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RESEARCH ARTICLE

Spectrofluorimetric study of the ageing of mixtions used in the gildings of mediaeval wall paintings

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Abstract
Introduction In the Middle Ages, we could find gildings on mural paintings. Gold, silver or tin leaves were applied according to distemper or mixtion technique. For the first one, a binder as glue is necessary, and for the second, a lipidic binder is used to stick the metallic leaf. Studies of gildings materials characterization show that the mixtion technique, with a mordant, is the most common. Linseed oil seems to be the binder used. It is always mixed with a siccative agent as lead. Because of bad conditions of conservation, the gildings do not resist anymore, only remain traces of metal or the adhesive under-layer. Thanks to the binder fluorescence, we can nowadays detect ancient gildings.
Objective The purpose of this paper is to study the degradation of the linseed oil, generally mixed with lead white to give a mordant for the metallic leaf, by spectrofluorimetry.
Materials and methods To understand in situ fluorescence, gildings recreations, linseed oil and lead white are aged in hygro-thermal and ultraviolet (UV) light (313 nm) climatic rooms and under UV irradiation. Irradiation wavelengths are chosen according to the maximum of absorption of linseed oil and the bibliography (296, 313 and 366 nm=mercury bands).
Results In comparison with results (in situ UV lamp, spectrofluorimetry), excitation wavelength chosen is 366 nm. Irradiations at 366 nm of linseed oil and linseed oil mixed with lead white show the most degrading effect in the fluorescence to the big wavelength. Lead white plays an important siccative role; it increases the intensity fluorescence and accelerates the drying of linseed oil. This study also allows to show that 366 nm wavelength is good for the in situ observation.

Keywords Gildings · UV fluorescence · Gildings recreation · Linseed oil · Lead white · Mixtion · Accelerated ageing

1 Introduction

Gildings are elements of decoration sometimes found on mediaeval mural paintings. The study of the gilding techniques is particularly interesting from a historic point of view because of the aesthetic, symbolic and prestigious criteria which are at the origin of the realization of these golden decorations. In the Middle Ages, paintings, in particular by fresco, were decorated for the greater part with lights, metallic decorations, glass inlays to give more volume, relief and to add reflections and brilliance to the colour (Pastoureau 1999). These additions were glued on the wall, by means of an organic binder, which confers them a bigger fragility. Of these metallic decorations often remain some traces because their mode of application

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makes them sensitive to the numerous factors of degradation, in particular environmental, to which they are subjected during centuries. Often, only remain the rests of organic binders which served to glue the metallic leaf and thanks to their detection, it is possible for us to locate an ancient gilding today.

So, traces of gildings were discovered in some murals, thanks to the yellow fluorescence brought about under an ultraviolet (UV) source (Mounier et al. 2010a, b). As an example, on the murals of the chapel of the ancient abbey house in Moissac, a very intense yellow fluorescence was observed on the haloes of the most important characters (Fig. 1), in particular that of the Christ. This fluorescence directed our sampling, and the analysis of the micro-samples showed the presence of an ancient gilding on a tin leaf glued, thanks to a mixtion layer composed of linseed oil and lead white.

This empirical approach was insufficient. It was necessary, for a more systematic study of the metallic decorations in murals, to study the phenomenon of the organic binders' fluorescence. Indeed, two main techniques of gilding are used: by tempera or by mixtion (Théophile 1996; Cennini 1991). In the first case, the pigment is mixed with an organic binder as glue or Arabic gum which allows to glue the metallic leaf. In the second case, a lipidic binder, as linseed oil, is used associated with a siccative as litharge (PbO). This last technique is most frequently found on mural paintings, that is why this study concerns the influence of the degradation of the linseed oil on the fluorescence.

The objective was to observe the degradation of binder under (linseed oil) light ageing and the role played by the lead white. This study also allows discussing the relevance of the wavelength used for the in situ observation (366 nm) with devices usually used for that purpose.

Fig. 1 Yellow fluorescence on the halo of one of the characters represented on the mural paintings of the vault of the ancient abbey home in Moissac

2 Materials and methods

2.1 Samples preparation

Analyses have been carried out on linseed oil and on a mixture of oil and lead white, deposited on glass slides. Linseed oil+lead white were also applied on a calcareous support. These samples have been set dry for 1 year in daylight at room temperature. Lead white was also studied apart.

Gildings recreations have been prepared by a restorer (SINOPIA) according to ancient techniques and stratigraphic structure found in mediaeval mural paintings. The gold leaf was applied according to the mixtion technique (mixture of linseed oil and lead white) on a support at fresco (mortar: *arricio* and *intonaco*) and a sublayer of red ochre. Table 1 presents a summary of samples, their conservation conditions and their reference name.

2.2 Accelerated ageing

Several simulations have been carried out to take various parameters into account: the dark, the daylight, UV radiation and humidity rate. Two types of ageing were tested: UV ageing and hygro-thermal ageing (Table 2).

Photochemical irradiation experiments of linseed oil and linseed oil+lead white were carried out by using a high-pressure Hg/Xe lamp equipped with a monochromator (Jobin-Yvon) (power, 1,760W). The irradiation zone measures 1.3×0.6 cm. The distance between the sample and the UV source was 17 cm; width of the slits is 10 mm.[1]

Three wavelengths were chosen: 296, 313 and 366 nm (V_{Ir296}, V_{Ir313} and V_{Ir366}), according to the data collected in the bibliography. Maximum time irradiation lasted until 159 h and the fluorescence follow-up to various times duration (Table 2).

The gildings recreations were submitted to an artificial ageing by exposure to controlled UV radiations by UV B of 313 nm wavelength (V_{313c}) (QUV Accelerated Weathering Tester). During the ageing, the samples have been kept in a constant temperature of 45°C. The irradiance of the source is 0.71 W/m^2 when samples are placed at the distance of 4.5 cm imposed by the configuration device. The exposure to UV lasted 400 h (approximately 17 days).

