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PII: S0026-265X(17)30842-1  
DOI: doi:[10.1016/j.microc.2018.03.032](https://doi.org/10.1016/j.microc.2018.03.032)  
Reference: MICROC 3105  
To appear in: *Microchemical Journal*  
Received date: 28 August 2017  
Revised date: 20 March 2018  
Accepted date: 23 March 2018

Please cite this article as: Alessia Artesani, Francesca Gherardi, Sara Mosca, Roberto Alberti, Austin Nevin, Lucia Toniolo, Gianluca Valentini, Daniela Comelli, On the photoluminescence changes induced by ageing processes on zinc white paints. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. *Microc*(2017), doi:[10.1016/j.microc.2018.03.032](https://doi.org/10.1016/j.microc.2018.03.032)

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## On the photoluminescence changes induced by ageing processes on zinc white paints

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### Abstract

Recent research is focusing on the study of interaction mechanisms between pigments and binder, as they are crucial for understanding paint ageing and conservation issues. In this work, we investigate these mechanisms and follow the changes induced by ageing on zinc white paint by employing Fourier Transform Infrared (FTIR) and Time-Resolved Photoluminescence (TRPL) spectroscopies. The two techniques, applied on thermally aged mock-up samples and on a 19<sup>th</sup> oil painting, provide complementary information on the effect of the binder on the ZnO pigment particles. The characterization of the infrared absorption spectra confirms the well-known tendency of the formation of amorphous metal carboxylates in zinc white paint following ageing. At the same time, the ageing of paint film produces significant changes in the photoluminescence emission from defect centres of ZnO. The emission that is mostly affected by the changes of the micro-environment is the blue band (430 nm) - associated with surface defects - whereas the green emission (530 nm) is stable. The results demonstrate that the evolution of the pigment-binder system has detectable consequences on the crystalline structure of the pigment particles and we speculate that the main cause of the modifications is the functionalization of the pigment particle surfaces. The possibility to follow crystal structure changes with time-resolved photoluminescence can thus support chemical studies by providing information about pigment-binder interactions, metal carboxylate formation and paint deterioration.

**Keywords.** zinc white; metal soap; thermal ageing; painting; Time resolved photoluminescence; FTIR

### 1. Introduction

Zinc white is a pigment made of ZnO and it was the most widely distributed white between the 1840s and the middle of the 20<sup>th</sup> C. when it was replaced by titanium white [1]. Following this, the pigment has been used mainly as an extender and filler in paints. The presence of zinc white has a major impact on the conservation of modern paintings, since the pigment is reactive to the formation of metal soaps [2][3][4]. The ageing of paint is a complex process that involves chemical reactions between pigments and binders and the photo-oxidative drying of the binding medium, as illustrate in the following.

Many studies have demonstrated that the ageing of binder alone can be simplified into two phases. The first phase is relatively short and stabilizes after 10-15 days (depending on binder), which corresponds to a touch-dry film [5][6]. In the second phase, the system is more stable, and slow processes take place which lead to the ageing of the film [6][7]. It is important to consider these two stages separately. The first phase implies a significant autoxidation process followed by polymerization of the network, which leads to the hardening of the film [7][8][9]. The presence of a metal-based pigment (such as zinc white) catalyses the cross-linking process and activates a series of other chemical reactions between the organic part of the binder and the metal compounds. One significant consequence of the interaction is the formation of metal carboxylates, which can be detected by Fourier Transform Infrared (FTIR) spectroscopy [8][10]. It has been shown that in the case of oil and metal-based pigments, the unbound fatty acids present inside the oleic binder bond to metal ions and, via a hopping mechanism, cause the migration of metal ions from the metal oxide to the binding medium where the metal ions attach to the polymer network and form metal carboxylates [11][12]. Another mechanism suggested to occur in paint material is the adsorption of the organic acids on the pigment particle surface [10][13]. Such a surface functionalization has not been experimentally demonstrated for paint materials, but it is widely observed between metal oxide surfaces and organic compounds [14][15]. Despite the lack of experimental evidence, the functionalization of metal oxide particle is highly plausible even in paint materials and in our previous study we supported this hypothesis [16]. In fact, by employing Time Resolved Photoluminescence (TRPL) spectroscopy, we detected a significant modification of the photoluminescence (PL) emission of the zinc white mixed with binder with respect to the pigment powder. These changes were not simply related to a superposition of the PL of zinc white and the fluorescence of the binding medium, but were ascribed to an intrinsic modification of the zinc oxide crystal structure. The results confirmed the strong effect of the drying binder on zinc white and opened up questions about the temporal evolution of such a system.

