



HAL
open science

Colourless Powdered Glass as a Drier for Red Lakes: On the Influence of Composition and Particle Size

Mathilde Tiennot, Odile Majérus, Daniel Caurant, Gilles Bastian, Myriam Eveno, Elisabeth Ravaud

► **To cite this version:**

Mathilde Tiennot, Odile Majérus, Daniel Caurant, Gilles Bastian, Myriam Eveno, et al.. Colourless Powdered Glass as a Drier for Red Lakes: On the Influence of Composition and Particle Size. *Studies in Conservation*, inPress, 10.1080/00393630.2023.2256122 . hal-04246628

HAL Id: hal-04246628

<https://hal.science/hal-04246628v1>

Submitted on 17 Oct 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Colourless powdered glass as a drier for red lakes: on the influence of composition and particle size

Mathilde Tiennot ^{*1}, Odile Majérus², Daniel Caurant², Gilles Bastian¹,
Myriam Eveno^{1, 2}, and Elisabeth Ravaud¹

¹*Centre de Recherche et de Restauration des Musées de France, 14 quai
François Mitterrand, 75001 Paris, France*

²*Chimie ParisTech, PSL Research University, CNRS, Institut de Recherche
de Chimie Paris (IRCP), UMR 8247, 11 rue Pierre et Marie Curie, 75005
Paris, France*

Abstract

Colourless glass particles are observed in oil painting layers from 15th-17th-century. Several historical sources mentioned the use of finely ground glass powder acting as a solid drier. To evaluate the siccative effect of the glass particles added to paint, this research focused on red lake reconstructions and followed their natural drying by means of Fourier Transform Infra-Red (FTIR) analyses. Three glasses with various sodium-potassium and manganese content in their composition were investigated.

Notable differences in drying rates were observed in each of the samples, indicating a relationship between both the composition - either enriched in or without any manganese - and size of the glass particles that were added as siccatives. This FTIR approach enhances different complex mechanisms involved in the siccative effect of glass powder mixed in paint layers.

Keywords

Powdered glass, Oil paint, FTIR, Red lakes, Historic sources, Drier

This is an Accepted Manuscript of an article published by Taylor and Francis in *Studies in Conservation* on September 2023, available at: <https://doi.org/10.1080/00393630.2023.2256122>

To cite this article: Mathilde Tiennot, Odile Majérus, Daniel Caurant, Gilles Bastian, Myriam Eveno and Elisabeth Ravaud (2023): Colourless Powdered Glass as a Drier for Red Lakes: On the Influence of Composition and Particle Size, *Studies in Conservation*, DOI: 10.1080/00393630.2023.2256122

*e-mail: mathilde.tiennot@gmail.com

1 Introduction

For over a century, scholars have begun to take note of references relating to use of powdered glass as an additive to paint [1]. Sporadic observations of transparent particles in oil paintings from 15th-17th-century have been reported since the 1970s (Figure 1). Evidence of this painting studio practice was presented and discussed in 2003 and 2004 during the international studies of a large corpus of paintings by Perugino and Raphael [2, 3, 4]. In subsequent years, additional studies have focused on glass additives found in German, Flemish, French, Spanish and Portuguese school paintings from 15th-17th-century [2, 3, 5, 6, 7, 8, 9, 10]. Several hypotheses have since been presented in an attempt to explain the addition of glass to oil paint mentioned in historical recipes and contemporary sources: a) to increase the transparency of the paint b) to modify the texture and application of the paint and c) to act as a drier. Our study focuses on the latter and aims to study the siccative effect of powdered glass on painting layers. In this introduction, we first review the historical sources mentioning explicitly the use of glass powders as driers, before presenting our experimental strategy.

Several historical sources, reviewed below, document the use of powdered and/or crumbled glass added to oil paint, particularly when the paint contains lake pigments. The siccative property of powdered glass is mentioned in various historical treatises that include additional technical information relating to paint preparation. These sources need a careful attention, as the word 'glass' could be mistranslated or misunderstood. Spring [8] and Van de Graaf [11], for instance, have already pointed out that terminology associated with "glass" could also refer to 'resin'.

The sources mentioned discuss the uses of glass in paint [7, 12, 13]. The first mention of glass as a paint additive can be found in 15th century manuscripts, referring specifically to powdered glass being added to aid in the grinding of pigments such as orpiment [14, 1]. To our knowledge, the oldest treatise indicating that pulverised glass can be used as a drier for paint is the Paduan manuscript (*Ricette per far ogni sorte di colori*), dated around 1580 and discussed in [1].

Another major historical source from the late 16th century is the anonymous French manuscript BnF Ms.Fr.640 [15]. According to our researches on this primary source document, it should be dated from 1585 [16]. This manuscript details the use of powdered/crushed glass as a drier when added to paint with a specific reference to lakes. In Folio 58v (58v in modern numbering, 56 of the historic numbering) for instance, the author indicated that "le cristallin estant broye [...] se broie avec la laque et avec l'aspalte qui ne seichoient de fort long temps sans cela", translated as "The *cristallin* glass being ground [...] is ground with lake and asphaltum which would not dry for a long time without it". This manuscript also mentioned in Folio 57r (57r in modern numbering, 55 historical one) that "la laque est longue a seicher a huile Et pour ceste occasion il faut parmy broyer du verre Mays il faut choisir du cristallin pour ce quil est plus net", translated as "Lake is long to dry in oil And for this occasion one has to grind it with glass But one has to choose *cristallin* glass because it is cleaner". The term "cleaner" in this context probably means with less impurities.

Then, in most of the 17th-century sources documenting, glass used as an additive to paint is described as a drier. From the early 17th-century, the de Mayerne manuscript describes in Folio 85v the glass as one of the driers a painter can use [17]: "les grands

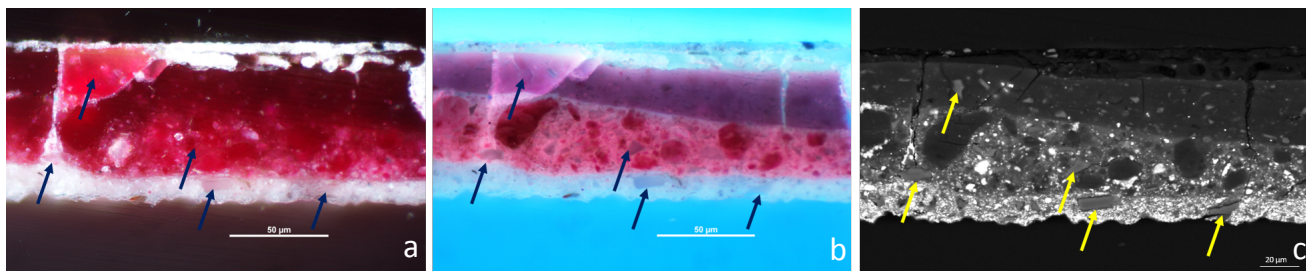


Figure 1: *Déploration sur le Christ mort*, Bronzino, 1540-1545, (Inv D799.1.29, *Musée des Beaux-Arts et d'archéologie de Besançon, France*) - Optical microscope, under UV light and SEM observations of a cross-section from the red drapery of Marie-Madeleine, revealing angular crumbled glass particles with irregular shape (indicated with arrows) (© M. Eveno)