Samples of linseed oil and linseed oil+lead white on glass slides and on limestone have been submitted to a thermo-hygrometric ageing (V_{HT}) in a climatic chamber (Vötsch VC 4018). The chosen protocol includes 8 h cycles (four phases of 90 min each), with ascents and descents of

[1] Samples were irradiated in a black room at ambient temperature (25°C to 29°C) and a relative humidity of 20 %; the temperature, measured with a thermocouple on the sample, was 26°C to 29°C.

Table 1 Samples summary, preparation, conservation conditions and their reference name before ageing

Samples	Preparation	Conservation conditions	References
Linseed oil (hl)	Spread in the brush on glass slide	Day light, ambient temperature during 1 year	V_0=1 year
Linseed oil+lead white (hl+bp)	Spread in the brush on glass slide and on limestone	Day light, ambient temperature during 1 year	V_0=1 year
Lead white (bp)	Deposited on glass slide		V_0=0 day
Gildings recreations (PM5)	According to a mixtion technique	Ambient temperature shielded from light during 2 years	V_0=2 years

30 min between every cycle. These conditions are similar to those studies on the alterations of pigments in mural paintings (Aze 2005). The phases, the temperature conditions and the relative humidity settled in this protocol are:

- High humidity: temperature (T)=18°C, relative humidity (RH)=85 %
- Low temperature: T=−10°C, RH=0%
- Dry heat: T=40°C, RH=25%
- Wet heat: T=30°C, RH=60%

This 8 h cycle was repeated 90 times for a total duration of 4 weeks.To facilitate the comparison of the organic binders with the gildings recreations, linseed oil deposited on glass slides was also subjected to the same hygro-thermal ageing.

2.3 Analytical methods

The UV–Vis absorption spectrum was realized for linseed oil deposited on a quartz slide with a spectrophotometer Hewlett Packard 8452A.

Fluorescence measurements were performed using a Fluorolog SPEX 212 spectrofluorimeter, equipped with double monochromators on both the excitation and emission beams. The excitation lamp is a 450 W high-pressure xenon lamp, and a thermoelectrically refrigerated photomultiplier (Hamamatsu R928) is used for signal detection, using the photon counting mode. Fluorescence signals are given in the following in "counts per second" (cps). Data acquisition and data processing were computer controlled (SpectrAcq Datamax run by the Grams/32 software). Both excitation and emission spectra (recorded with 4 nm bandwidth) were corrected for instrumental factors. The measurements are made in mode "front face". The emitted light is collected according to an angle of 22.5° with regard to the excitation beam.

Table 2 Accelerated ageing undergone on the different samples, notations and times of ageing

Samples	V_{HT}	V_{IR}			V_{313c}
		296	313	366	
Linseed oil (hl)	x	x	x	x	
Linseed oil+lead white (hl+bp)	x	x	x	x	
Lead white (bp)			x	x	
Gildings recreations (PM5)	x				x

For the hygro-thermal ageing (V_{HT}), the time duration of experiment was 720 hours. For the irradiation ageing to 296, 313 and 366 nm (V_{Ir296}, V_{Ir313} and V_{Ir366}), time irradiation is noted: T_0 (before ageing), T_{17} (after 17 h of ageing), and T_{159} (after 159 h of ageing). For the study to 313 nm controlled in climatic chamber (V_{313c}), the time to exposure was 400 h

x type of ageing undergone

3 Results

The linseed oil used in our samples focuses on an absorption spectrum, at initial state T_0, with three maximal intensities at 273, 286 and 326 nm. The spectrofluorimetric study was made out of different wavelengths excitations at 254, 273, 286, 313, 326 and 366 nm, very often mentioned in the bibliographical data (Larson et al. 1991; Karoui et al. 2006; De la Rie 1982a) and correspond to those of a mercury vapour lamp. Thoury (2006) also showed that the most interesting excitation wavelengths for the study of varnishes are between 300 and 366 nm.

For the excitation wavelengths of 254, 273 and 286 nm, the results are not really significant (very weak fluorescence). For the 313, 326 and 366 nm excitation wavelengths, the fluorescence intensity is much higher and the spectral envelope covers the domain of 350–600 nm (Fig. 2).

The 313 and 326 nm excitation wavelengths allow to study the evolution of two fluorophores families: the first one centred towards 380 nm (a) and the other at about 430 nm (b).

The 366 nm excitation wavelength allows to follow the fluorescence emitted in the visible range (400–600 nm) and, by concern of comparison between the results of laboratory and those observed in situ, with the eye as the detector. This wavelength was chosen for the whole study and for all the results presented below.

1. Irradiation ageing
   (a) Linseed oil fluorescence before and after ageing for an irradiation at 366 nm

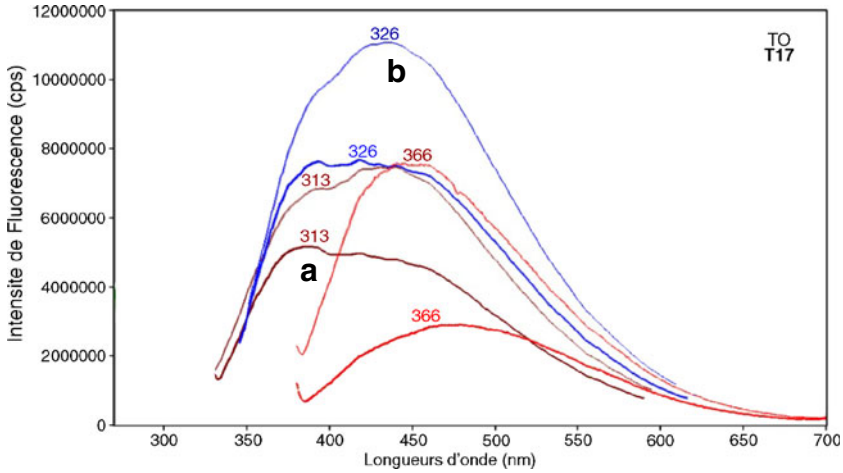

Fig. 2 Emission spectra at λ_{ex} 313, 326 and 366 nm before and after irradiation at 366 nm (V_{Ir366}) during 17 h (T_{17}). Two fluorophores families are present, one (*a*) at 380 nm and the other one (*b*) at 430 nm

Linseed oil deposited on glass slides 1 year before and then kept under daylight at room temperature (T_0) has been submitted to three series of irradiation (Tables 1 and 2). The layers of oil were not really regular, neither still dry.

