteristic of the measurement environment and the function of the device. This reference was made using a "perfect" white Lambertian diffuser with the same coating as that of the integrating sphere. Each measurement carried out has been normalized with respect to the "reference blank".

3.6. Rheological measurements

The rheological properties of the suspensions were investigated under simple shear conditions using a rheometer (Anton Paar MCR 102[®]) equipped with a plate-plate geometry of 25 mm in a narrow gap configuration of 0.5 mm (**Figure 2 c**)). In order to avoid slip at the plates, sand paper is glued onto both plates. All the experiments were conducted at a set temperature of 25 °C. The temperature was controlled using a Peltier temperature control device located below the lower plate. Each tested sample was transferred to the lower plate, taking care that no air bubbles were trapped in the sample. The upper plate was then displaced to achieve the required gap. A new sample was used for each shear stress measurement and the plates were cleaned with acetone after each test. Experiments were conducted with stress-controlled measurements by applying constant values ranging from 1 to 100 Pa during 6 min to ensure steady state and the stabilization of the shear rate value. Each paint formulation was characterized at least twice to ensure the reliability of the measurements.

4. Results and discussion

4.1. Optical measurements

Potential optical modifications due to the presence of glass particles include alterations to the reflectance and translucence of the pictorial layers and can be explored using diffuse reflectance and transmittance measurements [33]. The analysis of the transmittance, reflectance and

absorption of the lead white paint films, with and without glass inclusions, are shown respectively in Figure 3.