As previously mentioned, in addition to the important interaction in the first drying phase, in the second ageing stage, there is a progressive oxidation of the binding medium, that also involves the hydrolysis of ester bonds and cleavage of fatty acid chains

[6][7]. Despite some general considerations, the exact ageing mechanisms and their consequences on the metal-based pigment are, at present, not completely understood. In this work, we specifically investigate the consequences of ageing on zinc white paint. In order to provide a more complete view of the paint evolution, we analysed both thermally aged mock-up samples – made of a mixture of zinc white powder with three binders (drying oil, terpenoid resin and gum) – and an oil painting dated to the end of the 19th C. The chemical evolution and the photoluminescence with progressive ageing was evaluated for all samples, by FTIR and TRPL respectively. FTIR spectroscopy is sensitive to the formation of metal soap, which occurs in the binder medium, whereas TRPL spectroscopy provides information on the modifications induced in the ZnO crystal structure. The application of these two techniques on the selected samples thus gives complementary, but not disconnected, information regarding the interaction mechanisms in zinc white paint in the same samples.

## 2. Materials and Methods

**Sample preparation.** Paint mock-ups were prepared by mixing zinc white powder (46300, Kremer Pigmente GmbH & Co. KG, Aichstetten, Germany) with three different binders chosen as representative of different categories and typical of paint. Specifically, stand linseed oil (3320, Zecchi, Firenze, Italy) and chios mastic varnish in turpentine (3510, Zecchi, Firenze, Italy) were mixed with zinc white (1:1 in weight for each paint). A third paint was obtained by mixing 1 part in volume of zinc white, 1 part of gum arabic powder (2310, Zecchi, Firenze, Italy) and 2 parts of distilled water. Each painting material was homogeneously spread onto quartz discs (Corning(R) HPFS(R) 7980 fused silica) with thickness of about 0.1 mm. The samples were kept at room temperature (far from heat or light sources) for at least one week before the measurements. The naturally dried and unaged samples are referred as ‘pristine sample’ and their time of measurement is set equal to zero ( $t_0$ ). For thermal ageing, the samples were stored in an oven at 50°C for 20 days ( $t_1$ ) and 3 months ( $t_2$ ). The chosen temperature is moderate and guarantees an increase in the speed of polymerization process [6][7]. Following each step, Fourier Transform Infrared (FTIR) and Time-resolved photoluminescence (TRPL) spectroscopy were employed. It is worth noting that, since the zinc white mixed with gum arabic tends to crack, it was not possible to perform the test on this specific mock-up after 3 months and the results shown correspond to pristine and 20 days samples.

As a case study, a 19<sup>th</sup> C. oil painting entitle *Houses on the Estuary* (30 × 25 cm<sup>2</sup>) by an unknown artist was analysed (Figure 3). The only insight on the age of the painting is given by the back-stamp on the canvas. In particular, it is reported: “Winsor & Newton’s best artist’s canvas, Rathbone Place, London, W”. This suggests that the canvas is pre-1882, when the company name became Winsor & Newton Ltd [17]. The painting is in good condition, the canvas is made of linen and it is fixed on a wood frame with tacks on the corner and on the centre of each border. The study of the painting was obtained by combining the TRPL and micro-FTIR spectroscopy. The complexity of this case study required additional analyses to characterize the pictorial materials. Results from macro-X-ray fluorescence (XRF) mapping and micro-Raman spectroscopy are reported in the text and in the supplementary material.

**Time-resolved Photoluminescence (TRPL) spectroscopy.** The system is based on a Q-switching laser source (FTSS 355-50, Crylas GmbH, Berlin, Germany, pulse energy = 70  $\mu$ J, pulse duration = 1.0 ns, repetition rate = 100 Hz), emitting light pulses at 355 nm focused onto the sample with 1 mm spot-size. Additional details of the TRPL device are described in detail elsewhere [16] [18]. Here, the measurement and protocol adopted in this work are briefly reported. The measurements are based on the detection of a sequence of PL gated spectra at different delays with respect to laser pulses. In this work, the short-lived and the long-lived emission are detected by employing different gate widths. In this way, it is possible to separate the fluorescence from organic compounds and direct radiative recombination of pigment (short-living emission) from the photoluminescence emission related to defect states of the crystalline pigment (long-living emission). The short-lived emission was detected using a gate width of 5 ns and recording the emission decay kinetic for the first 50 ns following excitation and employing an exposure time of 0.2 s. The long-lived emission on the microsecond timescale is detected using a gate width of 1  $\mu$ s and recording the decay kinetic for 100  $\mu$ s following excitation, and exposition time of 5 s. The result is a TRPL dataset in which the rows represent the PL spectra recorded within temporal gates (quoted as gated spectra thereafter) and the columns represents the emission decay kinetic in spectral windows. The kinetic data were fitted to a multi-exponential decay model (with a maximum of three components) [19] using a nonlinear least square method. As synthetic parameter, the effective lifetime was then calculated as the average of the lifetimes weighted over the number of photons originating from each decay path [16] and the same parameter is applied for comparison purpose amongst different samples.