For every irradiation series, the same protocol was respected:

- Complete study by fluorescence at T_0, T_{17} and T_{159} (Table 2)
- Study of the fluorescence intensity evolution and of the spectral envelope, according to the ageing time.

After irradiation at 366 nm, the intensity of fluorescence decreases gradually with the irradiation time and the maximum shifts towards higher wavelengths (from 444 nm for T_0 to 480 nm for T_{159}) (Fig. 3).

The 296 and 313 nm irradiations also provoke intensity variations and a spectral evolution but in lower proportions. The normalization of spectra intensity at T_0 and T_{17} shows that before ageing, three samples have more or less the same spectral signature. Spectra are practically superimposed (Fig. 4). Seventeen irradiation hours at 296 nm does not provoke (or little) changes of the spectrum. On the other hand, the 313 nm irradiation lead to a shift towards high wavelengths but lesser than for the 366 nm irradiation. Contrary to the result obtained for the 366 nm irradiation, the spectral shift obtained after 313 nm irradiation comes along with an increase of the fluorescence intensity in the range (450–550 nm) and not of a decrease.

The excitation fluorescence spectra observed for the observation wavelengths of 450 and 520 nm allows to explain this spectral evolution (Fig. 5).

Before irradiation (T_0), spectra present a maximum towards 368 nm which corresponds to the absorption domain of the polyunsaturated compounds containing double bounds of type linoleic acid. After 17 h of ageing (T_{17}) and even more after 159 h of irradiation (T_{159}), this

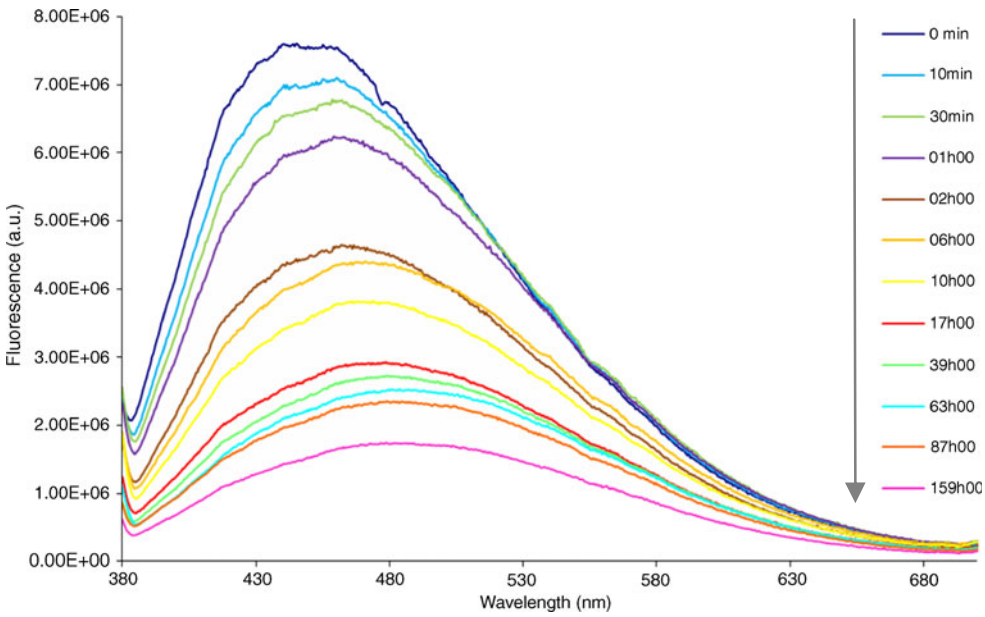

Fig. 3 Emission spectra of linseed oil aged at different times with a 366 nm irradiation (0 to 159 h)

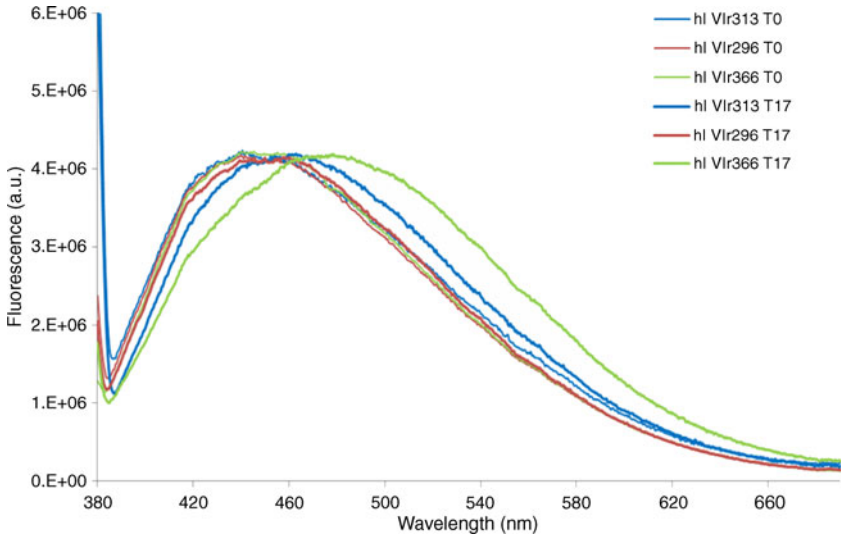

Fig. 4 Normalized emission spectra of linseed oil before and after 313, 296 and 366 nm irradiations (T_0, T_{17} and T_{159})

maximum disappears in favour of a maximum towards 330 nm. We can suppose that the polyunsaturated compounds had been transformed into smaller compounds which absorb in UV. This hypothesis was supported by the increase of the fluorescence in the range 350–400 nm, for λ_{ex} 313 and 326 nm, after irradiation (Fig. 2). In 1 year, samples have aged "naturally". There was formation of hydro-peroxides. During the irradiation, the photo-oxidation phenomenon amplifies the decomposition of peroxides, which explains the decrease of absorbance towards 368 nm. The formed radicals absorb towards the shorter wavelengths, here towards 330 nm (result consolidated by the increase of the fluorescence intensity (a) to the detriment of the fluorescence intensity (b) for λ_{ex} 313 and 326 nm) (Fig. 2).