siccatifs pour estre meslés parmy les couleurs sont l'alun bruslé, la couperose, l'umbre, la mine, le vert de gris", translated as "The strong siccatives to be bound with colours are burnt alum, vitriol, umber, red lead, verdigris". There is also a note in the margin that states the following: "Verre de Venise ou simplement broyé ou estient en eau plusieurs fois, seiché et broyé", which means "Venetian glass either ground or quenched into water several times, dried and ground". In Folio 18r, we can read that "Les couleurs qui ne seichent point le feront en y adjoustant le verdegris ou la couperose, ou du verre cristallin pulverisé impalpablement [...] La laque ne sèche jamais de soy meme", meaning that "The colours that do not dry will do with added verdigris or vitriol, or *cristallin* glass ground to an impalpable powder [...] Lake never dries alone". 'Impalpablement' is a precise term and means that the glass should be extremely finely ground until no granularity is detected. Throughout the 17th-century, several sources mention the use of finely ground glass powder to be used as a drier for colours that dry slowly when bound in oil, and especially for lakes. Such reference include the Turquet de Mayerne, Brussels, Baldinucci, and Pacheco manuscripts [17] (fol. 12r, 18r), [18] (p.388), [1], (p.200-202).

Several technical examinations confirmed the presence of colourless glass particles in various layers of paintings [3, 4, 7, 8, 10]. Observations of 15th-16th-century Italian and French school paintings at the Centre de Recherche et de Restauration des Musées de France (C2RMF) allowed the identification of these colourless glass particles in numerous easel paintings [2]. Based on SEM-EDS observations and 2D-image analysis of samples, the amount of glass particles as well as their morphology, length, size distribution within the painting stratigraphies and composition were evaluated, and reported for instance in [7, 8, 12]. Investigations have produced results similar to conclusions deduced from previous studies [2, 19]. Particles ranging from 5 μm to 50 μm can be observed, most of them are either in the range of 5-10 μm , and 20-30 μm . The surface of the glass particles detected varies from 2 to 20 % of the total layer area and they present an homogeneous distribution within the considered layer. The morphology and distribution of these particles in historic painting layers could be studied following the non-invasive imaging approach proposed in [20]. The influence of grinding processes on the morphology, size and size distribution and on physical behaviour of glass mixed in paint was evaluated by means of OCT and nanoindentation on dried red lake layers.

The chemical composition of the glass particles observed in paint layers was investi-

gated [21]. Previous studies detected manganese in the glass particles found in paintings [8]. As mentioned in sources since 1290, manganese oxides were commonly used to discolourise the glass and counter the natural greenish tint induced by iron impurities [22]. The manganese content has been suspected to be the source of the siccative effect [1, 7]. This hypothesis is studied in the present paper.

On another hand, the BnF Ms.Fr.640 manuscript, mentioned above, described carefully the siccative effect of glass added to paint [15]. This source pointed out that the glass to be used in this purpose should be *crystallin* glass (Folio 57r). The Folio 68r, related to casting of metal objects, provides a precise definition of *crystallin* glass, by comparison with *commun* glass (usual glass) : "Le cristallin est plus excellent car le commun ne tient que du sel de salicor, mayes le cristallin tient du sel de tartre et de salicor tout ensemble, qui tout deux servent à la fusion", translated as "The *crystallin* is better because the *commun* consists only in salt of salicornia, but the *crystallin* consists in salt of tartar and salicornia all together, both of them helping the fusion". With this description, the tartar and salicornia are respectively identified as the potash and sodium sources in glass composition. In light of the late sixteenth century definition from the BnF Ms.Fr.640 manuscript, mixed sodium and potassium or *crystallin* glass was identified as the accurate drier when added to paint and lakes. Thus, the impact of the chemical content of the glass on the drying rates has to be studied with respect to both sodium and potassium, and manganese contents.

In this study, we propose an experimental investigation to evaluate the possible siccative effect of powdered glass added to oil paint, focusing on red lakes. We investigated the first steps of the drying processes of fresh red lakes prepared with cochineal lake pigment in boiled linseed oil. The detailed oxidative polymerisation mechanisms of drying oils, consisting in an autoxidation based on the reaction of hydroperoxides with the double bonds, and followed by polymerisation by decomposition of the peroxide groups, have been described in various research publications [23, 24]. These chemical reactions occurring along the curing of the oil upon exposure to oxygen can be studied by Fourier Transform Infra-Red (FTIR) analyses of paint samples [25]. Such methodology can estimate the drying rates and leads to discriminate oxidation and isomerization steps by monitoring samples over time. We studied the differences induced by the addition of glass particles in the natural drying. To further discuss the effect of the nature of the glass added as a drier for cochineal lake, we considered three varieties of glass: i) a common soda-lime industrial glass, ii) a sodium-potassium glass enriched in manganese, iii) the same sodium-potassium glass without manganese. To evaluate the influence of the shape of the glass, we considered two ranges of particles sizes and studied their siccative effect. As mentioned earlier, this study is part of a larger experimental research on the various effects of the addition of crushed glass in paint layers [21, 20].

2 Experimental

2.1 Materials

Fresh red lake paint samples were prepared using cochineal pigment bound in linseed oil. The cochineal pigment was purchased at Sennelier (reference 133677 by Couleurs du Quai Voltaire), and the presence of carminic acid was confirmed by chromatography. The linseed oil was purchased at D. Plantes and was boiled for two hours at 120 °C [26].

Three varieties of glass with different chemical compositions were selected to evaluate the possible impact of the nature of the alkalis and total alkali content on the drying mechanisms associated with cochineal lake. The first glass particles result from the grinding of a commercial soda glass container, henceforth named *modern* glass. The second and third glasses were elaborated for this research [21]. The composition of the second and third glasses can be described as follows: A) the second glass is enriched in potassium and sodium according to the description of the *cristallin* glass in Folio 68r of the BnF Ms.Fr.640 manuscript, and slightly enriched in manganese and iron for our investigation. This glass is henceforth designed as Mn-enriched *cristallin* glass. B) The third glass has a similar composition as the second but does not contain manganese or iron. The manganese content was lowered on purpose to evaluate the impact of this element on the drying process. This third glass is henceforth designed as Mn-free *cristallin* glass. The chemical compositions of the raw glass materials, measured by Proton Induced X-Ray Emission (PIXE) analyses, are reported in Table 2.1 [21].

Caption of the Table 2.1: Composition of the *modern*, Mn-free *cristallin* and Mn-enriched *cristallin* glasses used for the research, measured by PIXE analyses and presented in [21]. 1 mol% Eu_2O_3 was added to the batch composition of the prepared glass to allow to follow possible glass alteration in paint by luminescence spectroscopy (Eu^{3+} ion is an optically active local probe that can be used to probe glass structure and alteration [27, 28]). These studies are not presented in the present paper.

We used two sets of glass particles, the first one with particles ranging from 25 μm to 32 μm , and the second one with particles around 10 μm in diameter [21]. The preparation of the particles at specific ranges was performed following a protocol presented in [29]. Manual grinding was first used employing a mortar and pestle in order to produce millimeter-sized glass particles. Smaller particles from 125 μm to 80 μm were separated using sieves. After a ultrasound separation of the $< 80 \mu\text{m}$ particles in ethanol, the fraction between 25 to 32 μm was obtained using the finest sieves easily available. Finally, sedimentation (employing Stokes law and using ethanol as the suspension liquid) was performed in order to separate particles that were less than 10 μm in length. This powder fraction was washed to eliminate the very fine particles, so that the particle size fraction finally obtained is estimated at 5-10 μm . Irregular angular shape similar to the one observed in historical paint layers (Figure 1) results from this preparation.