**Fourier Transform Infrared (FTIR) spectroscopy.** Micro samples from mock-ups and painted layers were collected and analysed by micro-Fourier Transform Infrared spectroscopy (FTIR), using a Nicolet 6700 spectrophotometer coupled with Nicolet Continuum FTIR microscope equipped with an MCT detector (acquired between 4000 and 600 cm<sup>-1</sup> with 128 acquisitions and 4 cm<sup>-1</sup> resolution) using a micro compression diamond cell accessory. The reported spectra represent the average of three measurements, baseline corrected using Omnic software. The FTIR spectra from stand linseed oil and mastic paints were normalized based on the intensity of the carbonyl C=O stretching vibration at approximately 1740 cm<sup>-1</sup>, to better highlight the metal carboxylate band absorption, as reported also in [8][12]. Spectra from gum arabic paints were normalized based on the intensity of C-O-C vibration at about 1050 cm<sup>-1</sup>.

### 3. Results

#### 3.1 Mock-up samples

The FTIR spectrum of each pristine sample ( $t_0$ ) corresponds to absorption bands of the binding medium, of the zinc carbonate and, in case of linseed oil and mastic, of amorphous zinc carboxylates and of zinc salts of resin acids, respectively (Figure 1). After zinc white pigment is mixed with the oil binder there is an increase in the absorption of the bands at about  $1580\text{ cm}^{-1}$  and at  $1420\text{ cm}^{-1}$  corresponding to the asymmetric and symmetric  $\text{COO}^-$  stretching, respectively (Figure 1a). The infrared absorption of these bands increases with natural ageing and is accelerated by thermal treatment [6][20]. This result is in accordance with the literature [8][12][21]. According to Hermans et al. [12], after pigment dissolution, zinc ions ( $\text{Zn}^{2+}$ ) diffuse into the oil network, where they interact and bind to carboxylate groups of the polymerized oil medium forming an amorphous carboxylate structure. A similar phenomenon occurs in resinous media, which are characterized by high concentrations of acid groups. The absorption spectrum of mastic resin is not expected to change after thermal treatment [22]. When instead it is mixed with zinc white, the carboxylic groups of terpenic acids easily reacts with the pigment producing zinc salts of resin acids, giving rise to the  $\nu$  stretching of  $\text{COO}^-$  (Figure 1b), which is similar to changes reported by others [23][24] [25]. A different behaviour is shown by the mock-up sample with gum arabic. FTIR measurements do not detect any differences between the absorption spectra obtained from gum arabic alone and when it is mixed with the pigment and after thermal ageing. After 20 days of thermal ageing, no amorphous zinc carboxylates are detected (Figure 1c), and FTIR analysis confirms the absence of detectable interactions between the glucuronic acids of gum arabic and the zinc oxide particles [26].

Time-Resolved Photoluminescence (TRPL) spectroscopy was performed on the mock-up samples. On the nanosecond timescale it is possible to detect both the photoluminescence emission from near-band-edge (NBE) recombination of ZnO at 380 nm and the fluorescence of the binder, centred at 500 nm. The thermal treatment does not provoke substantial changes in the shape and peak position of the typical narrow NBE emission with respect to zinc white in pristine samples for all the considered binders (Figure S1). The main effects on this luminescence signal following ageing are the increase of fluorescence emission from binders, particularly evident for linseed oil (Figure S1), and the decay kinetic of the NBE becomes slightly rapid (Figure S2).

At a delay of 500 ns following excitation, the NBE recombination and fluorescence from the organic fraction are completely absent and the detected PL emission is produced by electron-hole recombination from trap state (TS) levels of ZnO. This emission is the superposition of several intra-band transitions, which result in a broad spectrum. In previous work we showed that the typical photoluminescence emission of zinc white powder is modified by binding media [16]. Superimposed on the typical broad green emission centred at 530 nm (Green Luminescence, GL), microsecond TRPL analysis highlighted the presence of another distinct emission in the blue region peaked at 430 nm (Blue Luminescence, BL). The presence of this second peak is evident in all the mock-up samples and in case of gum arabic it is even more intense than the GL. The features and the decay kinetic of this BL band in pristine samples have been fully characterized [16].