The excitation spectra obtained by observation at 520 nm also shows an intensity increase in the superior range at 400 nm which explains the extension of the emission spectrum towards the high wavelengths. This corresponds to the formation of compounds which give yellow fluorescence.

(b) Addition effect of lead white

Lead white is the main pigment used up to half of the nineteenth century, both for the paintings and for the gildings because it can be used with a big variety of organic binders, in particular with siccative oils as linseed oil. To understand its impact on the binder fluorescence, lead white deposited on a glass slide was irradiated 17 h at 366 nm in the same conditions used for the linseed oil and for the mixture linseed oil+lead white.

Before irradiation, the fluorescence was very weak. After 17 h of irradiation, the lead white presents an intense fluorescence in the visible range (400–600 nm) and its excitation fluorescence spectrum covers the UV rays domain. Lead white is considered as a fluorescent white

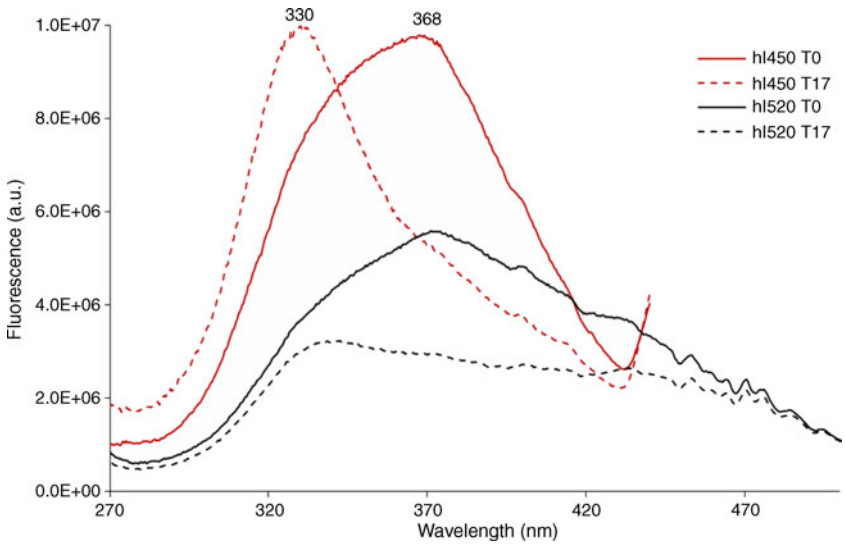

Fig. 5 Excitation spectra of linseed oil before and after 366 nm irradiation (λ_{ob}, 450 and 520 nm)

which absorbs UV and emits in the visible. After irradiation under 366 nm, the sample is slightly yellow. After irradiation under 313 nm, it turns brown.

For the sample of lead white mixed with linseed oil, before irradiation (T_0), it presents an important fluorescence with regard to the only linseed oil. After normalization spectra (linseed oil spectrum×1.6 factor), the spectral answer is globally the same, with a very light extension towards the higher wavelengths >500 nm (Fig. 6). As for the oil, during irradiation at 366 nm, the fluorescence intensity decreases gradually and the spectrum moves towards the high wavelengths. This shift is always more important than for the oil; the maximum of the spectrum at 444 nm for T_0, 484 nm for T_{17} and 500 nm for T_{159}.

This result confirms that the presence of lead white amplifies the yellowing. The spectrum of linseed oil+lead white after 17 h of irradiation is the same than for oil after 159 h irradiation (Fig. 6).

The increase of fluorescence is connected to the lead white fluorescence. The shift, more important towards the high wavelengths (bathochrome effect), is connected to the drying speediness of the film. By drying, the film structure becomes more and more waterproof to the oxygen. Lead white accelerates the drying of the oil, increases the cohesion of its molecules and amplifies the formation of fluorescent compounds. The reactions of photo-oxidation become unimportant, only contaminants are photodegradable and are transformed into compounds which get a yellow fluorescence.

By-products of the degradation process appear with, maybe, a reaction between the carboxylic functions of the oil and carboxylic metallic (Matteini et al. 2009). These hypotheses join those of De la Rie (1982a) who had shown the influence of lead white on the intensification of the linseed oil fluorescence. To explain this phenomenon, he suggests two mechanisms. Lead accelerates the drying process and new fluorescence appears due to the formed products of degradation, or lead influence the luminescence of the degradation products by formation of metallic complexes.

The study of the mixtion sample, before and after irradiation in 366 nm, confirms some observations made directly on mural paintings. The fluorescence signal is higher than for the only linseed oil. The phenomenon of yellowing is accelerated. Compared with the in situ observations, the presence of lead white can explain the strong fluorescence intensity. If this one is yellow, the presence of a lipidic binder is the most likely hypothesis.

Various factors influence the ageing of oil. The increase of the temperature accelerates the drying processes and the oil cross-linking. Afterward, the dried oil seems as relatively thermostable. The use of siccative pigments, salts of metals such lead, cobalt or iron, also accelerates the oil drying. The thickness of the film eventually can play a role. Differences of polymerization inside the oil film are indeed observed depending to the depth (Mallégol et al. 2001b; Stenberg et al. 2005).

2. Thermo-hygrometric ageing effect (V_{HT})

In the darkness, the temperature variations, in the range −10°C to +40°C, accompanied with the relative humidity variations from 0% to 85%, cause only weak modifications on the spectral answer but amplify the fluorescence intensity (Fig. 7). This increase can be explained by the absence of light in the chamber as results observed by De la Rie (1982b, part II) and by ourselves.