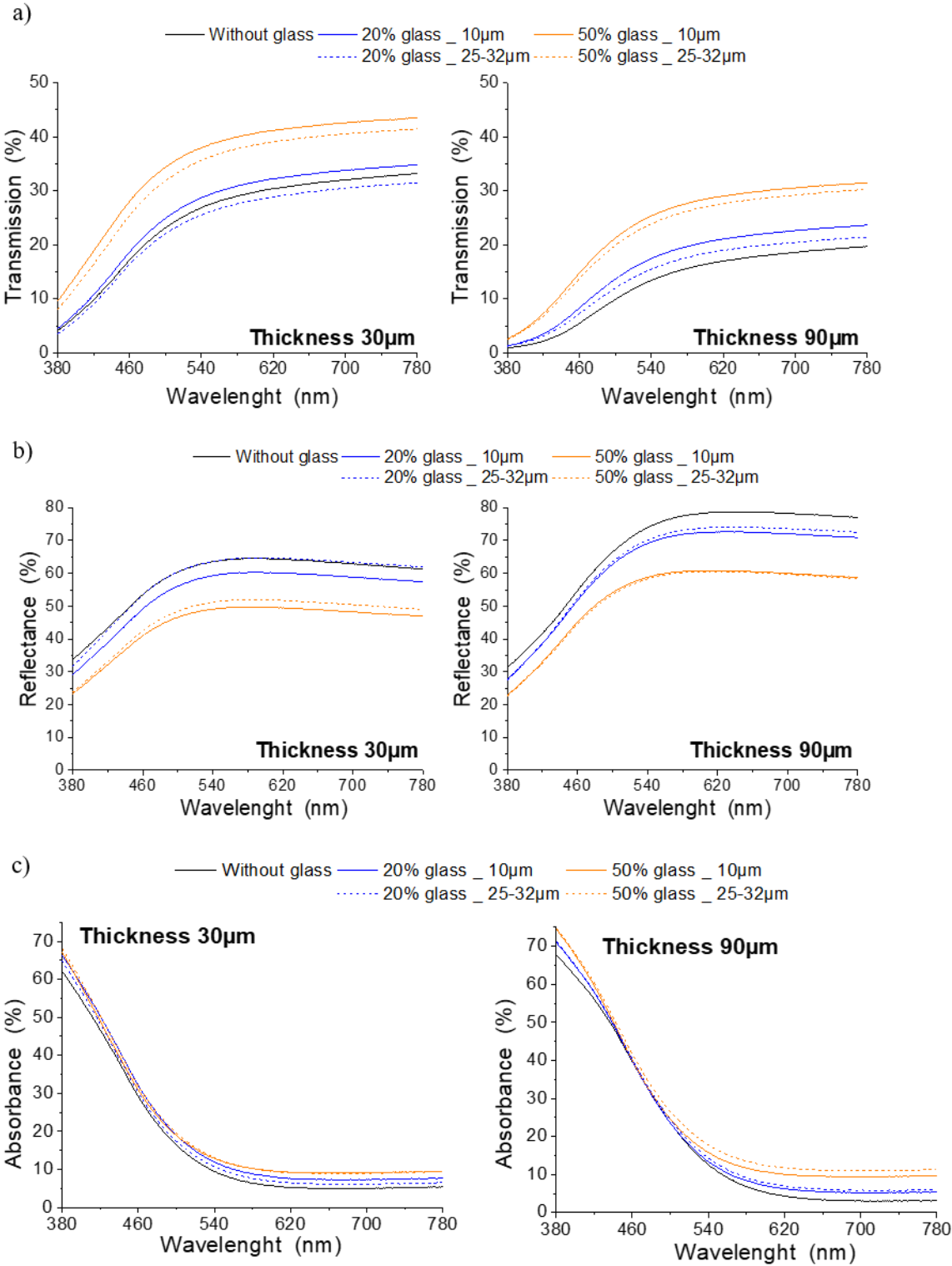


Figure 3. Spectra transmission comparison of low thickness films, left 30 µm and right 90 µm: white lead without glass (black line), and with glass with 20% and 50% by weight concentrations relative to

*the white lead pigment (blue and orange lines) and particle sizes 10 μ m and 25-32 μ m (dotted lines);
a) Transmission ; b) Reflectance ; c) Absorbance.*

For the film thicknesses studied, the optical properties are dominated by light scattering effects. There was no specular light transmission or reflection. The scattering of light inside the film layer is created by the presence of heterogeneities of different optical index compared to the ambient medium; the more the light is scattered, the more the reflectance increases. Overall, increasing the thickness of the film has the effect of increasing reflection (R) and decreasing transmission (T).

All the compounds in the paint films absorb at short wavelengths, whereas they do not absorb (or very little) at the longest wavelengths. The absorption, defined by $100\% - R - T$, in the short wavelengths will therefore increase with the thickness and will be little affected in long wavelengths.

The substitution of lead white by glass particles increases the transmittance and to a very small extent the absorption, and decreases the reflectance of the films. The decrease in reflectance and the increase in transmittance are due to a decrease in light scattering. Indeed, it is the particles of lead white, with a relatively high optical index (around 2) which create the diffusion of light, in comparison to the linseed oil, which has a relatively low index (slightly less than 1.5). This means that when lead white is substituted for glass (with an optical index only slightly higher than 1.5 very close to that of linseed oil), the light propagates in a more dilute medium.

The effect of the size of the glass particles on the optical properties of the lead white paint films is weak, but this weak influence is nevertheless difficult to interpret. For the absorption, there is no noticeable difference. For the reflectance and transmittance, smaller glass particles seem to scatter light less than larger ones. Until now, we have considered that glass and linseed oil to have approximately the same optical index. If the optical properties of two paint films of the same thickness but with two glass grain sizes, differ, we can assume that this is due to the

difference in optical index between the glass and the linseed oil, which creates slight diffusion. At constant concentration, [34] predicts an increase in the quantity of scattered light when the size of the scatterers decreases, because they become more numerous, which is the opposite of the observed results. The sizes of scatterers considered here are relatively large, and it is therefore possible that Mie resonances create a particular scattering enhancement for the chosen sizes [34] [35]. Another explanation could also be given by the thickness of the layers produced, which are not perfectly controlled.

From an optical point of view, the substitution of lead white by glass reduces the effects of light scattering. This has the effect of increasing the translucency of the pictorial layers, while decreasing their reflectance, and therefore their brightness.

4.2. Monitoring of the paint drying process via FTIR measurements

Over a period of 3.5 months the drying process was compared for 120 μm thick white lead paint films, with and without the substitution of 20% of the lead white pigment by weight with glass of particle size $\leq 10 \mu\text{m}$. Each presented spectrum is an average calculated from an FTIR 100x100 μm map, pixel size 1.56 μm , measured between 4000 and 750 cm^{-1} . Figure 4 illustrates the ATR FTIR spectra for 1, 8, 24, 48 hours and 3.5 months of drying respectively.

