



**HAL**  
open science

## Re-Interpretation of Old Master practices through optical and rheological investigation: the presence of calcite

Laurence de Viguerie, H Glanville, G. Ducouret, P Jacquemot, P Anh Dang, Ph Walter

### ► To cite this version:

Laurence de Viguerie, H Glanville, G. Ducouret, P Jacquemot, P Anh Dang, et al.. Re-Interpretation of Old Master practices through optical and rheological investigation: the presence of calcite. *Comptes Rendus. Physique*, 2018. hal-02401167

**HAL Id: hal-02401167**

**<https://hal.science/hal-02401167>**

Submitted on 9 Dec 2019

**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.

## **Re-Interpretation of Old Master practices through optical and rheological investigation: the presence of calcite**

L. de Viguerie<sup>1</sup>, H. Glanville<sup>1</sup>, G. Ducouret<sup>2</sup>, P. Jacquemot<sup>1,3</sup>, P. Anh Dang<sup>2</sup>, Ph. Walter<sup>1</sup>

1. Sorbonne Université, CNRS, Laboratoire d'Archéologie Moléculaire et structurale, LAMS, F-75005 Paris, France

2. Laboratoire Sciences et Ingénierie de la Matière Molle, CNRS UMR 7615, ESPCI Paris, PSL Research University, 10 rue Vauquelin, F-75231 Paris cedex 05, France.

3. Muséum National d'Histoire Naturelle, Sorbonne Université, CNRS, Institut de Minéralogie, Physique des Matériaux et Cosmochimie, F-75005 Paris, France

### **Abstract**

Lead white, composed of a mixture of cerussite and hydrocerussite (respectively  $\text{PbCO}_3$  and  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ), is often associated in paintings to other white pigments, especially calcite. By combining in-situ analyses with paint reconstructions, we attempt to get a better understanding of the role of this addition of calcite, and investigate how artists may have used it to modify the properties of their paint. Lead-based white pigments of a Dutch 17th century « *nuancier* », have been analysed as well as historical paintings. Two examples are given: one from a painting by Roger van der Weyden, in the 15th century, and one by Nicolas Poussin in the 17th century, from specific zones which indicate the addition of calcite. The combination of calcite and pigments enhances both the optical and the rheological properties. Visible reflectance spectroscopy was carried out on pure paints as well as mixtures, and indicated an increase in the transparency of the paint mixture in comparison to the pure lead white. Rheological measurements also indicated an increase in the elastic and viscous moduli, as well as of the yield stress again in comparison to the pure lead white. Calcite could thus have been used to assist in the creation of impasto effects in lead white paints.

### **Résumé**

**Keywords :** lead white, chalk, transparency, rheology, visible reflectance spectroscopy.

### **Introduction**

Up to the 19<sup>th</sup> century, lead white was the main white pigment used by artists, artificially synthesized from metallic lead and vinegar since antiquity for cosmetic and painting purposes. Lead white was generally preferred to calcite and gypsum, which were mainly used

in preparation layers, because of its optical properties (great opacity) and its known catalytic effect in speeding up the drying of oil [1]. Different qualities of lead white are referred to in the written sources (artists' correspondence, notebooks, price lists...), the result of different processes of preparation and different post-treatments, but also possible adulteration. As a consequence, a whole range of varieties of commercial lead white existed with different proportions of hydrocerussite  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$  and cerussite  $\text{PbCO}_3$ , and containing greater and lesser quantities of extenders such as chalk (calcite). In the 16<sup>th</sup> century, written sources refer to 'Venetian' lead white as having a superior reputation [2,3]. A price list from London dating from 1532, tells us that *ceruse* cost twice as much as *lead white* [4]. Maartje Stols-Witlox investigated the terminology of lead white in written sources from the 15th to the 19th century ; she mentions adulteration with chalk as a quite common practice to reduce the price of the pigment. De Mayerne, in the 17th century, indicates that « The best (lead white) is the one that breaks easily, in shells and [is] very white. In the Ceruse commune, there is half chalk » [5].

Thanks to improvements in analytical methods, the presence of calcite can be highlighted in numerous works of art. Whether the calcite is an addition by the manufacturer, or a later one by the artist, is impossible to ascertain, but the painter must have been aware of the paint modifications resulting from this addition. The aim of our present research is to define the possible consequences of the presence of calcite in paint, and especially in lead white paint.

In a first section, we give a few examples (from our investigations or in the literature) of identification of calcite in white paints: a Dutch 17th century « *nuancier* » and two historical paintings have been analysed *in-situ* via X-ray fluorescence and/or X-ray diffraction. Different qualities of lead white (of different compositions and containing more or less chalk) have been used in different layers or in different areas of historical paintings. Then we studied the rheological and optical properties of model systems, mixtures of commercial lead white and calcite, to investigate how the addition of calcite modifies the behavior of the paint. These properties are of crucial interest for the painter and have been under investigation for lead white alone in various publications [6, 7]. The painter would have had to take them into account while making his paint.

## **I. Experimental**

### ***1. Materials and paint preparation***

The oil used was linseed oil purchased from Laverdure, cold pressed and purified.

Lead white from Master Pigments (98 wt% cerusite), and Meudon white from Laverdure has been used for both the rheology and colorimetry measurements.

All the samples were prepared by hand-grinding. The pigment was first weighed and placed in the mortar with the appropriate amount of oil. The amount of oil required for wet grinding (i.e. oil absorption value) was first determined by adding oil gradually to the wet slurry under continuous grinding in the mortar. For the rheological measurements, as the aim is to measure the influence of the addition of calcite (and not of the oil content) we chose to keep the oil / pigment ratio constant at 15.7 wt% with an increasing amount of calcite compared to lead white. For the visible reflectance measurements we used the proportions described in table 1 (paints prepared by a restorer, in accordance to the oil absorption value).

The oil and pigment were mixed and ground in the mortar then a small portion of the paint was placed on the glass slab and ground with the muller for 3 min. To ensure a good reproducibility of the rheological measurements, we ground the mixture in the mortar during 2 mn before grinding with the muller on the slab. The paint was prepared just before the experiment and placed directly on the rheometer.

	% binder	Oil	Calcite	Lead white
A	10.8	13 mL (12.1 g)		100 g
B	48.2	28 mL (26.04 g)	28 g	
Mixture in weight	16.6	3 g	5 g	10 g
Mixture in volume	13.8	2.7 g	2 g	14.8 g

Table 1: Proportions used for the colorimetry measurements.