A similar result was obtained on samples prepared for the UV irradiations. During these irradiations, unexposed samples (to UV) were kept in the dark at room temperature. An increase of the fluorescence intensity was observed

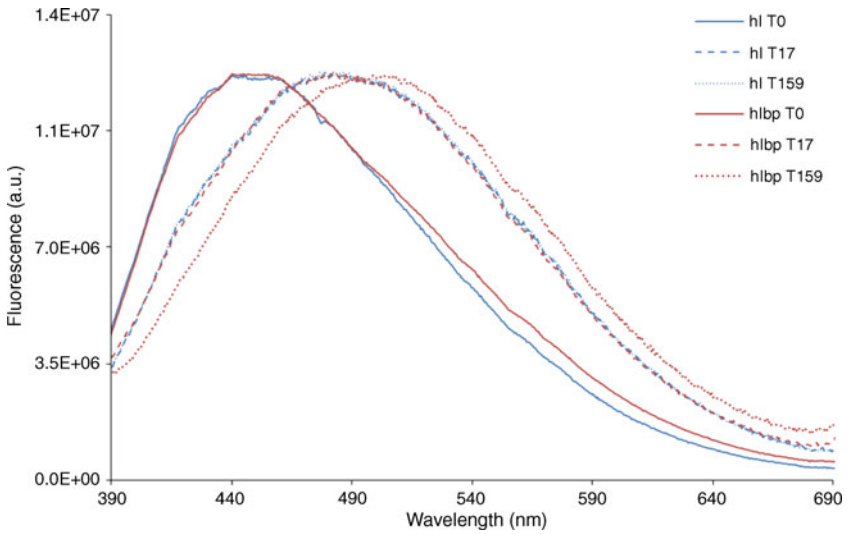

Fig. 6 Emission spectra normalized of linseed oil and linseed oil mixed with lead white before (T_0) and after 366 nm irradiation (T_{17} and T_{159})

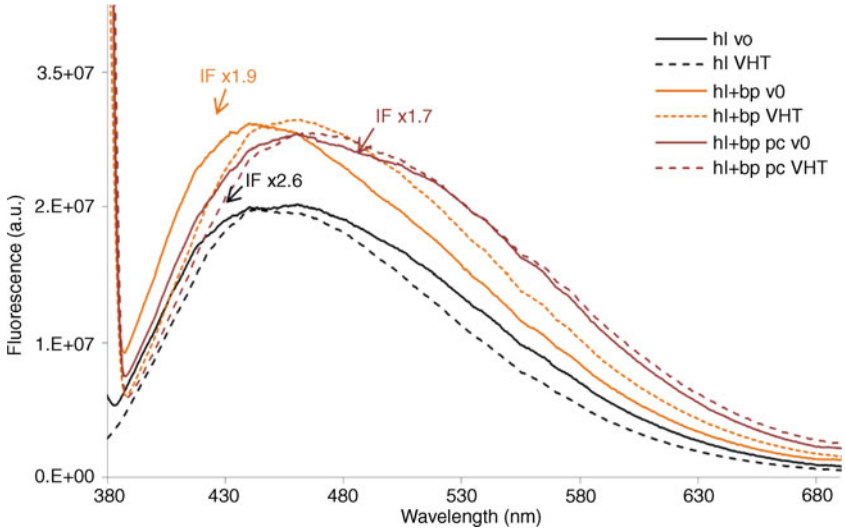

Fig. 7 Emission spectra of linseed oil and linseed oil+lead white, on a glass slide and on limestone, before and after hygro-thermal ageing (V_{HT}). Correction factors to normalized spectra are indicated (IF)

according to the time between the different irradiations (V_{Ir313}, V_{Ir296} and V_{Ir366} nanometres).

From the beginning to the first sample of linseed oil 313 nm irradiation and of the last one at 366 nm, it has lasted 1,200 h and the fluorescence intensity increased by an approximately 5 factor (Fig. 8). This result is in agreement with that obtained with the thermo-hygrometric ageing (2.6 for 720 h).

The extension towards the big wavelengths of the linseed oil+white lead spectrum (shift, 440 to 462 nm; so 22 nm after 720 h) can be explained by the faster contaminants oxidation which leads to a yellowing of the sample. In the case of linseed oil, the sample is less dry, the peroxides oxidation is not finished and no (or very few) reactions occur. That explains a spectral answer which varies with the proportion of peroxides and the formed radicals: no yellowing phenomenon.

The thermo-hygrometric ageing of linseed oil+lead white on calcareous support gives similar results: intensity increase and a very light shift of the spectrum, which are interesting for the comparison with the in situ measures (Fig. 7).

3. Gilding recreation according to ancient techniques

To make the link between the theoretical study and the in situ observations, ageing studies were carried out on gildings recreations (Table 1). The metal leaf was taken away from the zone corresponding to the analysis zone in order to show the mixtion layer.

After thermo-hygrometric ageing and UV-controlled ageing (313 nm), no significant shift of the maximum of fluorescence is observed. Only the fluorescence intensity increases slightly (Fig. 9). This result is in agreement with that obtained with the linseed oil+lead white on calcareous

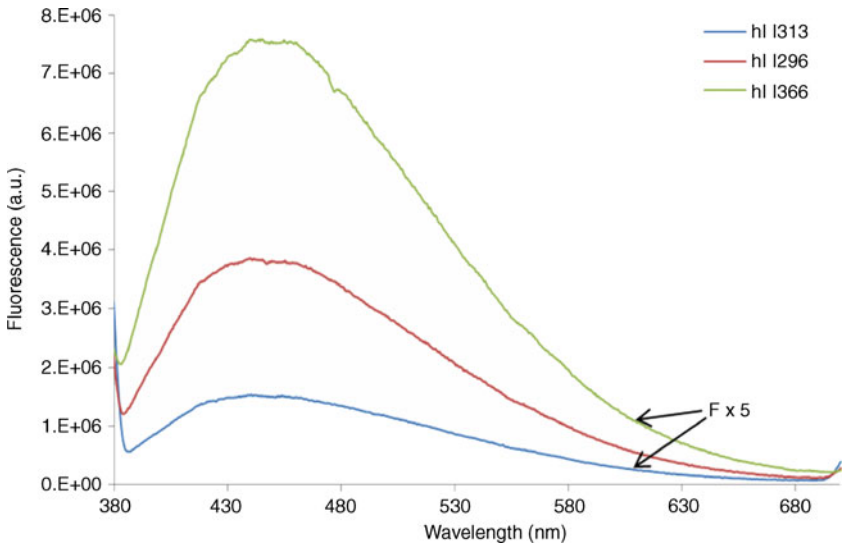

Fig. 8 Emission spectra of linseed oil before ageing to V_{Ir313}, V_{Ir296} and V_{Ir366}. Fluorescence intensity was multiply by 5 between the first sample analysed and the last one

support but also with those obtained for the irradiation under UV at 313 nm during 17 h.