2.2 Red lake samples

Five red lake samples were prepared and stored under controlled laboratory conditions ($T = 21 \text{ }^\circ\text{C}$, $\text{RH} = 50 \%$). First, the required proportions of oil to cochineal pigment was determined to provide an easy-to-apply red lake, with a deep colour and glaze effect, as

Composition (%mass)	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MnO	Fe_2O_3	Eu_2O_3
<i>Modern glass</i>	73.2	1.5	11.7	0.8	11	0.01	0.1	
Mn-free <i>Cristallin</i> glass	69.6	0.5	16.7	5.4	6.7	<0.05	<0.1	1.0
Mn-enriched <i>Cristallin</i> glass	67.5	0.7	16.2	5.1	6.5	2.0	1.1	0.9

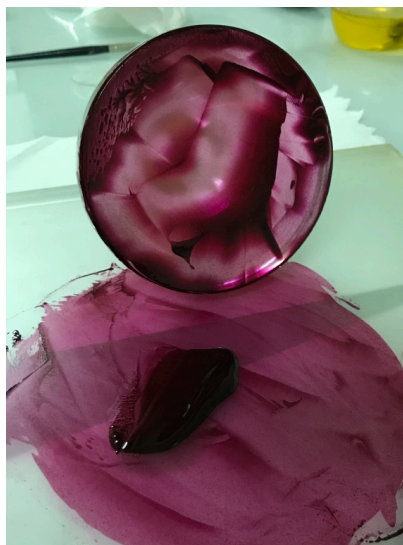


Figure 2: Preparation of the red lakes fresh paints, with cochineal bound in linseed oil using a mortar and a glass board (©M. Tiennot)

well as an adequate consistency for brush application. The reference red lake consists of 0.3 g of cochineal pigment in 0.42 ml of linseed oil, mixed together with a mortar and a glass board (Figure 2). Then, we studied the effect of the addition of 20 % in mass (with respect to the pigment's mass), ie 0.06 g of powdered glass, and mixed the oil-pigment and glass together under the same protocol.

2.3 Analytical protocol - FTIR spectroscopy analyses

FT-IR analyses were carried out to evaluate the drying and curing processes of the samples, by following the evolution of the degree of oxidation and isomerisation. Spectral changes, like variation in intensity, disappearance/appearance or broadening of the IR absorption peaks were used as markers of the oil curing steps. The natural drying under laboratory conditions ($T = 21\text{ }^{\circ}\text{C}$, $\text{RH} = 50\%$) was followed directly on the paint film applied on ZnSe discs, using a Frontier spectrometer, in transmission mode. The spectra are 20-scans summation over a range from 4000 cm^{-1} to 500 cm^{-1} at a 4 cm^{-1} resolution. The rotation of the supporting disc does not modify the acquired spectrum. We studied the impact of glass as a siccative additive for fresh lakes, and performed the analyses during the first four months of drying. The reactions were followed along the drying at and after the application, at 3 hours, 24 hours, 1 and 2 weeks, 2, 3, and 4 months.

2.4 Spectral Changes Corresponding to Oil Polymerization

After the paint samples were prepared, the autooxidation and polymerization of the linseed oil was followed as the paint was exposed to atmospheric oxygen over a period of time. The various steps involved with the drying processes, reflected by the structural changes of the oil polymer, have been followed by IR analyses in previous studies [23, 30, 31, 24, 25]. Based on these studies, the following spectral changes can be expected:

- The amount of the cis-double bonds present will decrease and ultimately disappear, which is highlighted by the corresponding decrease of the bands at 3010 cm^{-1} and 722

cm^{-1}

- A decrease in peak intensities at 2927 cm^{-1} and 2855 cm^{-1} , markers that indicate advanced stages of oxidation
- The C=O peak at 1744 cm^{-1} may progressively shift to 1740 cm^{-1} and can show a broadening in association to oxidation products
- A decrease in peak intensity at 1652 cm^{-1} (assigned to - CH=CH vibrations) as well as the formation of the shoulder peak at 1633 cm^{-1} (assigned to the conjugated C = C carboxyles); both are the markers of the isomerisation process
- the triglycerides region and the triad at $1238 - 1164 - 1101\text{ cm}^{-1}$ may show a broadening and increase during oxidation processes.

We focus on the differences on these specific spectral regions and bands to evaluate the effect of glass particles as a drier for the cochineal lake and to underline the differences induced in the drying processes. The significant evolution on the spectra and their initiation time are indicated on the figures.

3 Results

3.1 Monitoring the Natural Drying Processes Associated with Red Lake Paint

The spectra acquired for the sample of pure cochineal lake bound in oil during the first few weeks monitoring are presented in Figure 3. Some features can be related to the carminic acid of the cochineal used as a pigment for the red lakes, like the 660 cm^{-1} and 1562 cm^{-1} bands assigned to aromatic functions, the 771 cm^{-1} and the 880 cm^{-1} band (OH group) [32, 33]. The signal of the specific bands assigned to the carminic acid do not evolve during the early stages of the drying.

On another hand, some modifications of the signal are observed in the $1600\text{-}1652\text{ cm}^{-1}$ region (Figure 3). The appearance of a shoulder associated with the 1633 cm^{-1} peak, attributed to the conjugated C=C, was initiated after 1 week of drying, as well as the decrease of the 1652 cm^{-1} band. Both of these observations are related to the isomerisation process of the linseed oil. A slight decrease of the cis C=C 3010 cm^{-1} band is initiated after 3 months of drying.

3.2 Siccative effect of powdered glass

3.2.1 Modern glass

The IR absorption spectra of the samples prepared with the *modern* glass particles with sizes ranging from 25 to $32\text{ }\mu\text{m}$ show an evolution of the $1600\text{-}1652\text{ cm}^{-1}$ region along the first weeks of drying, with the progressive decrease of the 1652 cm^{-1} peak and the 1633 cm^{-1} shoulder appearance (Figure 4).

The size of the *modern* glass particles does not influence the drying: the spectra obtained with the addition of the $10\text{ }\mu\text{m}$ particles present the same modifications with time than the ones observed for the lakes with the 25 to $32\text{ }\mu\text{m}$ particles (Figure 4). Moreover, the addition of *modern* powdered glass does not induce significant difference in the chemical

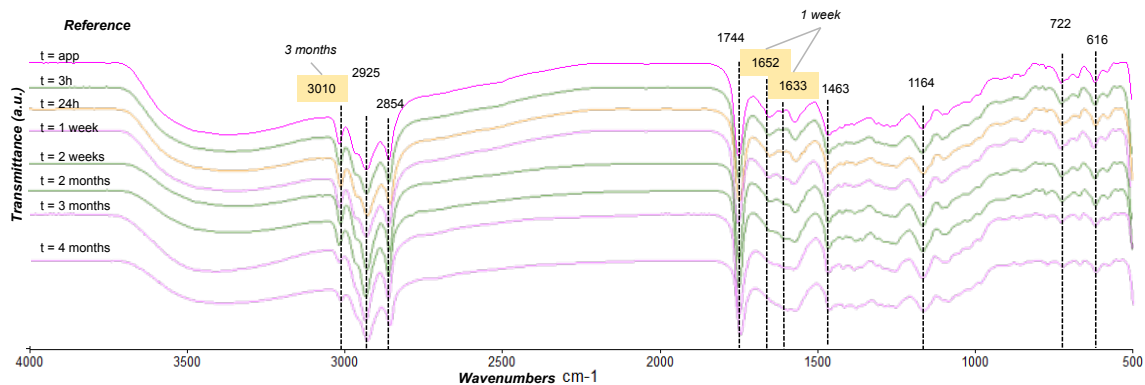


Figure 3: Evolution of the FTIR spectrum of reference cochineal lake bound in linseed oil, in the range of 4000 cm^{-1} - 500 cm^{-1} from the application of the paint to 4 months of natural drying

evolution of the red glaze layer. The results are similar for the red lake used as reference and when *modern* glass is added to the layer.