The thermal treatment has important consequences on the intensity of TS emissions. First, it affects the relative intensity of the TS emission with respect to the NBE, halving the intensity of the former after three months of ageing. In Table 1 the variation of the integrated PL intensity of the NBE/GL ratio, normalized to the pristine case, is reported. The tendency of the TS intensity to decrease with respect to the NBE recombination is observed for all mock-up samples and the effect is particularly strong when the pigment is mixed with gum arabic. Another consequence of the thermal treatment is the decrease of the relative intensity of BL emission with respect to GL. This decrease is only minor after 20 days of exposure at  $50^\circ\text{C}$ , where the  $I(\text{BL})/I(\text{GL})$  ratio reduces of a factor around 15-20 % (Table 1). The BL/GL intensity variation is greater after three months of treatment, where the intensity ratio diminishes of a factor around 50 % with respect to the pristine sample (Table 1). The superposition of different PL emission bands associated with different trap state levels is highlighted by the changes in the relative intensity after thermal ageing, which causes an apparent red-shift of the GL peak, as noticeable from Figure 2. Despite such important intensity effects, the decay kinetics of the mock-up samples are minimally affected by the thermal treatment. The parameters resulting from the exponential fitting of the decay kinetic are listed in supplementary material. Here, we report only the average lifetime values. The average effective lifetime for the BL emission is  $\tau_{\text{eff}} = 4.9\ \mu\text{s}$  ( $\sigma = \pm 0.2\ \mu\text{s}$ ), independent of binders and thermal ageing (Table S1). The GL lifetime of zinc white mixed with linseed oil or mastic does not change after thermal treatment and the results obtained for the two binders are equal to  $\tau_{\text{eff}} = 4.4\ \mu\text{s}$  ( $\sigma = \pm 0.2\ \mu\text{s}$ ), as shown in Table S2. The average value obtained for zinc white mixed with gum arabic is longer (as already reported in [16]),  $\tau_{\text{eff}} = 5.8\ \text{s}$  ( $\sigma = \pm 0.5\ \mu\text{s}$ ), but again not significantly altered following thermal ageing (Table S2).

#### 3.2 Case study: 19th C. oil painting

Preliminary measurements were carried to identify the main pigments in the oil painting that is characterized by the presence of different pigments. XRF reveals a high concentration of Zn in the white areas: the sky, the white clouds on the left, the white chimney of the central house and also the water (in lower concentration) (Figure S4, S5 and S6). Micro-Raman spectroscopy on a painting cross-section clarifies the stratigraphy (Figure S3): calcium carbonate and lead white were applied as primers on the canvas. Barium sulphate is detected by micro-Raman as a component of the white paint layer in mixture with Zn and the presence of Ba is confirmed by XRF mapping (Figure S3). Barium sulphate is expected in commercial zinc white pigment since it was usually added as a lightening agent in tube paints [1]. Micro-FTIR spectroscopy was carried out on the oil painting by collecting micro

samples from the painting surface. Six points were analysed: one point of the grey cloud (point P1), two points of the white chimney of the central house (point P2 and P3), and three points of the white cloud in the centre/right areas (point P4, P5 and P6), as reported in Figure 3. FTIR spectroscopy identifies the presence of a drying oil as the binder (possibly linseed oil) used to mix the pigments and a ketone resin as top protective layer (Figure S7) [27]. This synthetic varnish suggests a recent application on the painting since this resin was commercially produced for painting conservation by the end of the 1960s [28]. In addition, FTIR spectroscopy confirms the presence of lead carbonate and barium sulphate, as shown in Figure 4a for P6 and reported in the supplementary material (Figure S7). In the FTIR spectra, the broad absorption at 1500-1600  $\text{cm}^{-1}$  suggests the formation of metal soaps as a result of interactions between the pigment and the organic binder. As shown in the inset (Figure 4b), the spectra are characterized by the carbonyl band (1738  $\text{cm}^{-1}$ ) of the esters of the oil binder (fixed to 1 for the normalization) and by a second band at shorter wavenumber (around 1709  $\text{cm}^{-1}$ ) with different intensities. The latter band can be attributed to both residues of ketone resin in the micro-samples collected from the painting and the carbonyl group of fatty acids. The most interesting features is the band centred at around 1580  $\text{cm}^{-1}$  and associated with amorphous metal carboxylates COO-Zn. This signal can be observed in all analysed samples and its intensity is much higher compared to the absorption from the carbonyl peak (by a factor of 2 or 3). Moreover, despite slight changes in the shape and intensity of the band at 1580  $\text{cm}^{-1}$ , it is always possible to detect a peak at 1536  $\text{cm}^{-1}$  that perfectly matches the zinc palmitate/stearate signal (typical spectrum reported in Figure 4b) [29]. Infrared spectra with similar features are also reported in literature for other naturally aged oil paintings [2][10].

TRPL spectroscopy was performed on points close to the micro-sampling area. For all selected points at nanosecond time-scale the detected PL emission is the one typical of zinc oxide NBE emission, with a peak at 380 nm (see supplementary material). At the microsecond time-scale the broad emission centred at 530 nm is detected. The decay kinetic analysis confirms an emission with a lifetime compatible with the well-known zinc oxide green emission ( $\tau_{\text{eff}} = 4.8 \mu\text{s}$  ( $\sigma = \pm 0.4 \mu\text{s}$ )). No BL emission was detected in the oil painting. Instead in the wavelength range 400-430 nm the photoluminescence emission is quite weak, preventing analysis of decay kinetics (Figure 5a). The comparison of the two-dimensional TRPL dataset provides a better comprehension of the differences between the PL emission from the painting (point P6) and the one obtained from the pristine mock-up sample made of zinc white mixed with linseed oil (Figure 5b). The overall shape is modified with the absence of the BL band, while a similar decay kinetic for the GL emission can be recognized. The complete photoluminescence spectra and lifetime analyses are reported in the Supplementary Material (Table S3 and Figure S8). We finally exclude the possibility of artefacts in the photoluminescence emission from trap states due to absorption by ketone resin. In fact, this varnish, as well as other resins, has a high absorption in the UV region (250-300 nm) and a complete transparency in the visible region [27]. The absence of a microsecond PL emission from the carboxylate was demonstrated in previous work [16].