By considering the age of samples (2 years) and the various undergone accelerated ageing, we can deduce that the metallic leaf plays a protective role against the degradation of the adhesive layer. Whatever the type of ageing, the maximal wavelength did not change (Fig. 9). It is in approximately at 454 nm. The weak fluorescence intensity before ageing can be explained by the fact that linseed oil and lead white, in the initial state, are not fluorescent.

The more the metallic leaf is incomplete, the more the mordant is going to degrade because of bad preservation conditions (desquamation due to the climatic variations, to bad weather, microorganisms and restorations) (Daniel and Mounier 2010). The organic binder deteriorates faster directly in the air contact and light, submitted to temperature variations and atmospheric pollution.

These results explain why the observation of these gildings recreations, under UV Wood lamp at 366 nm, does not show significative difference in fluorescence whatever the ageing type.

4. Sites studies

Observations under UV lamp permit to detect ancient gildings remains on 15 sites. Micro-samples have been realized on the fluorescent zones according to symbolic iconographic theme. In all case, analysis show the presence of metallic leaves applied according to the mixtion technique. To identify the family binder, we observe cross sections under UV light with a microscope and IRTF analysis have been carried out.

For example, in the Saint-Andre cathedral of Bordeaux, the UV lamp allowed to detect also gilding traces on the Virgin crown in the funeral paintings of Arnaud de Puylehaut. The fluorescence was light yellow, little intense. The sample analyses show that the crown was "gilded" with a silver leaf on a minium and linseed oil under-layer (Mounier et al. 2010c; Daniel and Mounier 2010).

In the Saint-Etienne cathedral of Cahors, gildings were discovered on the western portal. Tin and gold leaves are localized on floral motives, as fleur-de-lys (Czerniak et al. 2007), on haloes and music instruments. A sample has been taken out of a halo figure; it counts four layers. SEM/EDS, Raman spectrometry and Fourier transform infrared (FTIR) analysis allow to identify materials. On the wall, an orange layer composed of minium and red ochre was applied. Then, a white layer of lead white, calcite and a lipidic binder is put to receive a thickness layer of yellow ochre. Finally a gold leaf (1 μm) was deposited (Fig. 10a).

The observations of the cross sections under UV source coupled with a microscope show that the mordant layer gives a yellow fluorescence (Fig. 10b). According to the in situ observations with the Wood lamp, the yellow fluorescence given under UV light on microscope, and the results of analysis, the spectrometric study of linseed oil mixed to lead white also support all this results.

Experiments on spectrofluorimetric analysis have been carried out on real samples from different sites, but their small size (<1 mm) does not permit to obtain result for this preliminary study.

4 Discussion

This preliminary study is in agreement with the results presented in various papers. During the ageing of linseed oil, two phenomena took place simultaneously: formation of small compounds which absorb in the UV (max at 330 nm) and formation of compounds which absorb in the

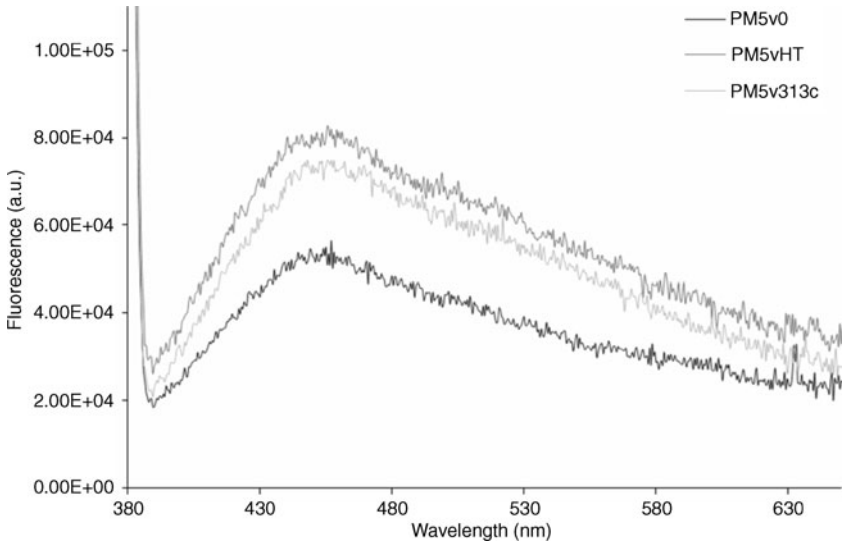

Fig. 9 Emission spectra of gildings recreations before and after hygro-thermal and UV 313c ageing (V_0, V_{HT} and V_{313c})

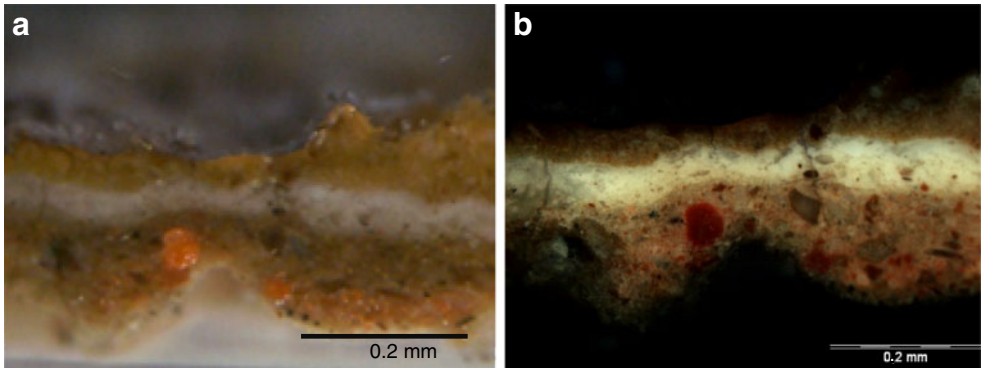

Fig. 10 **a** Cross section observed under microscope of a sample realized on a halo figure in the portal of the Cahors cathedral. From the wall to the surface: red ochre layer+minium, lead white+calcite+lipidic binder, yellow ochre and gold leaf. **b** Cross section observed under UV source coupled with a microscope of this sample. The mixtion layer composed of lead white+calcite+lipidic binder shows a yellow fluorescence