For comparative purposes, pigments from other providers were also purchased: lead white from Laverdure and Kremer, and Champagne chalk (calcite) from Kremer. All pigments were imaged by SEM (images in Supporting Information) and their elemental composition checked by SEM-EDX. We used the same experimental conditions on different paint mixtures. The aim was not to evaluate the influence of the pigment origin (and thus characteristics) on each investigated property, but to assess the effect of calcite whatever the origin of the pigment used. Colorimetry measurements were carried out with: each of the lead white pigments mixed with Meudon white from Laverdure, and only lead white from Kremer and Laverdure mixed with Champagne chalk from Kremer. Rheological measurements being more time consuming, measurements were carried out with lead white from Kremer and Master pigments mixed with Meudon white from Laverdure.

## ***2. Pigments and paint samples characterisation***

### *SEM*

SEM images were performed on carbon-coated powders of pigments deposited on carbon tape. For all observations, a SEM-FEG Zeiss ultra 55 (IMPMC, Paris) was used in secondary electrons detection with the following conditions : accelerating voltage 2 kV, working distance 2 mm.

### *Rheological measurements*

The rheological measurements were performed at 25°C. Yield stress and dynamic properties were measured on a stress controlled rheometer Haake RS600 equipped with a crosshatched, stainless steel plate-plate geometry (diameter: 35 mm, gap 1 mm). The sample, placed on the lower plate, is scraped when the gap is 1.2 mm, then the gap is set at 1 mm. After a waiting time of 5 minutes, a very short strain sweep at 1 Hz is carried out in the viscoelastic regime, followed by the frequency sweep in the range 0.1- 100 rad/s still in the linear domain.

Then an oscillating stress sweep is performed at 1 Hz from 0.1 Pa up to a stress value that goes far beyond (or exceeds) the linear regime. The measurement time of the last experiment is approximately 30 minutes.

Paint formulations display a gel-like behavior, both elastic modulus  $G'$  and loss modulus  $G''$  are roughly constant and  $G'$  is higher than  $G''$  on all the frequency range. The elastic ( $G'$ ) moduli reported in section III are measured in the linear viscoelastic plateau. The yield stress is calculated from tangent analysis by applying tangents to the strain-stress data in the linear strain region and in the flow region, the intersect of the two tangents is the yield stress value. Measurements were repeated on several samples to check the reproducibility.

### *Colorimetry*

Paint was spread on glass plates (to avoid interaction/ absorption effects) with a 30  $\mu\text{m}$  applicator from Erichsen. Two glass slides were prepared for each paint preparation, placed on an Erichsen contrast card. FORS analyses were carried out with a portable Ocean Optics model USB 4000 – Vis-NIR Fibre Optic Reflectance (FORS) spectrophotometer. The instrument was equipped with a couple of optic fibres (Ocean Optics RS monocoil), a halogen source lamp (Ocean Optics model HL-2000) and a high performance 3648-element linear

CCD-array detector, covering the 350-1000 nm wavelength range and of optical resolution 1.5 nm FWHM. To properly position the fibres on the samples, a device head was used with a 20° configuration to avoid specular reflectance. A constant sample-to-probe distance (ca. 4 cm) was preserved on the surface to be analysed. The diameter of the area analysed was 2 mm. Diffuse reflectance spectra were measured against a white standard with guaranteed reflectance at 98 % or more in the range studied. Acquisition time was 50 ms and a total of 20 scans were collected for each measurement. The device was also capable of providing colorimetric data (experiments in triplicate), following the CIE L\*a\*b\* chromatic space as defined by the International Commission on Illumination (CIE). L\* defines lightness and its values range from 0 to 100, a\* and b\* represent, respectively, red/green and yellow/blue tone axes. Data treatment was carried out with the Ocean View software package.

### ***3. Historical paints and paintings analyses***

#### *Corpus*

A Dutch treatise on color describing watercolour pigments and their mixing, written by A. Boogert in 1692, was investigated at the Bibliothèques Méjanes (Manuscript Ms. 1389, Aix-en-Provence, France). It has been digitalised and is available on-line [8]. The book is divided into two parts, the first one dealing only with pure pigments. For each pigment, the left-hand page describes the recipe used, and the right-hand page displays the pigment applied according to the recipe.

Two paintings are also presented here:

- The Gdansk triptych *Last Judgment* by Roger van der Weyden (and completed by Hans Memling) in the 15th century.
- *Venus presenting Aeneas with his Arms*, in the Musée des Beaux Arts of Rouen, painted in 1639 by Nicolas Poussin. The moment depicted is from Book VIII of the *Aeneid*, in which Venus presents her son with the arms she has had Vulcan prepare for him.

A third painting, *Orage* (the storm), by Nicolas Poussin is also cited. It was painted in 1651 and is also in the collection of the Musée des Beaux Arts in Rouen.

We focus here on the results obtained in specific areas of the paintings and their interpretation; more details on the analysis and a complete description of the palette, can be found in [9] in relation to the Gdansk triptych, and in [10] and [11] for the paintings by Poussin.

### *In-situ measurements*

*In-situ* XRF and XRD measurements have been performed using two portable systems developed in-house.

X-ray fluorescence spectroscopy has been performed thanks to a portable system which is the latest version of an instrument developed and used over the past 10 years. The X-ray source is a Moxtek (Orem, USA) Pd-anode tube 3W power at 30 kV. The Pd-XRF beam (diameter about 1 mm) strikes the surface of the object at 45° and the SDD (Amptek, active area of 25 mm<sup>2</sup>) is perpendicular to the surface. It also allows the measurement of points along a line, thanks to a motorised displacement system. The voltage used during the experiments was 30 kV and the current 50 mA, the acquisition time, 5 minutes. The XRF spectra were processed by the dedicated software PyMca [12]. The chemical composition of the glazes has been calculated from spectra using the PyMca software with the fundamental parameters method [13]; the flux has been estimated at  $1,9 \cdot 10^8$  thanks to a Pb reference sample.