The drying of linseed oil involves complex reaction mechanisms: the radical polymerization of linoleic and linolenic acids, di- and tri-unsaturated respectively, which are contained in the oil. The radicals of these acids are formed by the removal of a hydrogen atom belonging to a methylene group (CH_2) in the vicinity of a double bond. In the presence of oxygen from the air, hydroperoxides are formed which themselves provide radicals and lead to aldehydes, ketones and carboxylic acids. The polymerization step includes the recombination of the radicals [28-30].

The spectra for the wet paint samples (1 hour after application) contain bands characteristic for both the oil and the lead white pigment. The linseed oil bands occur around 3000 cm^{-1} , at ~ 2960

(shoulder), 2925 and 2855 cm^{-1} , caused by vibrations of the C-H bonds in the CH_2 and CH_3 groups. There is also a smaller peak $\sim 3010 \text{ cm}^{-1}$ linked to the cis-type unsaturated group (C=C-H) and a band at 1740 cm^{-1} , resulting from the carbonyl (C=O) stretch. The principal band from the lead white occurs at $\sim 1400 \text{ cm}^{-1}$, representing lead carbonates, besides a band at $\sim 3540 \text{ cm}^{-1}$ assigned to the (OH) stretch vibration of hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) [36]. The spectrum for the sample containing glass particles also shows a broad band between 900 and 1100 cm^{-1} which is due to the contribution from the asymmetric stretching vibrations of Si-O-Si bonds.

During the first 8 hours, no difference is observed in the spectra between the paint drying processes for films with and without glass. After 24 hours, the isomerization cis trans CH=CH is evidenced from the diminution of the band at 3010 cm^{-1} . After 48 hours, the drying of the film containing the 20% by weight of glass is more advanced than that of the film without glass, showing signs of isomerization and oxidation. The peak around 3010 cm^{-1} , attributed to the cis-type unsaturated CH group (C=C-H), has disappeared, which signifies the total isomerization of the cis double bonds in the fatty acids to a trans configuration [24]. The glass-containing film has a carbonyl band around 1740 cm^{-1} , which is broader and slightly offset compared to the film without glass. After 3.5 months the paint films both with and without glass are dry and their spectra are more similar to each other. The spectra for the two samples show decrease in the peak at 3540 cm^{-1} (OH str) assigned to the (OH) stretch vibration of basic lead carbonate. We have yet to explain the decrease in size of this band, however, it is known that even trace amounts of water can markedly affect the intensity of this peak [37].

According to this comparative evolution of paint with and without glass, the addition of 20% by weight of glass (relative to the pigment) to the lead white oil paint has an effect on the drying kinetics, in accelerating the drying process, within the first 24 hours. The spectrum for the lead white paint film without glass shows that the isomerization process only began after 48 hours

(decrease of 3010 cm^{-1} band). The accelerating effect on drying through the addition of glass to lead white is therefore highlighted.