blue (λ>400 nm) and emit in the yellow range (Mallégol et al. 2001a). These phenomena can be reversed according to the oil degradation processes. Indeed, the action of the light on the ageing process of a siccative oil is complex. First of all, we notice that a linseed oil film submitted to light dries more quickly and turns yellow. However, we observed that a film exposed to light and then placed in the dark turns yellow, but becomes again colourless if it is again exposed to light (De la Rie 1982c). The same phenomenon has been observed on paintings, which darken when placing them in the dark and then appear to find their original tint when they are exposed to the light (Masschelein-Kleiner 1992).

At the same time, accelerated ageing was realized to study the yellowing. The yellowing is correlated to an increase of the absorbance of the oil in the range of 300–400 nm and an increase of the fluorescence intensity towards 500 nm. On the opposite, the bleaching which appears for a longer time exposure to light is accompanied with a decrease of the absorbance below 400 nm (Mallégol et al. 2001a). It is generally admitted that the yellowing is caused by the apparition of photo-unstable compounds, in particular combined polycetones, during the oxidation. A more recent hypothesis proposes that the oxidation of the impurities contained in oil can participate secondly to the yellowing (Mallégol et al. 2001a).

The fluorescence excitation spectra of the mixtion (lead white+linseed oil) confirm that the formed compounds are the same that for the linseed oil. That is due to the speed of the phenomenon: the film is thinner, more regular and dries more quickly.

Generally, "ageing", for an oil, is a succession of oxidation and auto-oxidation phenomena that can be described in several stages. First is about the phenomena of auto-oxidation which lead to the drying of the oil by cross-linking reactions (Lazzari and Chiantore 1999), which we call siccativation.

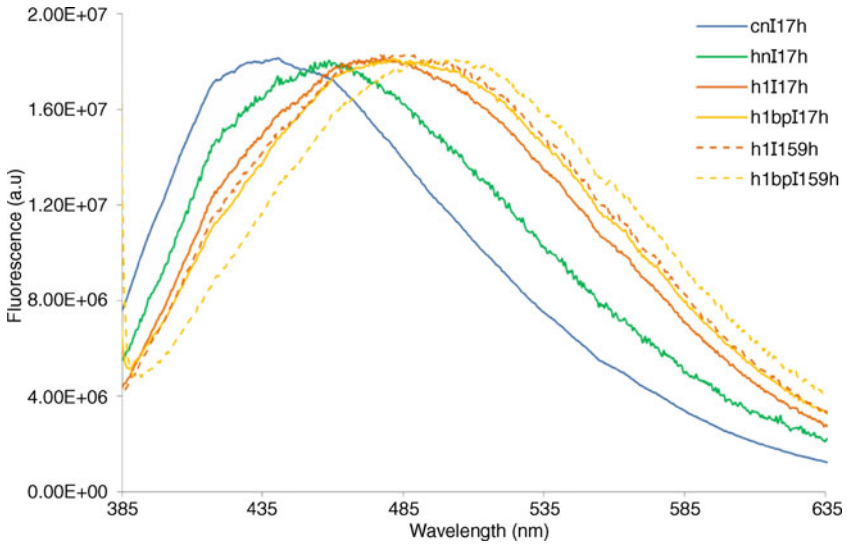

Fig. 11 Emission spectra after ageing at 366 nm, irradiation of nerve glue (T_{17}: λ_{max}=441 nm), walnut oil (T_{17}: λ_{max}=458 nm), linseed oil (T_{17}: λ_{max}=478 nm and T_{159}: λ_{max}=480 nm), linseed oil+lead white (T_{17}: λ_{max}=482 nm and T_{159}: λ_{max}=500 nm)

For the weak evolution of the spectral envelope of the samples aged on thermo-hygrometric conditions, it is necessary to keep in memory that before the ageing, samples were stored for 1 year in the natural light and at room temperature. Films not dried were subjected to the reversible phenomena of yellowing and bleaching according to the conditions of thermo-oxidation and photo-oxidation (Mallégol et al. 2001b). It explains the spectral answer, connected to these conditions, for the sample at T_0. The light gap of the spectral envelopes in the range 380–440 nm can be explained by the fact that in the dark, the photo-oxidation phenomena are non-existent. It is the thermo-oxidation phenomena that are facilitated and which lead to the decomposition of peroxides. This phenomenon is translated by a decrease of the absorbance towards 368 nm and a decrease of the fluorescence intensity in the range 380–440 nm (previous results and Mallégol et al. 2001b).

It was demonstrated that for temperatures ≤40°C, the oxidation of peroxides was in competition with another phenomenon connected to the kinetics of the decomposition of hydro-peroxides which gave radicals of low mobility. Consequently, the oxidation of contaminants is facilitated with regard to that of peroxides and leads to a yellowing of the sample. In the case of the addition of lead white, which accelerates the drying and consequently the decomposition of hydro-peroxides, the oxidation of contaminants is faster (Mallégol et al. 2001b).

Infrared analyses do not permit to show the degradation and oxidation phenomena of linseed oil on the recreated sample of mixtion in glass slide. However, FTIR/ATR is a good technique to identified binder family present in the real samples (lipidic binder), but it is a destructive method.

Spectrofluorimetry is an appreciable technique for this type of study which requires development to in situ analysis. Thereafter, we are purchasing an optical fibre coupled with a microscope on a spectrofluorimeter to study small samples. We are expecting a spectrofluorimeter system to be portable to avoid sampling and give directly in situ analysis.