The two paintings have also been analysed thanks to a portable XRD/ XRF system; it is equipped with an air-cooled iMOXS source (IFG-GmbH, Berlin) operated at 28 W power and 40 kV voltage, with a copper anode and a poly-capillary semi-lens that provides a parallel beam [14]. XRD (Cu-K $\alpha$ ,  $\lambda = 0.154$  nm) has geometrical constraints, in particular an incident beam at 10° from the object surface. With adequate slits, the surface irradiated by X-rays is about 3 x 4 mm<sup>2</sup>. A 2-D detection of XRD is provided by an imaging plate perpendicular to the incident beam. XRF is measured with the Amptek silicon drift detector referred to previously, perpendicular to the object.

## **II. Results and discussion**

### ***1. Addition of calcite in historical samples***

We first take into consideration the Dutch «*nuancier*», composed of all the pigments available at this time, used in a water colour medium. It is an extraordinary source of information, being at the same time a painting and a book of recipes. On the page opposite each recipe, the corresponding paint is applied. Two recipes are dedicated to lead white. According to the titles, the first one (Figure 1, left) refers to a pigment called «*loot wit*», and the second one to «*schilp wit*» (Figure 1, right). XRF analyses were carried out on both. «*The first one, loot-wit, contains only lead and calcium. The most usual lead based white pigment at the time is lead carbonate; the most probable compounds containing calcium*

would be calcium sulphate or carbonate. As no sulphur is detected (a precise fit of the spectrum with PyMca allow us to discriminate the Pb M lines from the K line of S), one can assume the presence of calcite and lead carbonate (either cerussite, hydrocerussite or a mixture of both).” Quantitative data treatment of the XRF spectrum allows us to estimate the respective quantities of lead and calcium at respectively 49 wt% and 15 wt% i.e. 63 wt% of lead white and 37 wt% of calcite. The thickness of the layer has been estimated at 27 microns (the procedure for absolute quantitative data treatment is presented in [13] and is recalled briefly in Experimental section). The second paint, *schilp wit*, contains only lead according to the XRF spectrum, and would thus be only lead white. This is in accordance with historical sources [15] which refer to two sorts of lead white known in the 17th century: pure lead white, *schelpwit* (shell white, or, in English usage, flake white or fine white), and a mixture of lead white and chalk which was called *lootwit* (literally lead white) or *ceruse* (ceruse, common white or Spanish white). It would have been of interest to identify the crystalline phases present in both paints but we were not able to take samples, and it was not possible to perform *in-situ* XRD measurements due to the geometrical constraints of the book. Complementary measurements and /or historical reconstructions would also allow us to understand the degraded aspect of the *loot wit* paint sample, in contrast to the *schelp wit* one, more expensive and made of the pure lead white pigment. Without further investigation it is not possible to state here whether this degradation would be systematic with such pigment, or if this is an isolated case due to specific conservation/ storage conditions.

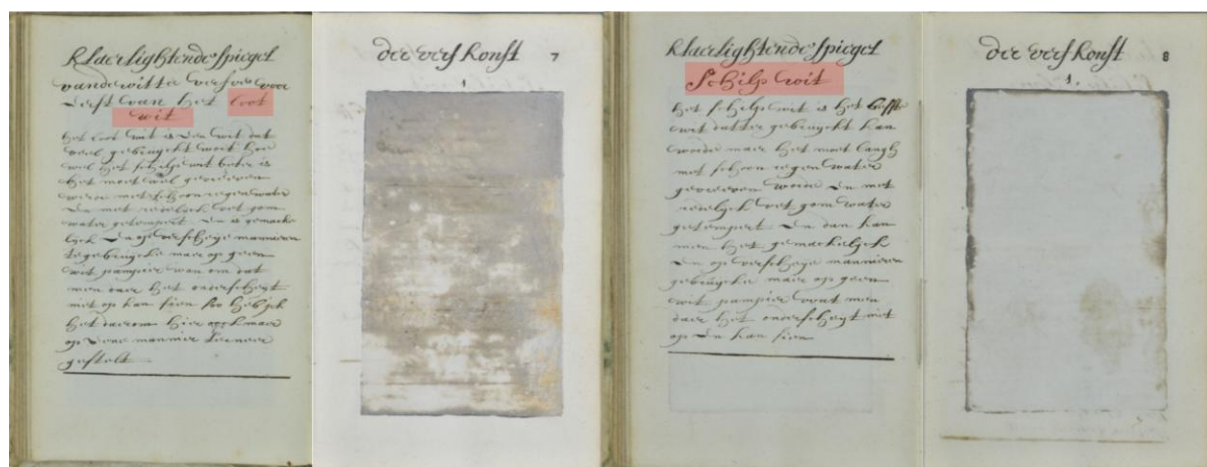


Figure 1 : Photographs of the two pages dealing with lead-based pigments. The name of the pigment has been highlighted in red : *lootwit*, on the left and *schelpwit* on the right.

Our team also highlighted the presence of calcite in several works of art; we describe here two examples where it can be interpreted in terms of optical effects.



A first example comes from the central panel of the Gdansk triptych *Last Judgment* (figure 2a). It was probably painted by Roger van der Weyden, and later completed by Hans Memling in the 15th century [9].