3.2.2 Manganese-enriched *crystallin* glass

The influence of the sodium potassium glass enriched in manganese added to red lakes on their drying rates is then illustrated in Figure 5. For both $10\text{ }\mu\text{m}$ and $25\text{-}32\text{ }\mu\text{m}$ grain sizes, the 1633 and 1652 cm^{-1} bands/shoulders also evolve after 1 week of natural drying (Figures 5).

Significant differences appeared in the evolution of the cis double-bonds at 3010 cm^{-1} . While there was no significant evolution of the absorption band for the previous samples (Reference and with *modern* glass in Figures 3 and 4), the decrease of the cis C=C bonds at 3010 cm^{-1} for the red lakes with $25\text{-}32\text{ }\mu\text{m}$ Mn-enriched *crystallin* particles starts after 2 months of drying (Figure 5). Compared with the drying rates identified for the reference cochineal lake (Figure 3), the decrease of the 3010 cm^{-1} band after 2 months of drying is a marker of the accelerated isomerisation processes induced by the powdered Mn-enriched *crystallin* glass.

Furthermore, when $10\text{ }\mu\text{m}$ particles of Mn-enriched *crystallin* glass are added to the paint, this 3010 cm^{-1} band disappears, starting from 2 weeks of drying, alongside the progressive decrease of the 722 cm^{-1} band (Figure 5). The combined evolution of these bands indicates a cis-trans isomerisation of the double-bonds, initiated during the 2 first weeks of natural drying. Moreover, with the addition of particles of $10\text{ }\mu\text{m}$ Mn-enriched *crystallin* glass, the intense 1744 cm^{-1} band shows a broadening and begins to shift at 1740 cm^{-1} , also after 2 weeks of drying (Figure 5). These broadening and shifting continue along the natural drying of this sample. Thus, the addition of particles of $10\text{ }\mu\text{m}$ of Mn-enriched *crystallin* glass clearly speeds up the isomerisation process of the oil.

3.2.3 Manganese-free *crystallin* glass

To evaluate the influence of the alkali content on the drying processes of the red lakes, the *crystallin* glass without manganese was added to paint. FTIR results obtained with

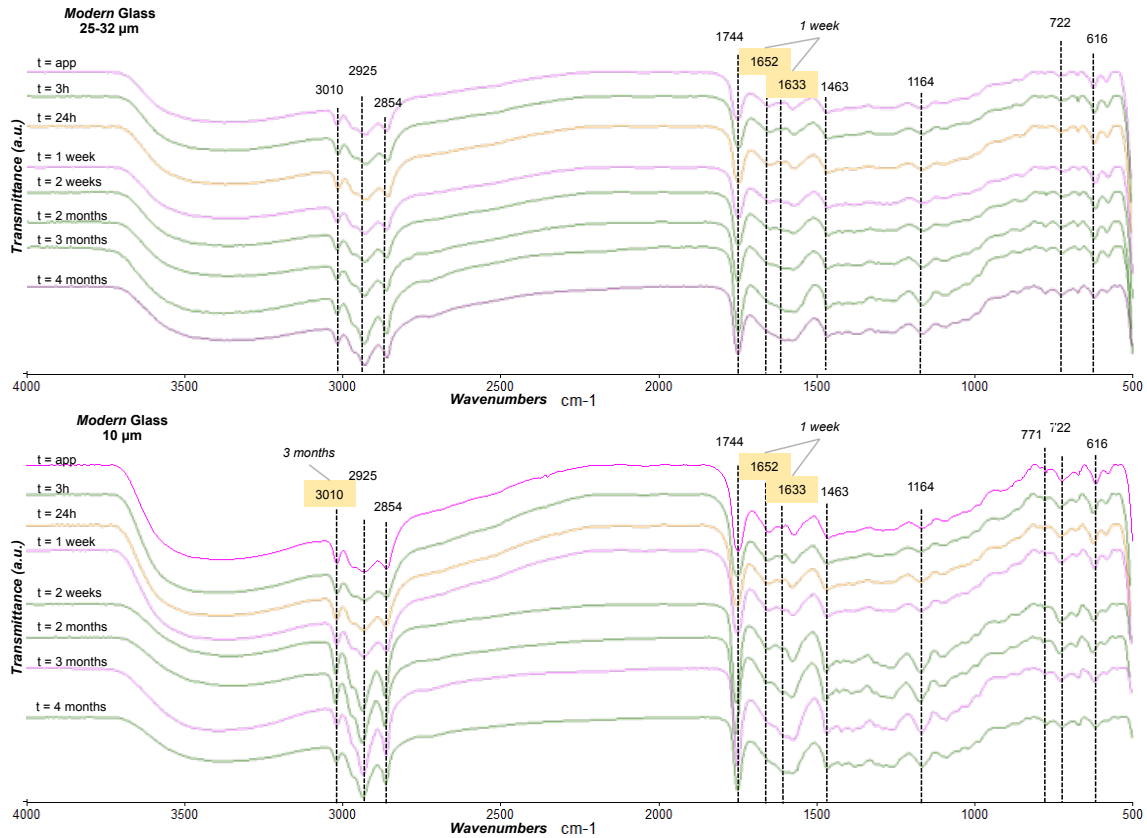


Figure 4: Evolution of the FTIR spectrum of cochineal lake bound in linseed oil with 25-32 μm and 10 μm particles of *modern* glass, in the range of 4000 cm^{-1} - 500 cm^{-1} from the application of the paint to 4 months of natural drying

the 25-32 μm particles and the 10 μm particles are presented in Figure 6. These two particles sets induce the same decrease of the 1652 cm^{-1} peak and the 1633 cm^{-1} shoulder appearance observed after the first two weeks of drying. However, major differences are identified in the drying evolution with the 3010 cm^{-1} evolution. The decrease of the cis C=C bonds at 3010 cm^{-1} starts after 1 month, and disappears after 2 months with the 25-32 μm particles of Mn-free *crystallin* glass, alongside the broadening of the 1744 cm^{-1} , as described for the Mn-enriched *crystallin* glass.

On another hand, the paint mixed with the 10 μm in size particles of the sodium potassium glass without manganese does not present significant evidence of accelerated drying processes during the first months.

In conclusion, these results illustrate differences in the drying process, with respect to the composition and size of the glass particles. We observed that :

- i) after 2 months, 25-32 μm particles of both sodium-potassium enriched glass with a high amount of manganese, and without manganese, induce an accelerated natural drying;
- ii) the 10 μm particles significantly speed up the drying process of the red lakes within two weeks, only when the glass contains a higher manganese content.

