



The ageing of model pigment/linseed oil systems studied by means of vibrational spectroscopies and chemometrics

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ABSTRACT

We used Fourier Transform - Near Infrared (FT-NIR) and micro-Raman spectroscopies to follow the changes occurring in a thin layer of linseed oil in the presence of lead white (basic lead carbonate) and zinc white (zinc oxide), which were due to the natural ageing process.

The curing of linseed oil is a very complicated process, owing to different mechanisms that occur simultaneously, ones which may be further modified by the presence of pigments and by environmental conditions (e.g. light, humidity, temperature). Both lead white and zinc white pigments affect this process, leading to the formation of films with different properties. Previous studies have already characterised the ageing of binders alone, including linseed oil. We investigated, by means of a combined analysis of the results of two different vibrational spectroscopy methods, the role of these two white pigments on the ageing of a linseed oil film. Model samples were prepared, and we followed their evolution over a 24-month period. Two ten-year-old oil mock-ups, which were prepared by using lead and zinc white pigments (comparable to contemporary oil painting), were analysed within the framework of the present results.

Lastly, we exploited the potentiality of Principal Component Analysis (PCA) on the combined FT-NIR and Raman spectra in order to define a possible ageing trend for two oil-white mixtures. Furthermore, we tested the statistical models by comparison with spectra related to the two ten-year-old mock-ups.

1. INTRODUCTION

Painters commonly use drying oils, such as linseed, poppy seed or walnut oils, owing to their capacity to form a continuous and thin film with good optical and mechanical properties within a reasonable length of time. The quality of this film and its stability over time are extremely relevant for a successful conservation and fruition of the works of art.

The aim of this work is to demonstrate the possibility of using Fourier Transform - Near Infrared (FT-NIR) and micro-Raman spectroscopies for the characterisation of changes due to the natural ageing process, in linseed oil films present in painting models, thanks to the observation of modifications in their vibrational spectra.

We used two different vibrational spectroscopy techniques, such as infrared absorption and Raman scattering, so as to cover both low-frequency fundamental vibrations and overtones in our experimental work. This use permitted access to an extended spectral region in which vibrational modes involved in the relevant chemical changes contributed either as fundamental modes or as overtones / combination

bands. In addition, the different physical process involved in the light-matter interaction can conveniently be exploited. Molecular vibrations can be triggered by the interaction of molecules with optical radiation if they are associated with changes in the molecular electric dipole moment (infrared active modes) or in the polarizability (Raman active modes), or both (infrared and Raman active modes). The use of a single spectroscopic method possibly limits the opportunities to follow the chemical change spectroscopically. For instance, Raman spectroscopy is better suited to identifying conformational changes and breaking/formation of CC bonds, while infrared absorption is more sensitive to the formation of polar bonds. Both types of vibrations provide information on the drying oil changes upon ageing, since the cross-linking process mostly involves the breaking of CC double-bond and CC single-bond formation, while the oxidation process involves the formation of C-O and C-OH bonds. Lastly, simple, dedicated and portable experimental tools exist to cover either one method or the other: this is very relevant for the possible implementation of low-cost, widespread monitoring methods used on paintings. However, spectroscopic information on the

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chemical changes in oils due to the drying process is not immediately accessible with the observation of a single band or of several specific bands. Many subtle spectral changes occur with the drying process. [1,2] Therefore, an advanced data analysis method is mandatory for a satisfactory study of this process. Chemometrics makes it possible to analyse complex spectral patterns and large sets of data concerning the search for common trends. [3,4] It has in fact been applied to studies on cultural heritage materials, including paintings, paper, and artistic artworks. [5,6] Interestingly enough, it is possible to carry out this numerical analysis on artificial spectra generated by merging data from different spectroscopic techniques. This enhances the level of information that we can extract from the different spectra, thanks to the cross-validation of the results obtained from the different techniques. For each sample we combined NIR and Raman data obtained from different spectral regions ($6000\text{--}3900\text{ cm}^{-1}$ along with $1800\text{--}1000\text{ cm}^{-1}$) in a single spectrum. The full set of data from the different samples was subject to Principal Component Analysis (PCA) in order to sort out possible spectral trends.

Here as follows, we provide details on the chemical processes that are involved in the drying and ageing of drying oils. This should help us understand the relevance of the different spectral signatures that we have identified in the vibrational spectra.