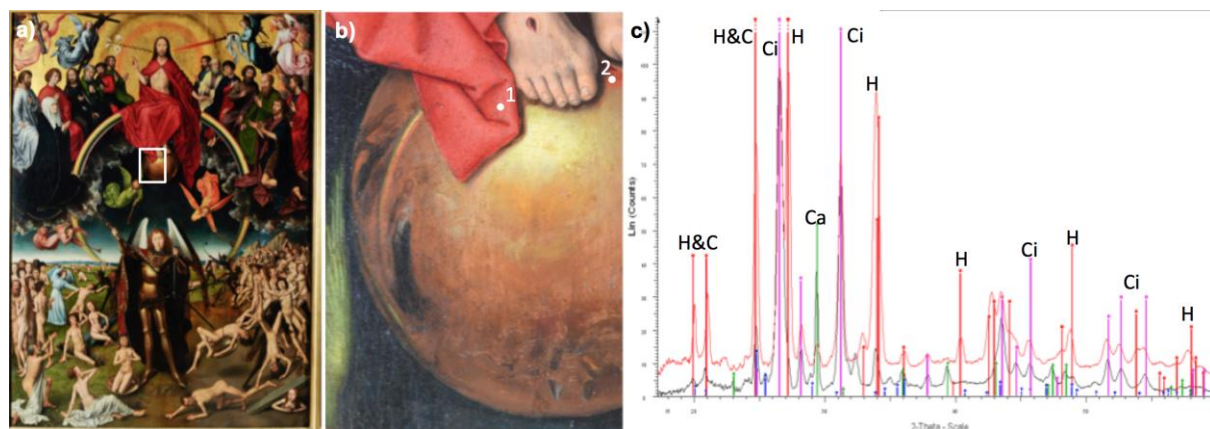


Figure 2: (a) Central panel of the Gdansk triptych *Last Judgment* by Roger van der Weyden, and completed by Hans Memling (15th century, 2.235 x 0.725 m) a close-up detail is presented in (b) showing the location of the points analysed in XRD (1 and 2); (c) displays the readings in XRD of point 1 (red line) and point 2 (black line), corresponding to the red reflection on the sphere with: H for hydrocerussite, Ci for cinnabar (vermilion), Ca for calcite and C for cerussite. The XRD data of point 1 and 2 were collected with the same experimental conditions (same acquisition time).

The figure of Christ “in majesty” is standing on a golden sphere that exhibits various reflections and shadows. We compared the chemical composition between the red mantle of Christ and the red reflection of the mantle, visible on the top of the sphere (figure 2b). XRD measurements on the mantle indicated mainly hydrocerussite and vermilion, with a very small amount of calcite. In the red reflection, a comparable quantity of vermilion is present, whereas there is a much greater quantity of calcite as opposed to the hydrocerussite. As the presence of calcite cannot be explained in any other way, it would seem clear that it must have been used deliberately, probably to create optical effects on the sphere. In this instance it is difficult to conclude if calcite has been used to contribute to the red reflection, or just to the metallic effect on the sphere (small amounts of calcite can be found in other parts of it).

We further present here the results of analyses of two paintings by Nicolas Poussin in which calcite has also been identified in white areas, but also used in various other colours in different proportions. In *Orange*, calcite, hydrocerussite and cerussite were found in almost all of the points analysed in different proportions indicating different qualities of lead white and the addition of calcite [11].

*Venus presenting Aeneas with his Arms* (Figure 3a) is also a striking example of the presence of calcite as it seems to have been chosen deliberately by the painter.

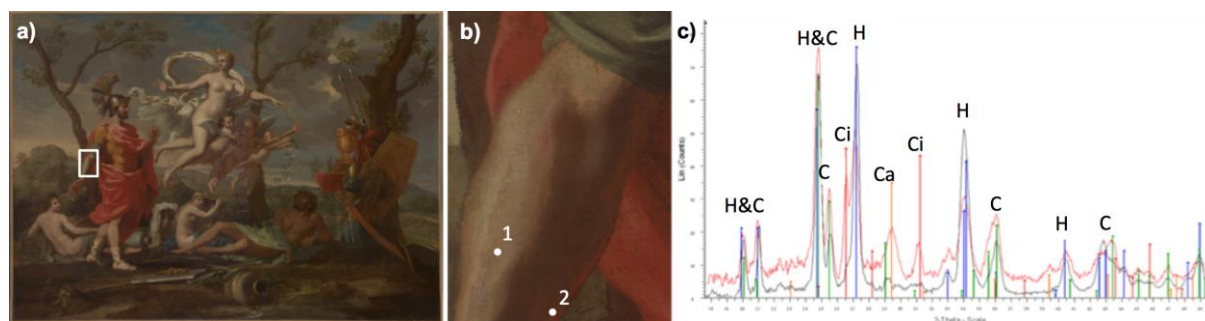


Figure 3: (a) *Venus presenting Aeneas with his Arms* ((Musée des Beaux Arts de Rouen, 1639, 1.07 x 1.46 m), a close-up detail is presented in (b) showing the location of the points analysed in XRD (1 and 2), (c) shows the readings in XRD of point 1 (black line) on the mid-tone of the flesh and point 2 (red line) corresponding to the red reflection on his arm, with : H for hydrocerussite, Ci for cinabar, Ca for calcite and C for cerussite.

We specifically investigated how shadows and effects of reflection have been created by the artist. Two points were analysed in XRD to understand the red reflection on Æneas' arm (Figure 3). The diffractogram indicates the presence of large amounts of lead white, both cerussite and hydrocerussite, in the mid-tone of the flesh with variations in the relative proportions. In the red reflection on the arm, a different form of the lead carbonate has been used, with a higher ratio of cerussite to hydrocerussite. Vermilion but also calcite are also clearly visible, present in small crystals (as indicated by the aspect 2D-diffractogram). It is not possible to know with any certainty whether the presence of calcite is due to a commercially available cheaper lead white pigment [16] or an addition made by the artist during paint preparation. Because Nicolas Poussin is known to have neglected no detail in his efforts to achieve a perfect resemblance to nature in his paintings, we can confidently suggest that this inclusion of calcite was chosen, and decided upon in order to achieve a specific effect in accordance with the optical properties that he desired of his paint.

In the literature, analyses have shown an increase in the presence of calcite in paint – both in grounds and preparatory layers and oil paint layers in 17<sup>th</sup> century works. The addition of calcite would increase the transparency of the paint layer, allowing the colour of the underlying ground or preparatory layer to play an optical role. The arrival in Italy of Northern artists, painting in oil as well as glue, who would ‘cut’ their lead white in this way to obtain optical effects through increased transparency, may have played a part in the adoption of the

practice by Italian painters [17]. Titian can be seen to have used different whites to this effect, a white containing a Ca based pigment for the shadows of the flesh of Lucretia's arm (*Tarquin and Lucretia*, 1572, Fitzwilliam Museum, University of Cambridge), thinly drawn over a red underlayer, giving it a pearly shade. The inclusion of calcite in paint is a 'mark' of Venetian painting, to the extent that one finds it also in the early works of El Greco, whose early years were spent in Venice.

In the literature, there are other examples of the presence of calcite [14-21]; already in 1967, Gettens [1] referred to several paintings, one by Rubens painted in 1616-1617 and two by Vermeer dating from 1670-1672, for which the *imprimitura* layer is a mixture of lead white and calcite. More recently, Bordalo et al. [18] combine XRF, Raman spectroscopy and SEM-EDX on panel paintings from the late 19<sup>th</sup> century. Two ground layers are present: the lower one shows mainly calcium with a low amount of lead and the upper one shows mainly lead with a small amount of calcium. Raman spectroscopy confirmed the presence of calcite ( $\text{CaCO}_3$ , peak at c.a.  $1080\text{ cm}^{-1}$ ), as also reported in [19] where the lead-based paint in a 16<sup>th</sup> century panel is a mixture of hydrocerussite and calcite.