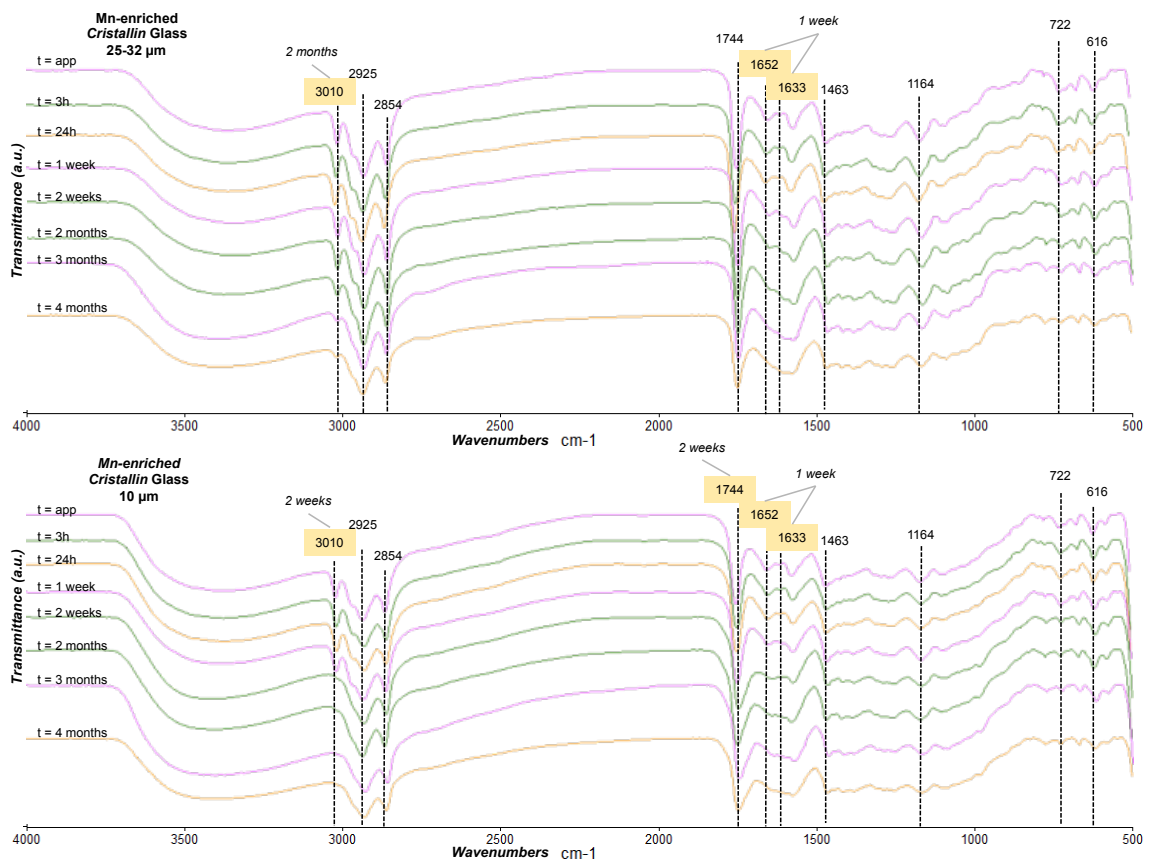


Figure 5: Evolution of the FTIR spectrum of cochineal lake bound in linseed oil with 25-32 μm and 10 μm particles of Mn-enriched *crystallin* glass, in the range of 4000 cm^{-1} - 500 cm^{-1} from the application of the paint to 4 months of natural drying

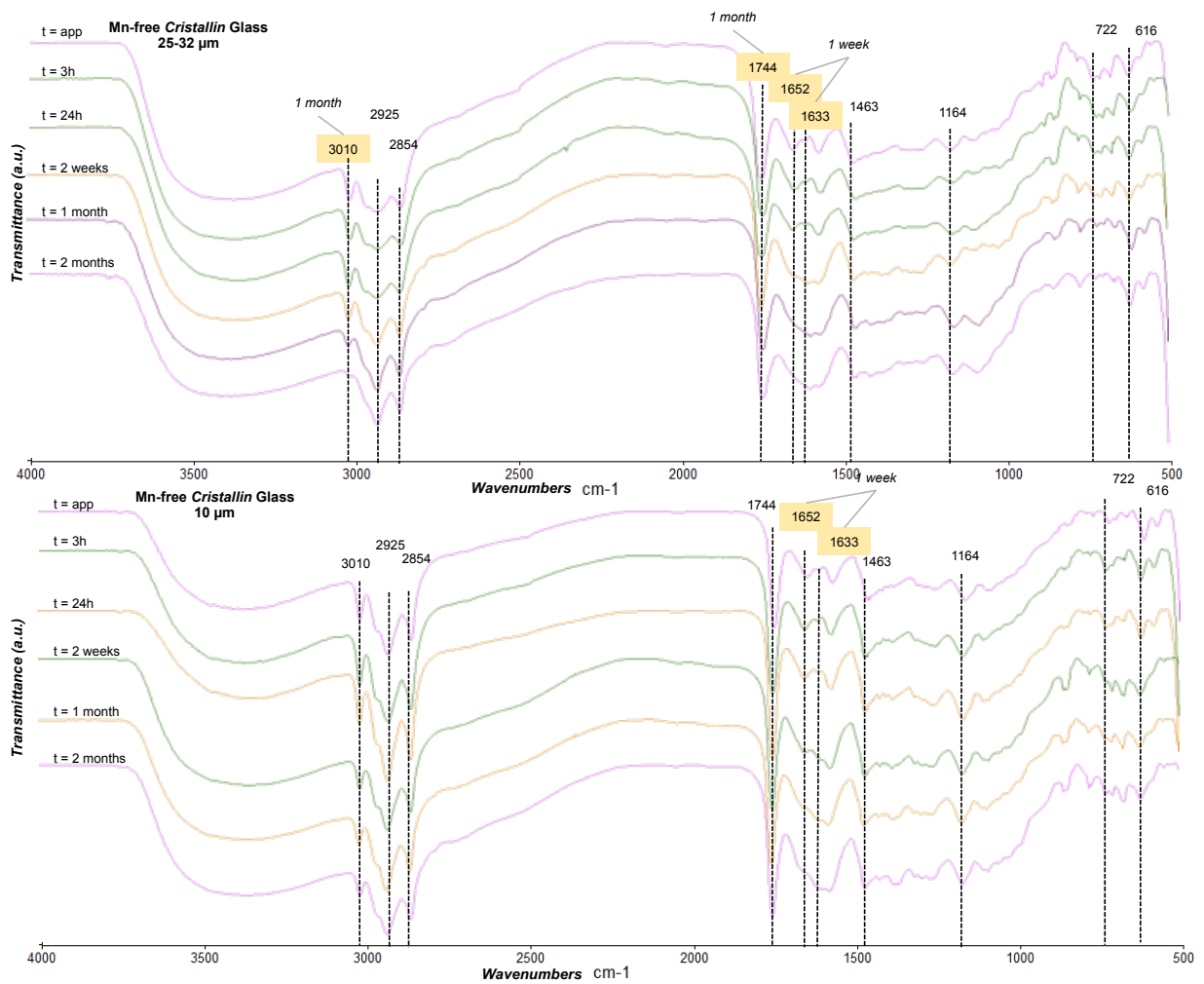


Figure 6: Evolution of the FTIR spectrum of cochineal lake bound in linseed oil with 25-32 μm particles of manganese-free *crystallin* glass, in the range of 4000 cm^{-1} - 500 cm^{-1} from the application of the paint to 2 months of natural drying

4 Discussion

In this study we were able to apply FTIR as a means of monitoring the natural drying processes associated with cochineal lake bound in linseed oil as well as evaluating the potential effect of the glass powder added as a drier. Our results point out differences in the drying with respect to the nature of the glasses we investigated, *modern*, Mn-free *crystallin*, Mn-enriched *crystallin*, as well as the size of the particles. The *modern* glass does not seem to influence the drying of the red cochineal lakes we prepared. An accelerated drying is identified with the 25-32 μm Mn-free and Mn-enriched alkali glass. The 10 μm particles of Mn-enriched alkali glass significantly speed up the drying process.