Since the fifteenth century, linseed oil has been used extensively as a medium for painting, owing to its capacity to form, within a reasonable time, a continuous thin film with good optical and mechanical properties. It is a fast-drying oil if compared to other products (e.g. poppyseed and walnut oils), due to its high concentration of linolenic acid [1]. The curing of this drying oil has been the subject of several studies [1,2,7–16]. It is commonly stated that the curing of this drying oil is due to a polymerization process that follows a process of autoxidation of the unsaturated fatty acid components. After an induction period, attributed to the presence of natural antioxidants, the oil absorbs large amount of oxygen, thus giving rise to the formation of hydroperoxide groups with concomitant conjugation and *cis-trans* isomerization of the double bonds. The subsequent decomposition of hydroperoxides into alkoxy (RO•) and peroxy (ROO•) free radicals leads to the formation of by-products (e.g. alcohols, aldehydes, ketones, carboxylic acids and peresters) and of *cross-link* reactions. [1,2,12,13,15,17,18] Although a film of linseed oil becomes *touch-dry* in a few days, the drying process continues for many years. [1] The autoxidation can also produce small chain acids, and oxidation at the C9 position of the unsaturated acids can result in the formation of azelaic acid, which is found in many oil paintings. [10,19]

Some inorganic materials, e.g. ones containing different metal ions, are known to decrease the drying time when in contact with the drying oils and to produce better polymerised films. They are therefore known as driers. Driers may act in different ways in order to alter the drying behaviour of oils, and may either increase the oxygen uptake through catalytic action or reduce the time when oxygen uptake begins (the induction period). [12,19–23] For this work, lead white (basic lead carbonate) and zinc white (zinc oxide) pigments were selected, since the literature reports a different type of reactivity with linseed oil. Lead white is active in the cross-linking steps of drying, and is responsible for an overall drying throughout the paint layer(s). [23] The film, which is made of lead white and linseed oil, maintains its flexibility for a considerable period of time. [24,25] Zinc white is able to improve the appearance and quality of the total oil-paint film. [23,26,27] It causes a specific and still unidentified drying process for linseed oil, and over the period of several years forms a hard and brittle oil-film. However, both white pigments can lead to the formation of metal carboxylates/metal soaps, thus promoting the triglyceride hydrolysis process (saponification reaction) [12,19,21–23,28–30]. Saponification generally causes a painting to darken and/or to become brittle [22].

2. EXPERIMENTAL

2.1. Linseed oil-paint models

Linseed oil from Zecchi (Florence, Italy) was selected as a binding medium, and was used just as it was supplied. Lead white and zinc white pigments, which were purchased from Sigma-Aldrich, were used directly in the preparation of the different samples. Two oil-paint models were prepared according to recipes reported in original treatises and artists' accounts [31,32] by mixing these pigments with linseed oil on the smooth surface of a glass surface. Initially, the powdered pigments were crushed in an agate mortar in order to obtain a homogeneously fine particle grain size without lumps. The exact concentration of the pigment with respect to that of the drying oil was not determined *a priori*. Instead, for each case, a mixture of similar consistency was used to prepare the paint models, so that they could be applied with a fine brush as a single thick layer on microscope glass slides and then be left to dry on a bench top. The paint films had rough non-homogeneous surfaces as would be expected in real samples. As references we also prepared samples made of linseed oil without any pigments.

Four replica samples were prepared for each material. The samples were left to age on a shelf at room temperature ($T: \sim 20\text{ }^{\circ}\text{C}$), with indoor conditions (RH: $\sim 50\text{--}55\%$) and exposed to indirect sunlight filtered through a glass window. They were measured at different delay times, after natural ageing. The powdered pigments were directly analysed without any preparation. The list of samples is reported in Table 1, with their denomination and the ageing time.

Lastly, measurements were performed on the two ten-years-old oil paint canvas mock-ups (Table 1), which were painted using lead white and zinc white mixed with linseed oil. The ground applied on the canvas, thus providing a uniform colour and texture, was a combination of linseed oil with calcite, gypsum and rutile. These canvas paint models were comparable to actual contemporary oil paintings.

None of the different samples examined showed any yellowing or darkness phenomena.

2.2. FT-NIR spectroscopy

FT-NIR reflectance spectra were recorded using a portable ALPHA FTIR spectrometer (Bruker Optics) equipped with an external reflection module. Total reflection spectra (including both the specular and diffuse reflection contributes) were collected *in situ*, in the $7500\text{--}3900\text{ cm}^{-1}$ spectral range with a resolution of 4 cm^{-1} over 128 scans and a 2 cm^{-1} sampling step. An area having a diameter of approximately 3 mm was analysed. The background was acquired using a gold mirror as a reference sample. Sixteen spectra were recorded for each model.

2.3. Micro-Raman spectroscopy

The Raman spectra were collected using a Renishaw RM2000 micro-

Table 1

List of analysed samples, with corresponding identification symbols and evaluated ageing times (units: months).

	Pigment	Drying Oil	Symbol	Ageing time	Dataset			
Neat drying oil	/	Linseed oil	L	3	L3			
				9	L9			
				24	L24			
Oil-paint models	Lead White (LW), 2PbCO ₃ ·Pb(OH) ₂	+ linseed oil	LWL	9	LWL9			
				24	LWL24			
				Zinc White (ZW), ZnO	+ linseed oil	ZWL	9	ZWL9
24	ZWL24							
Oil-paint mock-ups	Lead White (LW), 2PbCO ₃ ·Pb(OH) ₂	+ linseed oil	LWL	120	LWL120			
				Zinc White (ZW), ZnO	+ linseed oil	ZWL	120	ZWL120

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