The recent studies by Gonzales et al. give a more complete picture with identification and quantification of the different phases via XRD measurements. They first performed *in-situ* measurements on five drapery studies attributed to Leonardo da Vinci [20]. They demonstrate the use of different lead white grades for the different draperies with various amounts of calcite (all below 10 wt%), even within the same painting. Then they analysed fifteen lead white-containing painting samples, from Renaissance to late 19th century paintings, and found that in several samples calcite may reach 25 wt%, i.e. 40 vol%, of the pigment used [21]. However, despite the growing number of studies reporting the identification of calcite, it is usually not thoroughly discussed as a part of the master's technique and palette but generally attributed to the quality of the lead white [**Erreur ! Signet non défini., Erreur ! Signet non défini.**, 22].

In the *The Night Watch* by Rembrandt, K. Groen [23] reported that two lead white layers are used as underpainting: the lower one is composed of 25% of calcite whereas the upper one consists of lead white only. She underlines the fact that although the price could be a reason for such a mixture in a large painting, « *the differences in the percentage of chalk -(calcite)- so far discovered rather suggest that the chalk was not evenly distributed and thus that the mixing was perhaps done in the studio* ». In another publication, different paintings by Rembrandt were studied, the lead white paints contain a percentage of calcite from 5 to 15

wt% of chalk (13 to 45 vol%) [24]. Groen then goes on to discuss the rheological modifications obtained by the addition of calcite.

Based on this study and our own observations, we decided to define the influence of the presence of calcite on the properties of lead white based paint.

## 2. Modification of optical properties

The evidence that calcite was added to lead white (and other pigments bound in oil) in order to alter the optical properties of the paint derives largely from the analysis of paintings themselves.

In order to define the optical effect of adding calcite to white paints, we carried out visible reflectance spectroscopy on thin white layers (30  $\mu\text{m}$ ) placed on an optically black layer. We here report the results obtained for lead white from Laverdure. Other commercial lead white and Champagne chalk paints gave slightly different measurements, leading however to similar conclusions on the optical properties of the mixture. Paints made up with each pigment alone, and mixtures of 2 parts of lead white for 1 part of calcite (in weight and in volume) were prepared as detailed in the Experimental section. Their optical properties were compared by measuring the visible reflectance spectrum (figure 4) and the L, a, b coordinates (table 1).

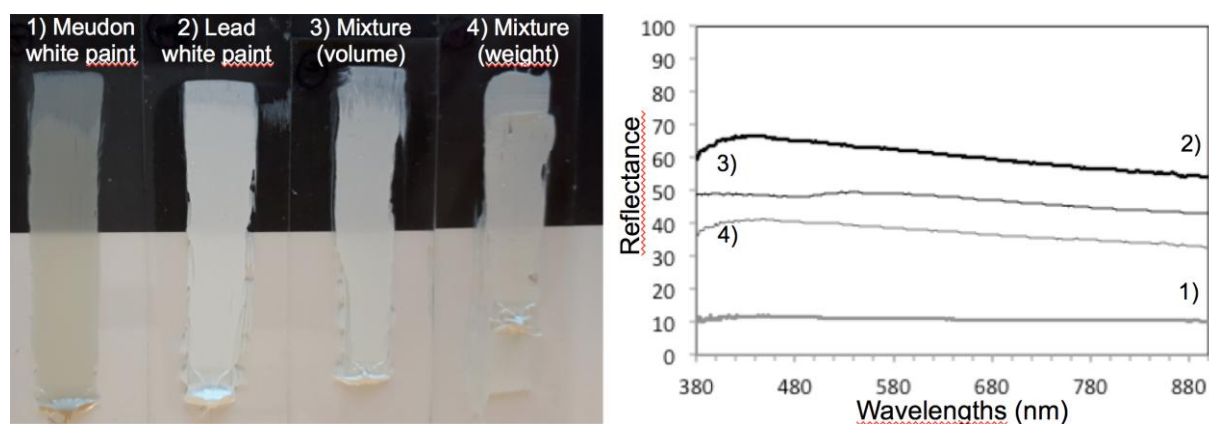


Figure 4: Photographs (left) and (right) visible reflectance spectra of the paint spread on a glass slide placed on the optical black (at  $t = 1$  week) of: 1) Meudon white paint, 2) lead white paint and 3) and 4) the mixtures lead white (2 parts) + Meudon white (1 part) respectively in volume and in weight. The oil/pigment proportions used are detailed in the Experimental section.

	Lead white		Meudon white		Mixture (vol)		Mixture (wt)	
	t = 1h	T = 1 week	t = 1h	t = 1 week	t = 1h	t = 1 week	t = 1h	t = 1 week
L	81	82.5	39	39.1	73.6	76	71.1	71.5
a	-0.7	-0.5	-0.2	0	-0.7	-0.4	-0.7	-0.5
b	-0.8	-2	-0.5	-0.4	-0.2	-1.5	-0.9	-1.9

Table 1: L, a, b measurements of the paint layers before and after drying. The mixture is 1/3 of calcite and 2/3 of lead white (by weight). As the paint is spread on a non-absorbent substrate, the variations in the “dried” state are small.

The L value of black is 0, whereas the one of white is 100. A completely opaque white layer placed on black would have L equal to 100, whereas a completely transparent one would have L equal to 0. Thus the variations of L observed here can be used to give us information about the transparency of the layer. The results are indicated in Table 1; the L value is higher for the lead white layer than for the calcite one. The L values of the mixtures are intermediary; the mixture by volume, containing less calcite, has a higher L value. This is also visible on the photographs of the slide (figure 4, left). The reflectance spectra of the mixtures are also in between the ones for the pure lead white paint, and the Meudon white one (figure 4, right).

The a and b values, which indicate the hue, are close to 0, but after drying (t = 1 week) a slight shift towards the “blue” colour (a zero and b negative) can be observed on the lead white base paints, as is also confirmed by their reflectance spectrum. This reminds one of Leonardo’s observations: “ (...) take a board painted in different colours amongst which a very fine black, and cover all of these with a very thin and transparent layer of lead white, and then he will see that (...) the white appear so blue » [p73 in 17].