#### 4. Discussion

In the present research, the synergic use of FTIR and TRPL spectroscopy reveals different aspects of the pigment-binder interaction and the temporal evolution of zinc white paint, which rapidly occurs upon ageing. FTIR spectroscopy is suitable to describe the formation and the evolution of metal carboxylates in different binders, while TRPL spectroscopy probes the modifications induced to the micro-environment of ZnO.

In agreement with literature [10][11][12], FTIR results confirm the chemical evolution of oleic and resinous paint - with amorphous zinc carboxylates formation - whereas these reaction products are not formed in the zinc white paint mixed with gum arabic. The detection of infrared bands from zinc carboxylate is suggested to be the evident consequence of the migration of  $\text{Zn}^{2+}$  ions from ZnO to the binding medium via a fatty acid hopping mechanism [12]. The phenomenon is dominant in the first drying phase, while during ageing it decreases, because it is affected by the mobility of the medium [30] and this explains the lack of significant increase of this infrared absorption band after thermal ageing. It is worth stressing that the thermal ageing can reproduce only in part the evolution of metal carboxylates of naturally aged paint material that generally corresponds to the enhancement of the broad band at 1580  $\text{cm}^{-1}$  and the formation of crystalline metal soaps, as found in the oil painting samples.

In contrast, ageing has a significant effect on the photoluminescence signal from trap state levels because of changes in the ZnO micro-environment. Generally, PL analysis conducted on zinc white paint shows that in touch-dry and unaged samples, the mixing with binder causes an increase of the TS intensity with respect to the zinc white alone [16], while with ageing, the trend is inverted and the intensity from TS drops. More interestingly, there is a change in the relative intensity of the BL with respect to the GL emission. In mock-up samples, under controlled thermal ageing, the BL/GL intensity ratio decreases and the trend suggests that after 7 months of soft thermal treatment ( $T=50^\circ\text{C}$  in dark), the BL emission should completely disappear. This tendency seems to be confirmed by the analysis of the 100-year-old oil painting, although in this case the authors cannot prove the presence of BL band in the original zinc white pigment. Overall, the case study confirms the presence of the broad GL emission in aged paint sample.

The optical behaviour of zinc white paint requires further discussion. It is worth stressing that PL emissions cannot be assigned to a single cause. In order to consider all the aspects related to this complex system, in the following, we discuss the results of this work in combination with previous published literature, indicating a speculative scheme to explain the paint ageing behaviour.

i) We observe that the GL emission shape and decay kinetic are independent of the ageing of samples. This band is characteristic of ZnO, present in both bulk materials and nanoparticles, and it arises from the superposition of several radiative recombinations

associated with different types of intrinsic defects. Despite extensive literature on this emission, there is still no consensus on its origin. Recent studies assign a strong contribution to the GL emission with the transition from shallow donor to the  $\epsilon(-/2-)$  state of Zn-vacancy at 0.87 eV above the valence band [31][32]. Therefore in this context, the migration of  $Zn^{2+}$  ions should have an effect on Zn-vacancies defects and indeed in previous work, we reported a notable variation in the GL decay kinetic with respect to the pigment powder [16]. Further ageing does not cause any additional change to the emission, since the migration of zinc ions is expected to occur mainly in the first drying phase of the paint film. The GL emission can thus be considered an additional fingerprint, together with narrow NBE emission, for detecting the presence of zinc white in oil paintings.

ii) The photoluminescence behaviour of the BL band suggests a dependence of this emission on the surface structure of ZnO that is subject to functionalization. In fact, it is known that ZnO has a high surface reactivity and is active to surface adsorption with many compounds, including carboxyl and hydroxyl groups typically present in binding media. When the metal oxide particle is exposed to these groups, the latter are electronically attracted to the oxide and surface adsorption takes place [14][33][34]. The general process has been extensively studied for nanocomposite applications because this property mainly depends on the surface volume ratio [14][35][36]. It has been proposed that the same process occurs between zinc white pigments and an organic binder [10][11][12] and the present research strongly supports the surface functionalization hypothesis. We speculate that the BL emission is associated with surface defects and that the adsorption of polar molecules on the ZnO surface influences its intensity due to local structural changes.