The *modern* glass composition contains higher Al_2O_3 and CaO contents, indicating a strong chemical durability. Indeed, a slight increase in Al_2O_3 content in the glass, by only a few 0,1 wt%, strongly improves the durability especially when subjected to a basic or neutral pH [34, 35]. Raising the alkaline earth oxides at the expense of alkali or SiO_2 also considerably increases the chemical durability in water, so that alkaline earth oxides are referred to as « stabilizers » [36, 37]. This stabilizing effect, attributed to the high ionic strength of alkaline earths with respect to alkalis and to structural aspects, culminates at about 10-12 wt% of CaO , beyond which value an opposite effect is observed. In historic glassware, the CaO/SiO_2 ratio is one important parameter which is used to evaluate the overall durability of the glass, having typically 5-10 wt% CaO , from poorly durable one having less than 5 wt% CaO (the terms « stable » and « unstable » are also used in this context) [38, 22, 39, 40, 41].

Thus, the *modern* glass, with its high Al_2O_3 and CaO contents, may be less likely to interact with its surrounding environment.

Furthermore, based on our FTIR results, the sodium and potassium content in the glass composition is of major interest for the siccative action. The greater efficiency of the two glasses with a high sodium and potassium content in enhancing the chemical transformation of the linseed oil may be related to the poorer chemical durability, as compared to the commercial *modern* glass. Indeed, alkali silicate glasses are chemically reactive to water. Their high content in alkali induces reaction processes like hydration, selective leaching by ionic exchange and hydrolysis [42, 43, 44, 36]. Such processes result in the release of chemical species from the glass (metallic cations and silicate anions), with alkalis typically being released faster than other species. Chemical durability directly refers to the kinetics of this glass-water reactivity, which is highly dependent on the composition of the glass.

An important parameter is the nature of the alkali, or $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratio. Potassic glasses are generally less durable than sodic glasses [45, 46, 47]. Mixed alkali glasses having both alkali types tend to be more durable in liquid water, because of structural and electronic modifications decreasing the alkali mobility (mixed alkali effect). However, this trend may not be true when this type of glassware is subjected to high levels of humidity as potassium-containing glass seems to be less durable against weathering [48, 49, 50]. Then, the nature of the alkali is a compositional parameter that also controls the stable/unstable classification of glasses [38, 22, 39, 40, 41]. From the composition of the materials we tested, a higher chemical reactivity with water - liquid and moisture content - of the two sodium-potassium bearing glasses is predictable, compared to the *modern* glass.

However, in the paint layers, the binding medium in which the drying processes reactions occur is oil, and the chemical reactivity as well as the degradation products of glass mixed in the oil-pigment systems is at stake. To the authors knowledge, the reactivity of glass in oil needs further investigation. Water is likely to be detected in the linseed oil during the natural drying. We can expect that the reactivity of the glass with liquid water and moisture content that may be present in the system, by releasing OH⁻ ions and alkalis, may induce chemical reactions with the triesters like saponification and produce fatty acids and alcohols. These species may act as ligands towards metallic cations of the glass, accelerating their release from the glass surface. The enhancement of the glass dissolution by organic acids has been put in evidence in several studies [51, 52, 53, 54] and attributed to protonation of the glass surface and chelation of the metallic surface sites by the anionic acid. Thus, the oil medium may be favourable to the extraction of cationic species from the glass, which may in turn be responsible for the siccative effect of glass particles. Further studies are necessary to investigate these hypotheses. Thus, these hypotheses may explain the effective siccative effect of the two sodium-potassium glasses. Moreover, the manganese content in glass also influences the natural drying rates of the red lakes, with respect to the size of the particles. The reactions and mechanisms involving manganese as related to drying rates and chemical processes seem to be active when the glass particles are the smallest. The finer the Mn-enriched *crystallin* glass particles, the stronger is their siccative effect on our cochineal lakes. This phenomenon may be in close correlation with the increase of the surface area, allowing the proposed reactions to occur. The accelerated drying rates may also be the consequences of the release of manganese ions in the drying paint system, activated during the grinding process used to produce finer particles. The influence of the grinding process of glass on the mechanical behaviour of lakes after natural drying was also investigated in [20], and the results indicate that the finer glass particles induce the higher effect on the properties. All these results illustrate the differences related to the extremely finely ground particles, described in the historic sources.

Practical recommendations about studio practices concerning the addition of glass, crushed and finely pulverized, as a solid drier for paint layers (especially red lakes), mentioned the higher efficiency of such glass particles. As early as the late sixteenth century, the nature of the glass, and the impact of the potash and soda sources, were identified as a key parameter to ensure a proper siccative effect of the glass particles in paints and lakes that need a long time to dry.

Based on this research, the combination of a higher sodium-potassium content and a higher manganese content, as well as the size of the particles, seem to be both crucial parameters for the efficient siccative effect of glass added to paint.

5 Conclusion

FTIR analyses allowed the investigation of the effect on the addition of colourless powdered glass on the drying of red lakes. A siccative action of glass particles added to colours that require a long dry time is mentioned in several historic sources, as well as the importance of the size. We studied the influence of the composition and size of the glass particles on the drying of cochineal lake. Differences are identified in the natural drying,

with various sodium-potassium and manganese contents. Our results illustrate that 25-32 μm particles of both soda-potassium enriched glass with a high amount of manganese, and without manganese, induce an accelerated natural drying of cochineal lakes and that only the 10 μm particles with a higher manganese content significantly speed up the drying process of the red lakes. Thus, the siccative effect of *crystallin* colourless glass, a soda-potassium glass enriched in manganese, and the influence of the particles size of the finely ground glass, added to cochineal lakes is observed and quantified by these FTIR analyses. Such modification of the drying rates may be related to the reactivity of the glass with the binding medium, that highly depends on the composition of glass. This research is a step further to uncover the rationale behind the addition of colourless glass to paint.

6 Acknowledgements

This work was supported by the Paris Seine Graduate School Humanities, Creation, Heritage, Investissement d'Avenir ANR-17-EURE-0021 – Foundation for Cultural Heritage Science.

The authors thank Isabelle Biron (C2RMF) for the fruitful discussions and help about the nature and composition of the glasses. The authors also thank Lucy Cooper and Berfin Karakalic for the preparation of the glasses considered in the present research.

7 Competing interests

The authors do not have any competing interest.