To explain the difference in transparency, one has to compare the refraction index of the paint layers, and the difference between the refraction index of the pigment and the one of the binder. For a single binder, an increase in the pigment index increases the reflection at the pigment-binder interface and at the air-paint interface, both of which limits the transmission of light in the medium, and thus its transparency. These effects explain the difference in the optical properties of lead white and calcite. Calcite has two refractive indices according to the orientation of the crystal as light passes through it:  $\varepsilon = 1.486$  and  $\omega = 1.658$ . The refractive index of liquid drying oil is c.a. 1.48 and increases to 1.54 according to [25]. Calcite ground in oil does not look perfectly white but yellowish and translucent. Gettens in [1] already stated that this property had been used by painters: “*Chalk was not used alone in oil-medium paints, because of its low refractive index and, hence, poor color and hiding power, although this quality has been exploited to achieve translucency in the paint film*”. The refractive index of lead white is higher and very different from that of oil, c.a. 2.1, which accounts for the well-known high opacity and hiding power of lead white paint.

The opacity of paint layers can also be strongly influenced by diffusion phenomena; the maximal diffusion is obtained when the wavelength of the incident light is the same as the size of the diffusing object. Meudon white has grains of the same size as the lead white from Laverdure (from 500 nm to 5  $\mu$ m) but displays different geometries. Meudon white as well as Champagne chalk designs ground chalk derived from marine ooze, mainly composed of fossil remains called coccoliths, clearly visible in SEM images, as calcareous platelets of various shapes, and of few micrometers diameter. The different lead white investigated all exhibit hexagonal pellets but of different granulometry (Supporting information and figure 5): the grain size of the pigment from Laverdure is much bigger as the one from Master Pigments (from 500 nm to 5  $\mu$ m vs ca. 100 nm). The lead white from Kremer is the most inhomogeneous with important size dispersion (from 100 nm to 5  $\mu$ m). Results obtained on the pure lead white paints are quite the same, the Laverdure's pigment being slightly more opaque which would indeed be explained by this size difference. However the effect of chalk on the layer opacity on the different lead white pigments seems to be unchanged. It is thus difficult to conclude if diffusion plays here an important role, based on these simple experiments and without a more systematic study on the pigment composition, grain size and distribution.



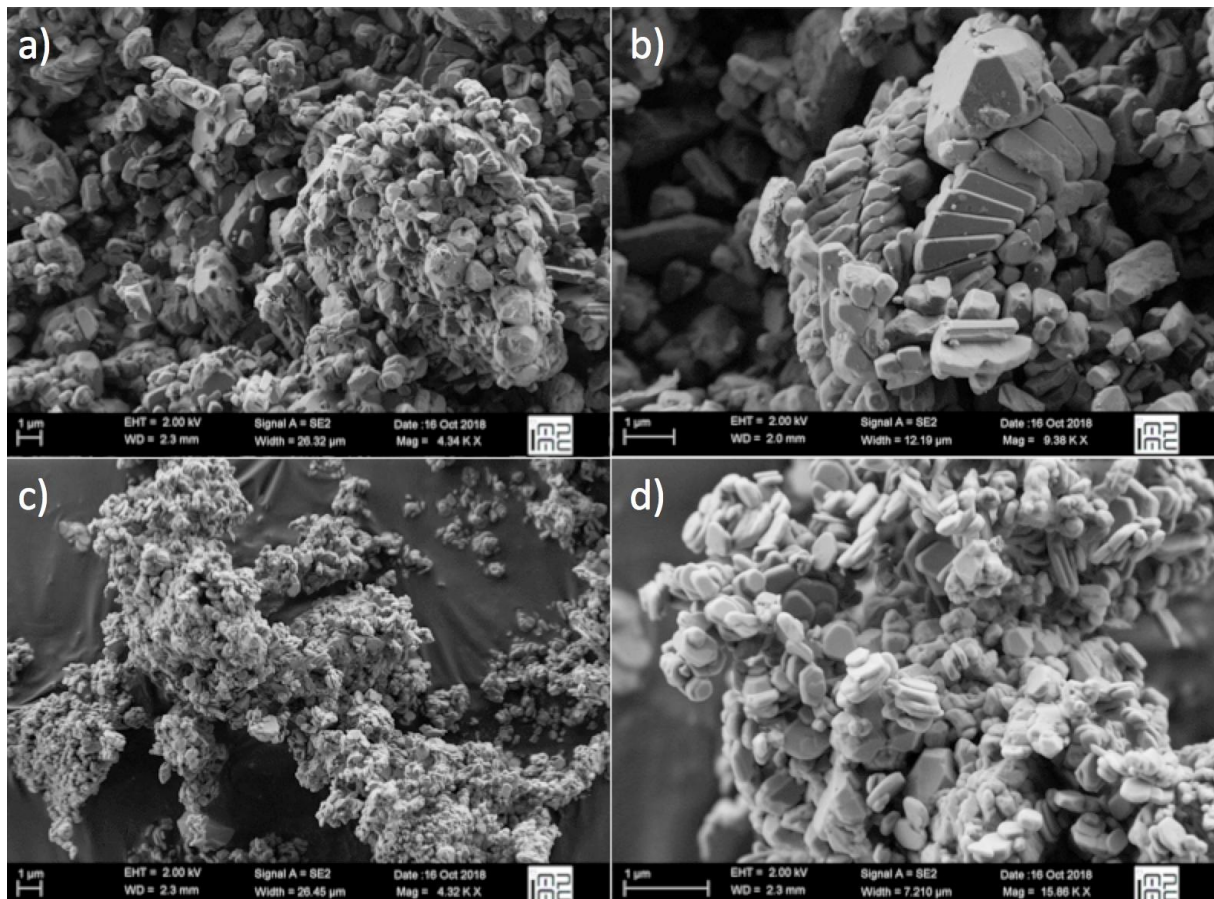


Figure 5: SEM images of a) and b) Meudon white from Laverdure and c) and d) lead white from Master's pigment.