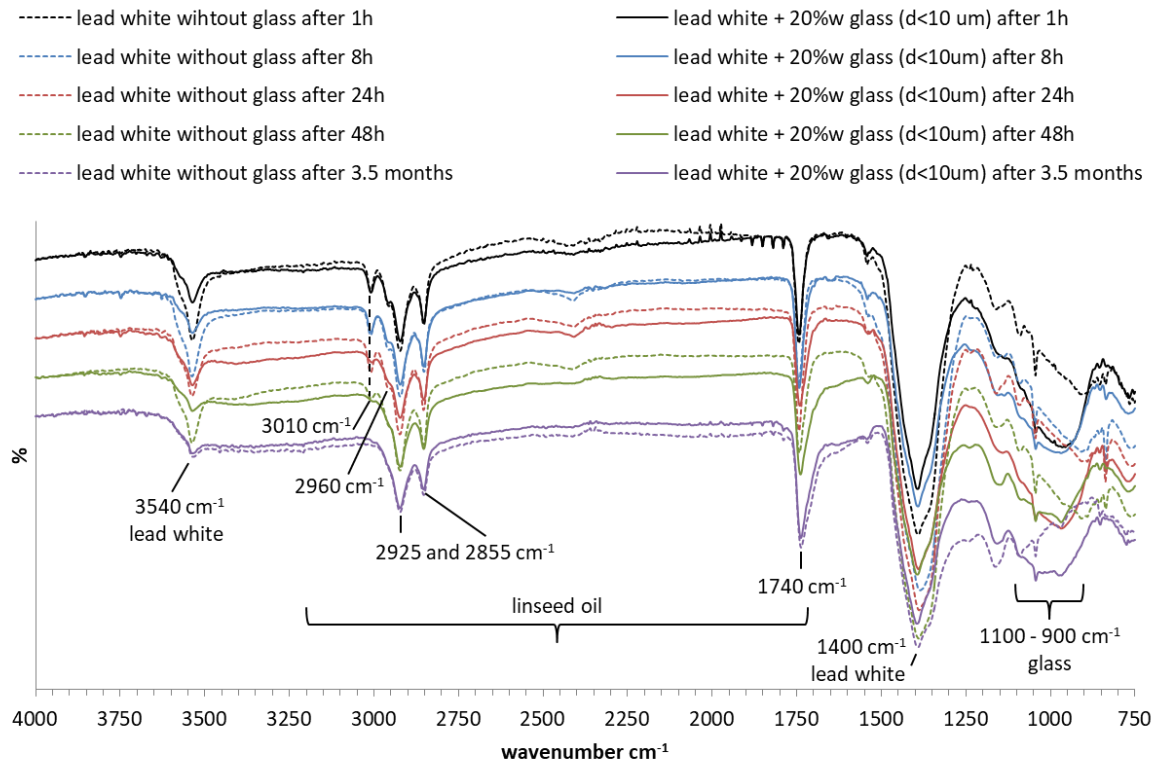


Figure 4. Comparison of ATR FTIR spectra for drying period ranging between 1h and 3.5 months: influence of glass inclusions/incorporation in the linseed oil based paint.

4.3. Rheological measurements

In order to assess the effect of lead white and glass inclusions on the rheological properties of the oil-based paint, we compared the flow behavior of the paintings. **Figure 5** illustrates the obtained shear flow curves for linseed oil, oil and lead white and oil and lead white containing glass inclusions with 5% solid volume fraction. As expected, and previously reported in literature [33], the paint suspensions behave as a simple yield stress fluid with shear-thinning behaviour, which can be well modelled using a Herschel-Bulkley model (Eq. (1)) [38]:

$$\tau = \tau_0 + \eta_{HB} \dot{\gamma}^n \quad (1)$$

Where $\dot{\gamma}$ is the shear rate, τ the shear stress, τ_0 is the yield stress, η is the consistency and n is the flow index behaviour. For such a model, the shear within the fluid can be observed when the applied stress exceeds the yield stress. Through shear rate condition, the fluid exhibit a shear thickening behavior for n higher than 1 and a shear thinning for n less than 1. A simple viscoplastic behavior (i.e like a Bingham fluid) is detected for n close to 1.

The suspensions containing different sizes of glass inclusions can be accurately modelled by a Herschel-Bulkley law and a same index $n = 0.5$, as predicted by the theory of Seth et al. [39]. This means that whatever the brushstroke velocity, the paint will have the same ability to structure itself through a shear-thinning behavior: the consistency does not depend on the shear rate, i.e. the velocity of the paint application by the brush.

From the Figure 5 lead white pigment tends to give the linseed oil a complex fluid behavior: the addition of lead white generates a yield stress the oil, the suspension does not flow while a critical shear stress value is not reached. Values of the computed yield stresses are in agreement with the work of Salvant Plisson et al. [28]. Increasing of the consistency and exponent index decreasing are also noted. As a consequence, lead white addition tends to liquefy the mixture while a shear stress is applied. Therefore, the lead white pigment strongly changes the rheological behavior of the pure linseed oil.