In order to sustain this hypothesis, we finally test the effect of mixing zinc white with two different solvents, a monocyclic saturated hydrocarbon (cyclohexane) and distilled water. Both solvents are free of carboxyl and organic hydroxyl groups, while they present different characteristics: water is a polar molecule and thus subjected to adsorption, as studied and reported in [37][38][39], whereas cyclohexane is a non-polar organic solvent. To avoid any evaporation, zinc white powder has been mixed with the two solvents in quartz cuvettes (precision cells QS 1 mm, Hellma). Figure 6 shows the results of the photoluminescence signal of zinc white (in the cuvette) and mixed with cyclohexane (Figure 6a) and water (Figure 6b). The result of this test clearly shows that in cyclohexane the relative intensity emission of BL/GL of zinc oxide is not modified, while a small but still significant increase of the BL emission is immediately detectable when ZnO is mixed with water, suggesting that surface functionalization has consequences on the BL emission properties of the material. It is noted that similar PL features have been reported by others on novel functional nanomaterials, highlighting the presence of a blue band (2.9 eV – 430 nm) when a polymer is deposited onto ZnO, without clarifying its possible origin [40][41][42]. The determination of the exact origin of the BL band is not straightforward and would require the identification of the nature of crystal defects in complex systems, which could include hard X-ray photoelectron spectroscopy (HAXPES) [43]. For this reason, other studies are needed to fully clarify the origin of the BL band.

## 5. Conclusion

In this work, the application of FTIR and TRPL spectroscopies provides complementary and new data on the complex phenomena involved in the pigment-binder interaction process. The characterization of the infrared absorption spectra of the paint films confirms the well-known tendency of amorphous metal carboxylate formation in zinc white paint, while photoluminescence offers new data related to the interactions of binder with the ZnO pigment particles. The interaction between a metal-pigment and binder, which represents a metal oxide-organic matrix system, produces significant changes in the emissions from trap state levels detectable with photoluminescence. The intensity of the blue emission band is sensitive to ageing, indicating that there is an evolution in the pigment-binder reaction, with consequences on the crystalline structure of the pigment particles. We speculate that the main cause of these modifications is the adsorption of carboxyl and hydroxyl groups, present in binding media usually employed in oil paintings, which are highly reactive and form bonds on the pigment particle surfaces. On the contrary, the broad green emission that is typically detectable in zinc white paint is stable and present in the pigment as powder and also in a 19<sup>th</sup> C. painting. We ascribe the latter band to recombination via deep trap states induced by Zn-vacancy defects, which are additionally affected by the  $Zn^{2+}$  migration phenomenon, associated with zinc carboxylate formation. The possibility to detect small crystal structure changes with methods based on luminescence opens up applications in future studies. This approach could in fact offer complementary information to future chemical studies on pigment-binder interactions, metal carboxylate formation and paint deterioration.

**Acknowledgment.** Research was partially funded by the Italian Ministry of Education, Universities and Research within the framework of the JPI Cultural Heritage-JHEP Pilot call through the Lead ART project 'Induced decay and ageing mechanisms in painting: focus on the interactions between lead and zinc white and organic material'.

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**Table 1** – Variation in intensity of the PL emissions with thermal aging in mock-up samples. On the left: ratio of the integrated PL intensity of the NBE (370-410 nm) and GL (510-550 nm). On the right: ratio of the integrated PL intensity of the BL (410-450 nm) and the GL (510-550 nm) emissions from trap states.

Zinc white mixed with							
I(NBE)/I(GL)	Linseed Oil	Mastic	Gum Arabic	I(BL)/I(GL)	Linseed Oil	Mastic	Gum Arabic
Pristine ( $t_0$ )	1	1	1	Pristine ( $t_0$ )	0.5	0.5	0.9
20 days aged ( $t_1$ )	1.1	2.0	4.2	20 days aged ( $t_1$ )	0.4 (↓-20%)	0.4 (↓-20%)	0.6 (↓-30%)
3 months aged ( $t_2$ )	1.4	3.1	-	3 months aged ( $t_2$ )	0.2 (↓-60%)	0.2 (↓-60%)	-

## Highlights

- Time resolved photoluminescence spectroscopy to study crystal defects in zinc white;
- Characterization of photoluminescence changes in zinc white paint;
- Study of thermal and natural ageing;

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**Figure 1** - FTIR spectra of mock-up samples after thermal ageing (unaged -  $t_0$ , 20 days -  $t_1$ , 3 months -  $t_2$ ). The zinc white is mixed with (a) linseed oil (zwlso), (b) mastic resin (zwm) and (c) gum arabic (zwga). The band at 1580 and 1420  $\text{cm}^{-1}$  are associated with the amorphous zinc carboxylate formation that occur only in zwlso and zwm.