### 3. Modification of rheological properties

Paint rheology is another important property to investigate in order to better understand artists' practices [26]. Indeed, according to Karin Groen's work on Rembrandt's paint [24], the addition of calcite can also be used to modify the rheological properties of paint. Maartje Stols-Witlox [5] writes in relation to the rheological effects of adding chalk: it can lead to « *somewhat greasy paint difficult to manage* » or be "*beneficial as it would facilitate the spreading of the paint*". Whether it is beneficial or not obviously depends on the painter's technique and practices, but what is certain is that the rheological properties of the paint are modified by this addition.

In order to assess this second effect, we compared the viscoelastic properties of white paints: lead white with an increasing amount of calcite. As reported elsewhere [6], lead white-based formulations exhibit unusual behaviour: when allowed to rest, they become spontaneously more fluent within a short time. This was the case here; thus, to ensure proper comparison, the paints were investigated just after preparation. Moreover, and for common time-dependent

suspensions, parameters such as the grinding time, the time between sample preparation and measurements, and the waiting time between measurements were strictly controlled. All the paints exhibit visco-elastic properties similar to paste suspensions. At low stress, the viscous modulus  $G''$  is lower than the elastic one  $G'$  and they are both nearly constant (“linear viscoelastic regime”). Beyond the so-called yield stress  $\tau_c$ , the system becomes viscous ( $G' \ll G''$ ) and the paint flows.

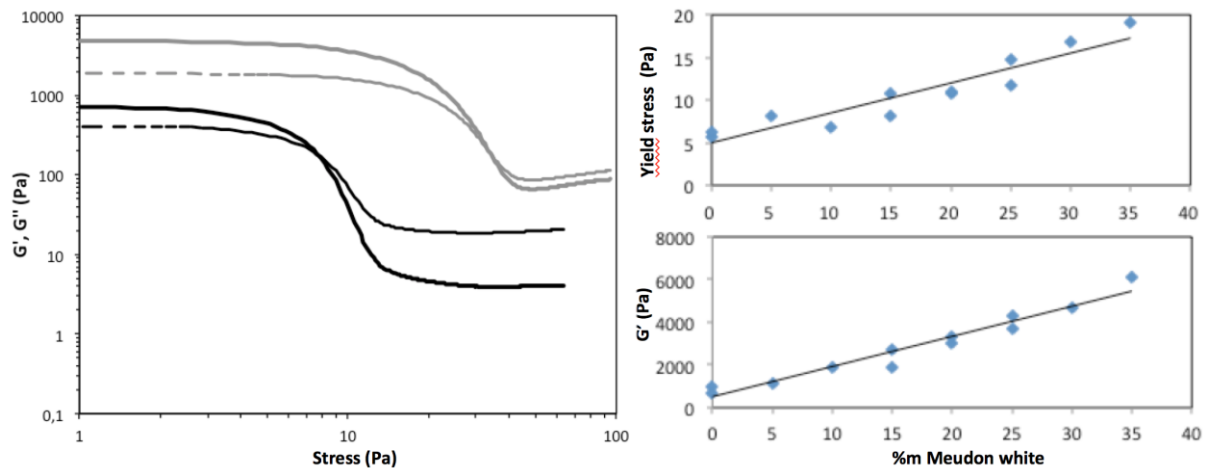


Figure 6: Rheological measurements on lead white based paints: left, viscoelastic properties of paints containing 0 wt% of chalk (black line) and 30 wt% of calcite (grey line). On the right, yield stress value and elastic modulus  $G'$  depending on the amount of chalk added to the lead white paint.

We compared the value of  $G'$  and of yield stress with different amounts of calcite (Figure 6); the oil content was kept constant at 15.7 wt%, (i.e. varied from 58 %vol to 45%vol). The addition of calcite induces the increase of  $G'$  and  $\tau_c$ . This result could be expected looking at their respective oil absorption value: around 8 wt % for lead white whereas it is much higher for calcite/ Meudon white. The value of  $G'$  is related to the number of « contacts » in the paint; one has also to consider the pigment granulometry. Chalk is indeed quite heterogeneous with numerous shapes of grain. This increase of elastic modulus and yield stress, can be seen as a way to allow impasto effects to be created with greater facility [Erreur ! Signet non défini.]. This is in full agreement with K. Groen’s observations on Rembrandt’s white paints, which could contain up to 15 wt% of calcite [24]. She suggested that this amount of chalk had been added by Rembrandt on his palette to obtain the consistency he wanted, to allow him to create the strong brushstrokes still visible on his paintings.

However these results have to be taken cautiously: as we chose to keep the binder/ pigment ratio constant, the paint samples were more model systems than accurate reconstructions. The



painter would have probably modified the binder ratio for each system. Although the modification induced appeared clearly here, other parameters can modify strongly the rheological behaviour of the paint: the lead white treatment, the nature and pre-treatment of oil, etc [Erreur ! Signet non défini.]... As well as for the optical properties, the pigments characteristics (cerusite/hydrocerusite proportion, grain size, distribution...) will have an influence on the rheological properties, even if the global effect of calcite remains unchanged. To go further, it will be interesting to investigate these same properties with lead white of different proportions of cerussite and hydrocerussite and pigments of different granulometry.

## **Conclusion**

*In-situ* measurements allowed us to detect lead white based paints containing high amount of calcite in a Dutch nuancier of the 17<sup>th</sup> century and in two historical paintings displaying different compositions of lead white. This presence of calcite has been highlighted in numerous works of art in the literature and is probably linked to a less expensive price but also modifications of the paint's properties, its rheological behaviour and its transparency. When the presence of calcite is identified in a white paint layer, it is not possible to prove conclusively whether the artist bought a less expensive lead white (which includes more or less calcite) which he has used as bought, or whether he has deliberately added calcite to achieve a desired effect, or even if he has added more calcite to his commercially prepared lead white paint. What appears to be undeniably the case, is that artists were aware of the different properties of their paint induced by the presence/addition of calcite, and that his use of this paint reflects either the artist's finances, his philosophy, the nature of the area to be painted in relation to the under and adjacent layers, the importance of the commission etc.

## **Acknowledgments**

The authors wish to thank the Bibliothèque Mejanès, the Gdansk museum and the Rouen museum for access to the works of art. We are also grateful to Victor Gonzalez for many interesting discussions on this topic.