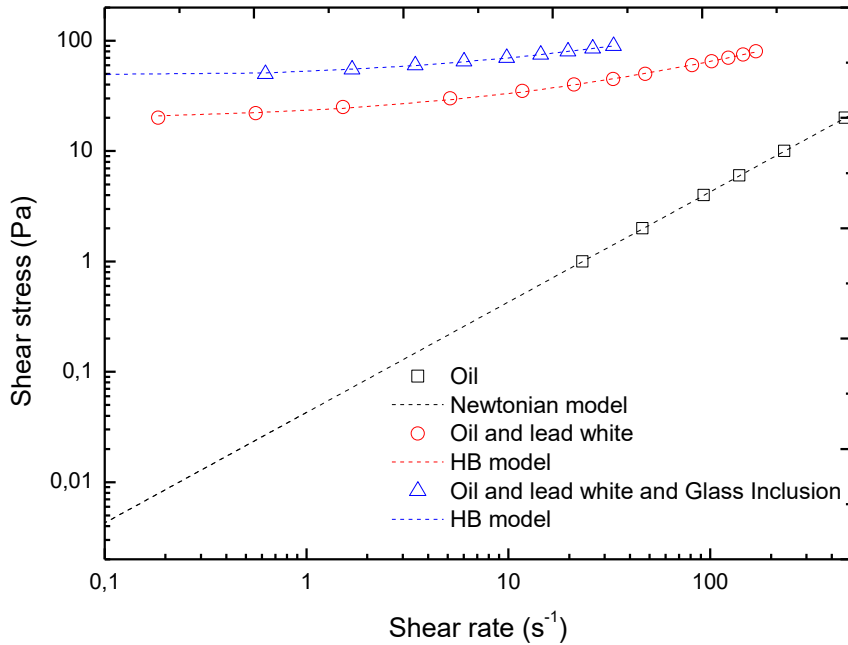


Figure 5. Examples of shear flow curves: experimental measurements and fitting using Newtonian model for linseed oil and Herschel-Bulkley model for ‘oil and lead white’ and ‘oil and lead white containing glass inclusions with 5% solid volume fraction’ suspension.

All the computed values of the yield stress are greater than the value of maximum shear stress leading to the yield value proposed by some authors [25] [40] following Eq. (2)

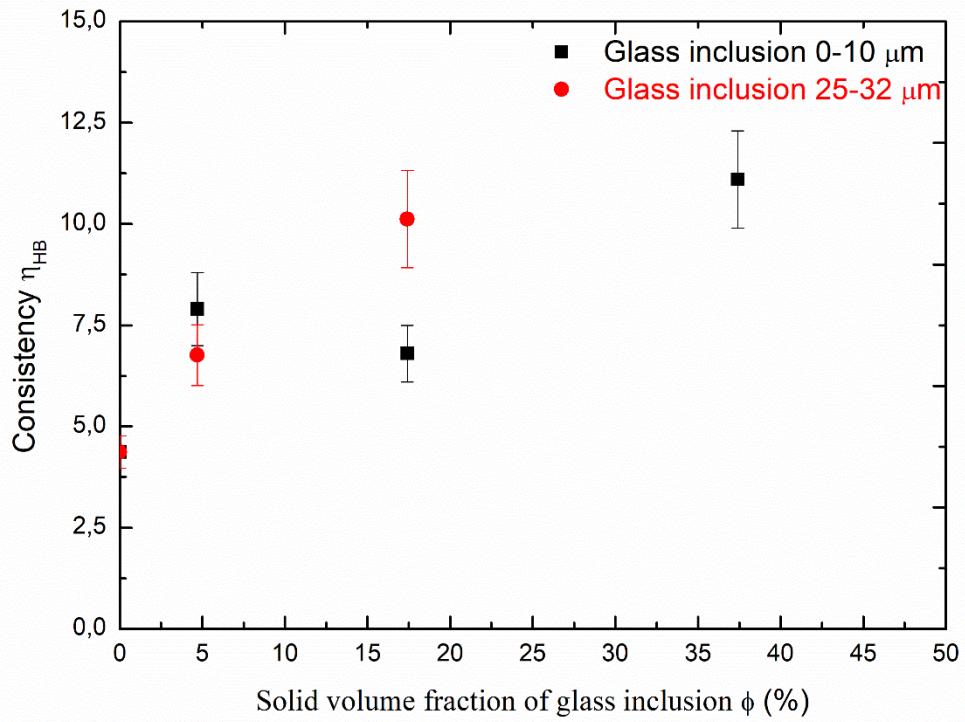
$$f = \frac{4\pi\gamma dh}{\lambda^3} \quad (2)$$

With d the depth of the brushmark into the paint, λ the average wavelength of brushstrokes and h the layer thickness. A value of 0.12 Pa was computed by Salvant Plisson et al. [41]. The gravity effect can be neglected compared to surface tension effect and the depth of the brushmark can be considered much lower than the brushstrokes average wavelength ($d \ll \lambda$) and also a small film thickness ($h \ll \lambda$).

Thus the yield stress values for paint samples of lead white in linseed oil are above this critical value, which could help to inhibit the levelling process of the paint (reduce the tendency of the paint to run).