**Figure 2** - TRPL gated spectra (delay: 500 ns, gate window: 10  $\mu\text{s}$ ) of pristine samples ( $t_0$ , black line), after 20 days ( $t_1$ , grey line) and 3 months ( $t_2$ , light grey line) of thermal ageing. Specifically, zinc white is mixed with (a) linseed oil (zwlso), (b) mastic resin (zwm) and (c) gum arabic (zwga). All spectra are normalized at the GL peak.

**Figure 3** - *Houses on the Estuary*, Unknown artist. Oil painting. Black numbers indicate the spots analysed by TRPL and micro-FTIR spectroscopy.

**Figure 4** - (a) micro-FTIR spectra from the painting in the area with white cloud. The recognized component are highlighted in the figure (zinc stearate, ketone resin, lead white, barium white and linseed oil). (b) micro-FTIR spectra from micro samples collected from the painting in the area with white and grey clouds and the house chimney (P1-P6) and spectrum of zinc stearate/palmitate.

**Figure 5** - (a) Example of gated spectrum (delay: 500 ns, gate window: 10  $\mu\text{s}$ ) of TS emission from the oil painting (zinc white and drying oil) compared with the TS emission from zinc white and linseed oil mixture mock-up sample (zwlso). (b) The complete two-dimensional TRPL datasets, taken as a function of emission wavelength and delay time of gating detection respect to laser excitation.

**Figure 6** - TRPL gated spectra (delay: 500 ns, gate window: 10  $\mu\text{s}$ ) of zinc white powder (black line) and zinc white powder mixed with (a) cyclohexane (grey line) and (b) distilled water (grey line). All spectra are normalized at the GL peak.