References

- [1] M.P. Merrifield, *Original Treatises, dating from the XVIIth to XVIIIth Centuries on the Arts of Painting* (1849)
- [2] E. Martin, J.P. Rioux, in *Postprints of the workshop on the painting technique of Pietro Vannucci, called il Perugino, organised by INSTM and LabS-TECH* (2003), pp. 43–56
- [3] M. Spring, in *Postprints of the workshop on the painting technique of Pietro Vannucci, called il Perugino, organised by INSTM and LabS-TECH* (2003), pp. 17–24
- [4] M. Spring, in *Raphael's painting technique: working practices before Rome, Proceedings of the Eu-ARTECH workshop*, ed. by S.M. Roy A (2004), pp. 77–86
- [5] C. Seccaroni, P. Muioli, I. Borgia, B. Brunetti, A. Sgamellotti, in *Proc LabS Tech Work Quad di Kermes, Florence.*, ed. by S.A.e. Brunetti BG, Seccaroni C (2004)
- [6] B.H. Berrie, L.C. Matthew, in *Scientific Examination of Art: Modern Techniques in Conservation and Analysis, Proceedings of the National Academy of Sciences*, ed. by M.A. (Ed.) (The National Academies Press, Washington, DC, 2005), pp. 12–26
- [7] K. Lutzenberger, H. Stege, C. Tilenschi, *Journal of Cultural Heritage* **11**(4), 365 (2010). DOI <https://doi.org/10.1016/j.culher.2010.04.003>. URL <https://www.sciencedirect.com/science/article/pii/S1296207410000579>
- [8] M. Spring, *Natl Gall Tech Bull* **33**, 4 (2012)
- [9] E. Arroyo, A. Cruz Lara, M. Espinosa, J. Ruvalcaba, S. Zetina, E. Hernández, S. Taylor, *MRS Online Proceedings Library* **1374**(1), 61 (2012). DOI 10.1557/opl.2012.1378. URL <https://doi.org/10.1557/opl.2012.1378>
- [10] H.P. Melo, A.J. Cruz, S. Valadas, A.M. Cardoso, A. Candeias, *Journal of Cultural Heritage* **43**, 261 (2020). DOI <https://doi.org/10.1016/j.culher.2019.11.001>. URL <https://www.sciencedirect.com/science/article/pii/S1296207419301049>
- [11] J.A. Van de Graaf, *The Burlington Magazine* **104**, 471 (1962)
- [12] M. Spring, *Heritage Science* **5**(1), 40 (2017). DOI 10.1186/s40494-017-0152-3. URL <https://doi.org/10.1186/s40494-017-0152-3>
- [13] E. Ancel, *L'utilisation du verre broyé dans les couleurs des peintures de chevalet à travers les sources historiques du xve au xviiie siècle*. Master's thesis, Ecole du Louvre (2019)
- [14] C. Cennini, *Il Libro dell'arte, Florence, Bibliothèque Laurentienne, 1437. Trad. Déroche, Colette, Cennino Cennini, Le livre de l'art (Il libro dell'arte), traduction critique, commentaires et notes, Paris, Berger- Levrault, 1991*, (1991)
- [15] Ms.Fr.640, *Recueil de recettes et secrets concernant l'art du mouleur, de l'artificier et du peintre.*, vol. Ms.Fr.640, XVIe century (Bibliothèque nationale de France. Département des Manuscrits)
- [16] E. Ravaud, G. Bastian, E. Itié, in *Back to basics : Proceedings of the sixth symposium of the ICOM-CC Working Group for Art Technological Source Research* (Rijksmuseum, Amsterdam, 16-17 June 2014)
- [17] T. Turquet de Mayerne, *Pictorja Sculptorja et quae subalternarum artium*, british library, london edn. (1620)
- [18] F. Pacheco, *Arte de la pintura, su antigüedad, y grandezas. Descriuense los hombres eminentes que ha auído en ella, assi antiguos como modernos, del dibujo, y colorido; del pintar al temple, al olio, de la iluminacion, y estofado; del pintar al fresco; de las encarnaciones, de polimento, y de mate; del dorado, bruñido, y mate. Y enseña el modo de pintar todas las pinturas sagradas* (Seville, 1649)
- [19] L. Cooper, A. Pierre, E. Ravaud, Y. Mélinge, O. Majérus, D. Caurant, G. Bastian, M. Eveno, C. Andraud, A. Tournié, *Journal of Cultural Heritage* **61**, 238 (2023). DOI <https://doi.org/10.1016/j.culher.2023.05.001>. URL <https://www.sciencedirect.com/science/article/pii/S1296207423000560>

- [20] M. Almasian, M. Tiennot, L.D. Fiske, E. Hermens, *Heritage Science* **9**(1), 66 (2021). DOI 10.1186/s40494-021-00527-y. URL <https://doi.org/10.1186/s40494-021-00527-y>
- [21] L. Cooper, A. Pierre, G. Bastian, M. Eveno, O. Majérus, D. Caurant, C. Andraud, A. Tournié, Y. Mélinge, E. Ravaud, *Projet vip : Influence de l'addition de verre broyé sur les propriétés physico-chimiques des couleurs employées en peinture à l'huile (artistique)* (2019). Rapport, Fondation des Sciences du Patrimoine
- [22] M. Verità, in *Modern methods for analysing archaeological and historical glass*, ed. by K. Janssens (Wiley, 2013), pp. 515–533
- [23] M. Lazzari, O. Chiantore, *Polymer Degradation and Stability* **65**(2), 303 (1999). DOI [https://doi.org/10.1016/S0141-3910\(99\)00020-8](https://doi.org/10.1016/S0141-3910(99)00020-8). URL <https://www.sciencedirect.com/science/article/pii/S0141391099000208>
- [24] J. Mallécol, J.L. Gardette, J. Lemaire, *Journal of the American Oil Chemists' Society* **77**(3), 257 (2000). DOI <https://doi.org/10.1007/s11746-000-0042-4>. URL <https://aocs.onlinelibrary.wiley.com/doi/abs/10.1007/s11746-000-0042-4>
- [25] L. de Viguerie, P. Payard, E. Portero, P. Walter, M. Cotte, *Progress in Organic Coatings* **93**, 46 (2016). DOI <https://doi.org/10.1016/j.porgcoat.2015.12.010>. URL <https://www.sciencedirect.com/science/article/pii/S0300944015303878>
- [26] C. YVEL, *Le métier retrouvé des maîtres* (Flammarion, 1991)
- [27] N. Ollier, G. Panczer, B. Champagnon, G. Boulon, P. Jollivet, *Journal of Luminescence* **94-95**, 197 (2001). DOI [https://doi.org/10.1016/S0022-2313\(01\)00277-0](https://doi.org/10.1016/S0022-2313(01)00277-0). URL <https://www.sciencedirect.com/science/article/pii/S0022231301002770>. International Conference on Dynamical Processes in Excited States of Solids
- [28] E. Molières, G. Panczer, Y. Guyot, P. Jollivet, O. Majérus, P. Aschehoug, P. Barboux, S. Gin, F. Angeli, *Journal of Luminescence* **145**, 213 (2014). DOI <https://doi.org/10.1016/j.jlumin.2013.07.051>. URL <https://www.sciencedirect.com/science/article/pii/S0022231313004432>
- [29] F. Alloteau, *Contribution à la compréhension des mécanismes de l'altération atmosphérique et étude d'un traitement de protection à base de sels de zinc. application à la conservation des objets en verre du patrimoine culturel*. Ph.D. thesis, Université de recherche Paris Sciences et Lettres – PSL Research University, 2017 (2017)
- [30] J.D.J. van den Berg, *Analytical chemical studies on traditional linseed oil paints*. Ph.D. thesis, University of Amsterdam (2002)
- [31] J. Mallécol, J.L. Gardette, J. Lemaire, *Journal of the American Oil Chemists' Society* **76**(8), 967 (1999). DOI 10.1007/s11746-999-0114-3. URL <https://doi.org/10.1007/s11746-999-0114-3>
- [32] M. Koperska, T. Łojewski, J. Łojewska, *Analytical and Bioanalytical Chemistry* **399**(9), 3271 (2011). DOI 10.1007/s00216-010-4460-7. URL <https://doi.org/10.1007/s00216-010-4460-7>
- [33] D. Guillermin, T. Debroise, P. Trigueiro, L. de Viguerie, B. Rigaud, F. Morlet-Savary, S. Balme, J.M. Janot, F. Tielens, L. Michot, J. Lalevee, P. Walter, M. Jaber, *Dyes and Pigments* **160**, 971 (2019). DOI <https://doi.org/10.1016/j.dyepig.2018.07.021>. URL <https://www.sciencedirect.com/science/article/pii/S0143720818309938>
- [34] T. Wassick, R. Doremus, W. Lanford, C. Burman, *Journal of Non-Crystalline Solids* **54**(1), 139 (1983). DOI [https://doi.org/10.1016/0022-3093\(83\)90088-1](https://doi.org/10.1016/0022-3093(83)90088-1). URL <https://www.sciencedirect.com/science/article/pii/0022309383900881>
- [35] J.P. Hamilton, C.G. Pantano, *Journal of Non-Crystalline Solids* **222**, 167 (1997). DOI [https://doi.org/10.1016/S0022-3093\(97\)90110-1](https://doi.org/10.1016/S0022-3093(97)90110-1). URL <https://www.sciencedirect.com/science/article/pii/S0022309397901101>. Practical Implications of Glass Structure
- [36] L. Hench, D. Clark, *Journal of Non-Crystalline Solids* **28**(1), 83 (1978). DOI [https://doi.org/10.1016/0022-3093\(78\)90077-7](https://doi.org/10.1016/0022-3093(78)90077-7). URL <https://www.sciencedirect.com/science/article/pii/0022309378900777>