5 Conclusions

The spectrofluorimetry is a suited technique to follow the evolution of binders during ageing and permits to verify characteristics of the linseed oil ageing.

This study allowed to show that 366 nm wavelength is effective for the in situ observation of oil binders used for the gildings techniques. The excitation at 366 nm proposes a correlation between the in situ observations and the laboratory study. The ageing of the linseed oil provokes a shift of the maximum fluorescence towards the higher wavelengths which is even more pronounced with lead white. The addition of this pigment accelerates the phenomenon and gives a brighter signal. The mixtion layer shows, under UV light coupled with microscope, a yellow fluorescence on various sites. The same study, led in parallel on a walnut oil and a nerve glue, shows that we can recognize the nature of the fluorescent organic binders, thanks to the in situ observed colour at 366 nm (Fig. 11), which goes to the same direction as the results obtained previously (Mounier et al. 2010b). After irradiation at 366 nm, nerve glue gives a blue fluorescence, walnut and linseed oil in the green-yellow and linseed oil+white lead towards the yellow, especially after a long irradiation time (159 h).

Obviously, the presence of fluorescence is not always associated to the presence of an ancient gilding. It is thus necessary to couple this observation with the localization of the fluorescence in the image and the iconographic programme because these metallic decorations are especially employed to heighten symbolically important zones of the image (haloes, stars, crowns, St. Peter's keys) and the observation of layers because their aspect is different from the mural paintings (thicker, fat, metallic tracks, black altered zones for silver or tin). By considering the case of the gilding, the presence of a fluorescence in a zone with strong symbolism may indicate the presence of a gilding (or of a light); the colour and the fluorescence intensity also inform about materials and, thus, about technique: if the fluorescence is blue-green, we are in the presence of a proteinic binder; if it is yellow, it is a lipidic binder. If it is yellow and very intense, we are certainly in the presence of a mixtion (lead white+oil).

References

Aze S (2005) Altérations chromatiques des pigments au plomb dans les œuvres du patrimoine, thèse de doctorat de l'Université d'Aix Marseille, 210 pages

Cennini C, XIV^{e}, réédité en (1991) Il libro dell'arte, Berger-Levrault, Paris, p.188-313

Czerniak V, Stouffs J-M, Tessariol M, Daniel F (2007) Le décor peint et la polychromie du portail occidental de la cathédrale Saint-Étienne de Cahors. Tome LXVII, Mémoires de la Société Archéologique du Midi de la France, pp 97–112

Daniel F, Mounier A (2010) Alteration of gildings on mediaeval mural paintings, Réunion intermédiaire de l'ICOM CC "Multidisciplinary conservation, a holistic view for historic interiors" http://www.icom-cc.org/54/document/alteration-of-gildings-on-mediaeval-mural-paintings/?id=797. Accessed 23–26 Mar 2010

De la Rie ER (1982a) Fluorescence of paint and varnish layers (part I). Stud Conserv 27:1–7

De la Rie ER (1982b) Fluorescence of paint and varnish layers (part II). Stud Conserv 27:65–69

De la Rie ER (1982c) Fluorescence of paint and varnish layers (part III). Stud Conserv 27:102–108

Karoui R, Kemps B, Bamelis F, De Ketelaere B, Merten K, Schoonheydt R, Decuypere E, De Baerdemaeker J (2006)

Development of a rapid method based on front-face fluorescence spectroscopy for the monitoring of egg freshness: 1-evolution of thick and thin egg albumens. Eur Food Res Technol 223:303–312

Larson L, Shin K, Zink J (1991) Photoluminescence spectroscopy of natural resins and organic binding media of paintings. J Am Inst Conserv 30(1):89–104

Lazzari M, Chiantore O (1999) Drying and oxidative degradation of linseed oil. Polym Degrad Stab 65:303–313

Mallégol J, Lemaire J, Gardette J-L (2001a) Yellowing of oil-based paints. Stud Conserv 46(2):121–131

Mallégol J, Gonon L, Lemaire J, Gardette J-L (2001b) Long-term behaviour of oil-based varnishes and paints. 4. Influence of film thickness on the photooxidation. Polym Degrad Stab 72:191–197

Masschelein-Kleiner L (1992) Liants, vernis et adhésifs anciens. Bruxelles, Institut Royal du Patrimoine Artistique, 3e éd. 123 p

Matteini P, Camaiti M, Agati G, Baldo MA, Muto S, Matteini M (2009) Discrimination of paintings binders subjected to photo-ageing by using microspectrofluorometry coupled with deconvolution analysis. J Cult Herit 10:198–205

Mounier A, Daniel F, Bechtel F (2010a) Gilding techniques in mural paintings: three examples in the Romanesque period in France. Proceedings of the 37th International Symposium of Archaeometry "Archeometry 2008", Siena, 12–16 May 2008 (in press)

Mounier A, Dayet L, Belin C, Daniel F (2010b) Etude de la fluorescence des liants employés dans les dorures sur peintures murales médiévales, Archéosciences–Revue d'archéométrie (in press)

Mounier A, Daniel F, Bechtel F (2010c) L'illusion de l'or–Imitation de dorures dans les peintures murales médiévales. Archéosciences–Revue d'archéométrie (in press)

Pastoureau M (1999) Le temps mis en couleurs: des couleurs liturgiques aux modes vestimentaires (XIIe–XIIIe siècles), Bibliothèque de l'école des Chartres, Vol. 157, N1, p.111-135

Stenberg C, Svensson M, Johansson M (2005) A study of the drying of linseed oils with different fatty acid patterns using FTIR-spectroscopy and chemiluminescence (CL). Ind Crops Prod 21:263–272

Théophile (Moine), XII^{e} s., réédité en (1996) *Essais sur divers arts*, publié par le Cte Charles de l'Escalopier, réédition Laget, Nogent Le Roi, pp 39–44

Thoury M (2006) Identification non-destructive des vernis des œuvres d'art par fluorescence UV. Thèse de doctorat, Université Pierre et Marie Curie Paris VI