## **References**

---

[1] R.J. Gettens, H. Kühn, W.T. Chase, Lead White, in : A. Roy (Ed.), Artists' Pigments – A handbook of their History and Characteristics, Vol. 2 , National Gallery of Art, Washington, DC, 1993, pp. 67-82.

---

[2] M. Merrifield, *Medieval and Renaissance Treatises on Painting*, Dover Publications, London, 1967, pp. cli.

[3] L.C. Matthew, *Vendecolori a Venezia: The Reconstruction of a Profession*, *The Burlington Magazine* 144, 1196 (2002) 680-686.

[4] B. Berrie, L. Matthew, *Lead white from Venice: a whiter shade of pale?*, in : M. Spring (Ed.), *The National Gallery Technical Bulletin 30th Anniversary Conference Postprints, Studying Old Master Paintings - Technology and Practice*, Archetype Publications, London, 2011, pp. 295-301.

[5] M. Stols-witlox, *The heaviest and the whitest: lead white quality in north western European documentary sources, 1400-1900*, in : M. Spring (Ed.), *The National Gallery Technical Bulletin 30th Anniversary Conference Postprints, Studying Old Master Paintings - Technology and Practice*, Archetype Publications, London, 2011, pp. 284-294.

[6] J. Salvant Plisson, L. de Viguerie, L. Tahroucht, M. Menu, G. Ducouret, *Rheology of white paints: how Van Gogh achieved his famous impasto*, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 458 (2014) 134-141.

[7] V. Gonzalez, D. Gourier, T. Calligaro, K. Toussaint, G. Wallez, M. Menu, *Revealing the Origin and History of Lead-White Pigments by Their Photoluminescence Properties*, *Anal. Chem.* 7, 89 : 5 (2017) 2909-2918.

[8] Bibliothèque Méjanes.

<http://bibliotheque-numerique.citedulivre-aix.com/records/item/35315-traite-des-couleurs-servant-a-la-peinture-a-l-eau> (accessed 10 October 2018).

[9] I. Szmelter, P. Walter, H. Rousselière, *New Information Provided by Multidisciplinary and Combined Studies, Including Radiography, XRD and XRF, of the triptych the Last Judgement from National Museum in Gdańsk: Rogier van der Weyden and Hans Memling co-authorship*, *Opuscula Musealia* 23 (2015) 61-73.

[10] H. Glanville, H. Rousselière, L. de Viguerie, Ph. Walter, *Mens agitat molem »: new insights into Nicolas Poussin's painting technique by X-ray diffraction and fluorescence analyses, chapitre 15*, in: A. Sgamellotti, B.G. Brunetti, C. Miliani (Eds.), *Science and Art: the Painted Surface*, Royal Society of Chemistry, 2014, pp. 314-335.

[11] L. de Viguerie, Ph. Walter, H. Glanville, *Some preliminary remarks on Nicolas Poussin's painting technique in L'Orage: complementary X-ray fluorescence / X-ray diffraction study*, *Kermes* 94/95 (2015) 97-106.

[12] V.A. Solé, E. Papillon, M. Cotte, Ph. Walter, J. Susini, *A multiplatform code for the analysis of energy-dispersive X-ray fluorescence spectra*, *Spectrochim. Acta B.* (2007) 62:63–8.

- 
- [13] L. de Viguerie, A. Duran, V.A. Sole, A. Bouquillon, J. Castaing, Ph. Walter, Quantitative X-ray fluorescence analysis of an Egyptian faience pendant and comparison with PIXE, *Anal Bioanal Chem.* 395 (7) (2009) 2219–25.
- [14] A. Gianoncelli, J. Castaing, L. Ortega, E. Dooryhée, J. Salomon, Ph. Walter, et al. A portable instrument for in-situ determination of the chemical and phase composition of cultural heritage objects, *X-Ray Spectrom.* 37 (2008) 418–423.
- [15] J. A. Van de Graaf, The Interpretation of Old Painting Recipes Source, *The Burlington Magazine* 104, 716 (1962), 471-475.
- [16] R. Spear, A century of Pigment prices : seventeenth-century Italy, in : J. Kirby, S. Nash, J. Cannon (Eds.) *Trade in Artist Materials – Markets and Commerce in Europe to 1700*, Archetype Publications, 2010.
- [17] H. Glanville, Veracity, verisimilitude and optics in painting in Italy at the turn of the 17th century, *Kermes* 84 (2012) 59-84.
- [18] R. Bordalo, C. Bottaini, C. Moricca, A. Candeias, Material characterisation of a florentine painter in portugal in the late 19th century: paintings by Giorgio Marini, *Int. J. conserv. Sci.* 7, 4 (2016) 967-980.
- [19] E. Stanzani, D. Bersani, P.P. Lottici, Ph. Colomban, Analysis of artist's palette on a 16th century wood panel painting by portable and laboratory Raman instruments, *Vibrational Spectroscopy* 85 (2016) 62-70.
- [20] V. Gonzalez, T. Calligaro, L. Pichon, G. Wallez, B. Mottin, Leonardo da Vinci's drapery studies: characterization of lead white pigments by 1-XRD and 2D scanning XRF, *App. Phys. A* 121, 3 (2015), 849-856.
- [21] V. Gonzalez, T. Calligaro, G. Wallez, M. Eveno, K. Toussaint, M. Menu, Composition and microstructure of the lead white pigment in Masters paintings using HR Synchrotron XRD, *Microchem. Journal* 125 (2016) 43–49.
- [22] M. Eveno, A. Duran, J. Castaing, A portable X-ray diffraction apparatus for in situ analyses of masters' paintings, *Appl Phys. A* 100 (2010) 577–584.
- [23] E. Van de Wetering, C. M Groen, J.A. Mosk, Summary Report on the Results of the Technical Examination of Rembrandt's Night Watch, *Bulletin van het Rijksmuseum* 24, 1/2 (1976) 68-98.
- [24] K. Groen, Investigation of the use of the binding medium by Rembrandt, *Chemical analysis and rheology*, *Zeitschrift für Kunsttechnologie und Konservierung* 11, 1997, 207-227.
- [25] F. Perego, *Dictionnaire des matériaux du peintre*, Belin, Paris, 2005.
- [26] L. De Viguerie, G. Ducouret, T. Moutard-Martin, F. Lequeux, Ph. Walter, Historical evolution of the oil painting media: a rheological study, *CR. Phys.* 10, 7 (2009) 612-621.