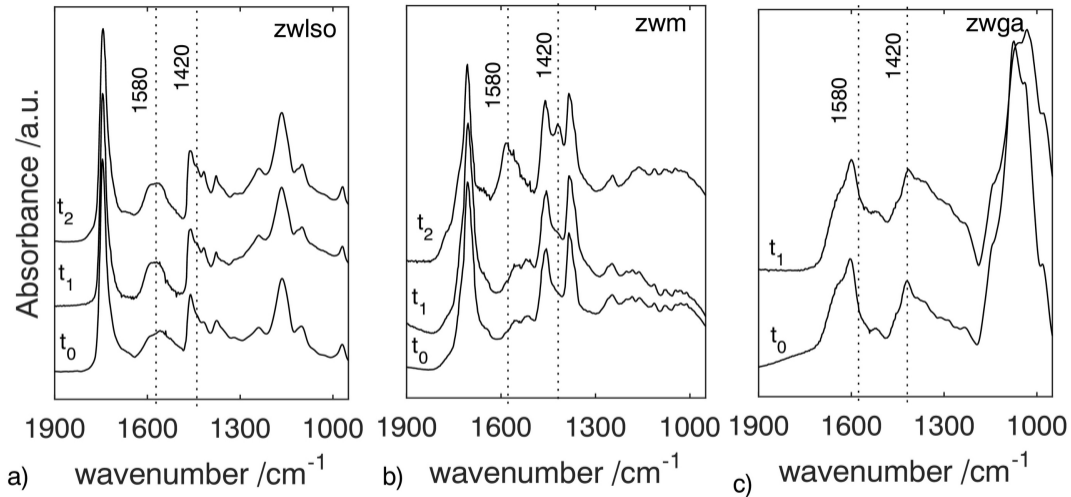


Figure 1

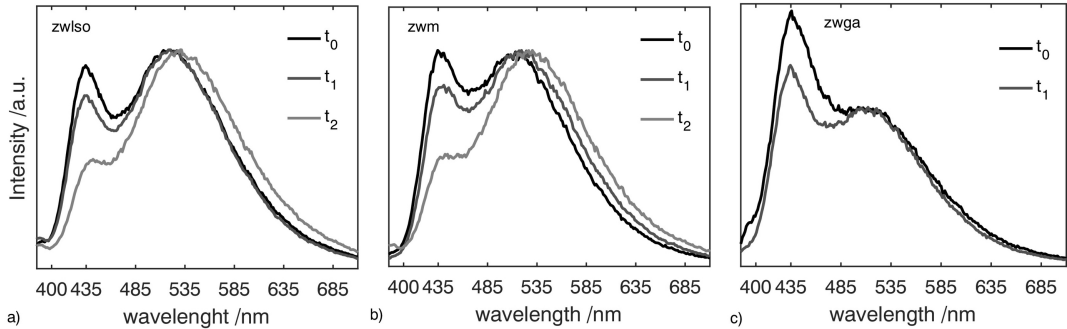


Figure 2



Figure 3

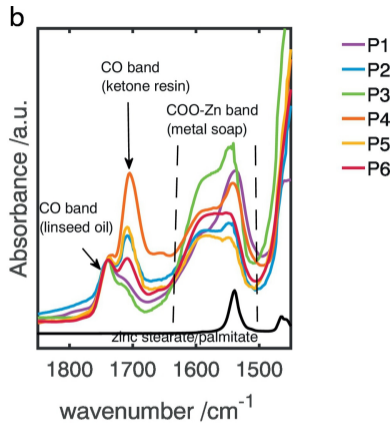
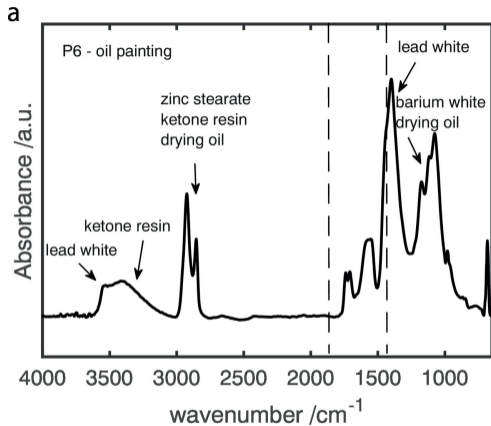


Figure 4

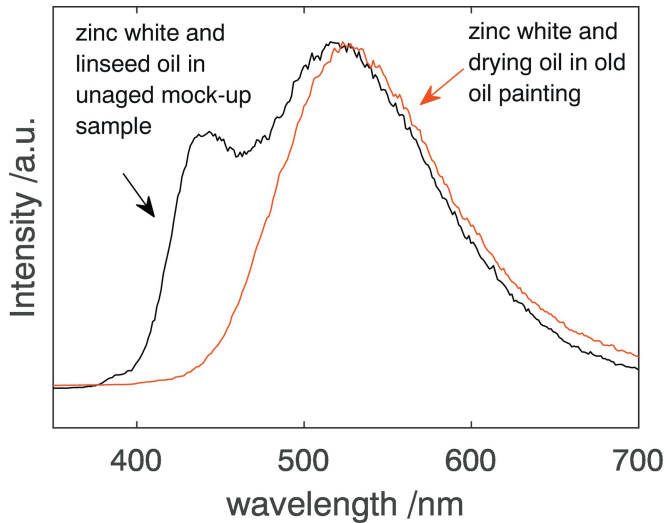
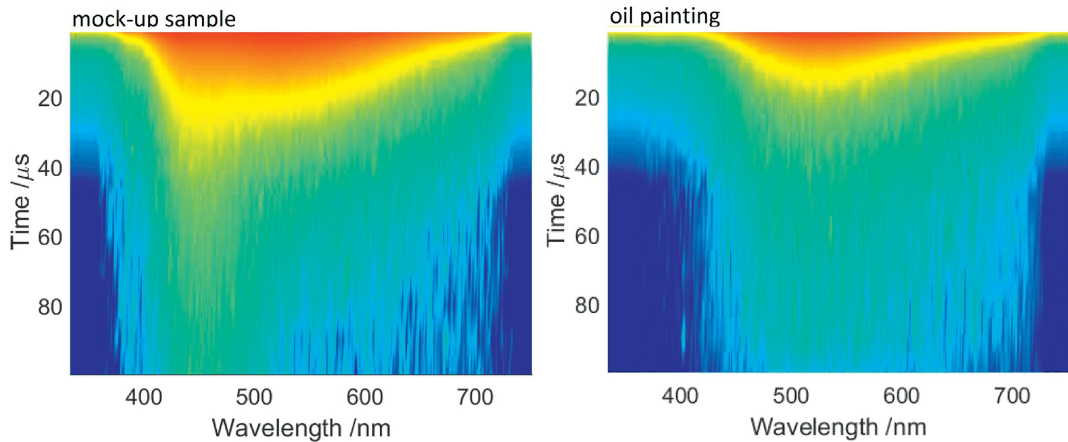
**a****b**

Figure 5



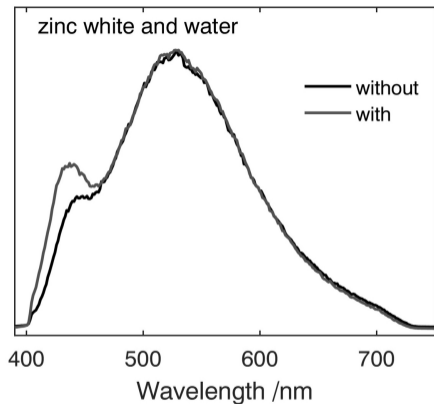
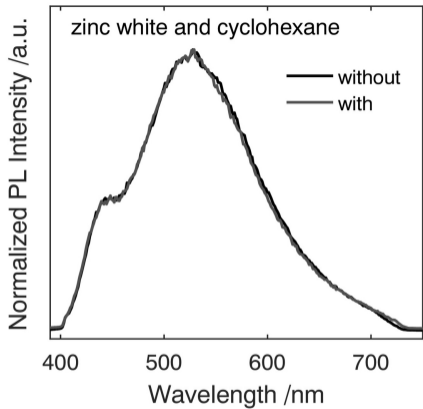


Figure 6