- [37] F. Angeli, D. Boscarino, S. Gin, G.D. Mea, B. Boizot, J. Petit, *Physics and Chemistry of Glasses* **42**(279-286) (2001)
- [38] J.J. Kunicki-Goldfinger, *Studies in Conservation* **53**(sup2), 47 (2008)
- [39] M. Melcher, M. Schreiner, *Glass Degradation by Liquids and Atmospheric Agents* (John Wiley and Sons, Ltd, 2013), chap. 7.2, pp. 609–651. DOI <https://doi.org/10.1002/9781118314234.ch29>. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/9781118314234.ch29>
- [40] C. Iliffe, R. Newton, *Verres et refractaires* **30**(1), 30 (1976)
- [41] S. Davison, R. Newton, *Conservation and restoration of glass* (Routledge, 2003)
- [42] R. Conradt, *Journal of the American Ceramic Society* **91**(3), 728 (2008). DOI <https://doi.org/10.1111/j.1551-2916.2007.02101.x>. URL <https://ceramics.onlinelibrary.wiley.com/doi/abs/10.1111/j.1551-2916.2007.02101.x>
- [43] W. Lanford, K. Davis, P. Lamarche, T. Laursen, R. Groleau, R. Doremus, *Journal of Non-Crystalline Solids* **33**(2), 249 (1979). DOI [https://doi.org/10.1016/0022-3093\(79\)90053-X](https://doi.org/10.1016/0022-3093(79)90053-X). URL <https://www.sciencedirect.com/science/article/pii/002230937990053X>
- [44] B. Bunker, *Journal of Non-Crystalline Solids* **179**, 300 (1994). DOI [https://doi.org/10.1016/0022-3093\(94\)90708-0](https://doi.org/10.1016/0022-3093(94)90708-0). URL <https://www.sciencedirect.com/science/article/pii/0022309394907080>. Proceedings of the First PAC RIM Meeting on Glass and Optical Materials
- [45] B. Bunker, G. Arnold, E. Beauchamp, D. Day, *Journal of Non-Crystalline Solids* **58**(2), 295 (1983). DOI [https://doi.org/10.1016/0022-3093\(83\)90031-5](https://doi.org/10.1016/0022-3093(83)90031-5). URL <https://www.sciencedirect.com/science/article/pii/0022309383900315>
- [46] M.F. Dilmore, D.E. Clark, L.L. Hench, *Journal of the American Ceramic Society* **61**(9-10), 439 (1978). DOI <https://doi.org/10.1111/j.1151-2916.1978.tb09355.x>. URL <https://ceramics.onlinelibrary.wiley.com/doi/abs/10.1111/j.1151-2916.1978.tb09355.x>
- [47] K. Wittstadt, G. Maas-Diegeler, W. Hiller-König, H. Grieb, *Crizzling - exploring degradation and simulation on model glasses* (Hermann, 2019), vol. Glas. Atmos. Alter. - Cult. Heritage, Ind. Nucl. Glas., pp. 185–195
- [48] M. Melcher, M. Schreiner, *Journal of Non-Crystalline Solids* **352**(5), 368 (2006). DOI <https://doi.org/10.1016/j.jnoncrysol.2006.01.017>. URL <https://www.sciencedirect.com/science/article/pii/S0022309306000573>
- [49] A. Rodrigues, S. Fearn, M. Vilarigues, *Corrosion Science* **145**, 249 (2018). DOI <https://doi.org/10.1016/j.corsci.2018.10.010>. URL <https://www.sciencedirect.com/science/article/pii/S0010938X18313398>
- [50] F. Alloteau, O. Majérus, V. Valbi, I. Biron, P. Lehuédé, D. Caurant, T. Charpentier, A. Seyeux, *npj Materials Degradation* **4**(1), 36 (2020). DOI [10.1038/s41529-020-00138-1](https://doi.org/10.1038/s41529-020-00138-1). URL <https://doi.org/10.1038/s41529-020-00138-1>
- [51] L. Rybarikova, I. Kourilova, *Ceramics-Silikaty* **40**, 94 (1996)
- [52] L. Rybarikova, I. Kourilova, *Ceramics-Silikaty* **41**, 61 (1997)
- [53] S. Gin, N. Godon, J. Mestre, E. Vernaz, D. Beaufort, *Applied Geochemistry* **9**(3), 255 (1994). DOI [https://doi.org/10.1016/0883-2927\(94\)90036-1](https://doi.org/10.1016/0883-2927(94)90036-1). URL <https://www.sciencedirect.com/science/article/pii/0883292794900361>
- [54] C. Altavilla, E. Ciliberto, S. La Delfa, S. Panarello, A. Scandurra, *Applied Physics A* **92**(1), 251 (2008). DOI [10.1007/s00339-008-4499-x](https://doi.org/10.1007/s00339-008-4499-x). URL <https://doi.org/10.1007/s00339-008-4499-x>