Our results indicate that the glass inclusions do not influence the yield stress requirement for the inhibition of levelling process. The Figure 6 a) and b) respectively show the evolution of the consistency and the yield stress as a function of the solid volume fraction of the glass inclusion: The addition of the glass inclusion does not modify significantly the yield stress of the paints. Also, the consistency, ie. the ability of the paint to flow under the brush increases linearly as a function of the solid volume fraction. This linear change may be due to the dispersing effect of glass inclusions within the pigment particles, which could lead to a better lubrication of the paint. However, since the shear rate value during the application of the paint using a paintbrush would be higher than 10^2 s^{-1} , the role of the glass inclusions would not be perceivable to the painter. It can also be noticed that when applying paint with a brush, viscosity at high shear rate should be low (around 0.5 Pa.s) [42]. Since the viscosity of the paint containing glass particles is an order of magnitude higher, we would not expect that brushing properties are the key parameter for justifying the incorporation of glass inclusions into the paint.

a)



b)

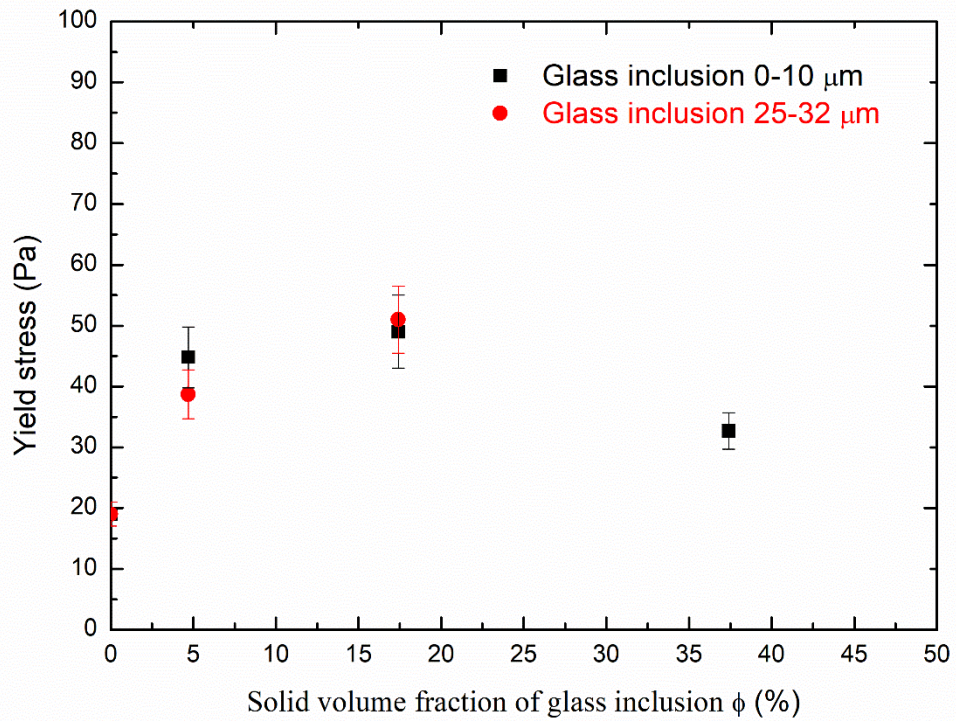


Figure 6. a) Consistency η_{HB} versus and b) yield stress vs. volume fraction ϕ of glass particles: experimental measurements with glass inclusion inferior to 10 μm and ranging 25 to 32 μm .

5. Conclusion

This paper examined the influence of non-reactive soda lime glass particles on the physicochemical behavior of oil paint mixtures containing lead white. Specifically, changes to the rheological, optical and siccative properties induced by the presence of glass particles in partial substitution of the lead white pigment in paint mixtures were studied. Glass particles substituted to lead white oil paint provide interesting optical and chemical modifications without significantly altering the rheological properties of the paint and potentially impacting on the painting techniques of the artist. We then showed that the accelerating effect on drying through the addition of glass to lead white might have been useful to artists during the painting process, especially for the first layers. We also highlighted that the transparency is increased with the addition of glass particles to the paint and could be an advantage for example to better see the underdrawing under a thin lead white priming layer. Further studies are currently under way to continue/deepen this research in examining the effects of reactive glasses with compositions close to those of ancient glass and with other non-siccative pigments such as red lakes.

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7. References

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