

The role of zinc white pigment on the degradation of shellac resin in artworks



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ABSTRACT

The stability and degradation behaviour of natural resins have been investigated by many authors for their important role in conservation chemistry but resin compositions and related degradation issues are not completely understood. In particular, shellac and its interaction with conservation materials during the ageing processes is still almost uninvestigated. In this work, some results of an extensive investigation on stability under thermal and photo-oxidative ageing of natural materials employed in the field of artistic production and artworks conservation are presented, and in particular, the ageing behaviour of shellac in presence of zinc white (ZnO) is described. This work underlines the importance of natural resin/pigment interactions from the point of view of the conservation of paintings since their decaying paths may be dramatically affected. During the photo-oxidative ageing of zinc white and shellac mixtures, the formation of zinc oxalate has been also detected. The formation of oxalates and the different degradation products from natural resins in presence of pigments are of particular interest considering the way the different degradation processes (double bond formation, ester formation, hydrolysis and polymerization) and the new chemical species (oxalates, metal soaps) can affect the removability of layers and, more generally, the cleaning processes, modifying in many cases the boundary between painting and varnish layers, and the aesthetical aspects of the work surfaces.

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1. Introduction

Natural resins are complex mixtures of isoprenic structures (terpenes) and sometimes, such as in the case of shellac, a polymeric fraction could be present. Natural resins are commonly and widely employed in the Cultural Heritage field and in conservation as finishing layers or varnishes, for their appreciated optical and preservative properties. In many cases they have been used mixed with drying oils in order to obtain oleo-resinous binders with particular aesthetical properties, or else pure as binders in retouching paintings. In all these applications the resins come in contact with pigments by direct mixing or by interaction with the underneath painting layer often impoverished by natural binder migration.¹ Moreover, the usual conservation treatments for varnish substitution place fresh natural resin in contact with painting pigments

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¹ An imperfect preparation layer or repainting on a previous partly decayed painting layer can let the fresh binder penetrate leaving a painting leaner in binder.

increasingly exposed as consequence of previous solvent-based cleanings. Shellac, in particular, is the most used and appreciated finishing in historical wooden furniture [1,2] but it has been also used by many artists as painting varnish mixed with other softer resins [3]. Chemically, shellac is a complex mixture of mono and polyesters coming from hydroxy aliphatic acids (mostly aleuritic acid) and many different cyclic sesquiterpene acids [4–10]. It also contains variable amounts of wax (5–6%) and dyestuff (0.5–1%). The stability and degradation behaviour of natural resins have been investigated by many authors for their important role in the conservation chemistry but compositions and related degradation issues are not completely understood. In particular, shellac and its interaction with conservation materials during the ageing processes is almost uninvestigated.

In this work, some results of an extensive investigation on stability of natural materials employed in the field of artistic production and artworks conservation will be presented, and, particularly, the ageing behaviour of shellac in presence of zinc white (ZnO) will be described. It is well known that the presence of pigment influences dramatically the response of polymers and resins towards thermal and photo-oxidative stresses [11].

The correlation among the different simulated artificial ageings and the natural ageing which occurred to the objects is a critical point. We studied, separately, the effect of a 60 °C and 300 °C thermal ageing and a solar simulated one trying to evaluate the decay behaviours related to the different ageing factors (temperature and UV–VIS radiation). The aim was, supported by results, conservators observations and bibliographic references, to find detectable parameters and decay patterns that can help in the study naturally aged works of art.

Mixtures of a large number of painting binders and varnishes (drying oil, natural resins, proteinaceous binders) with the most common historical pigment, in different ageing conditions (solar simulated, thermal at 60 °C and thermal at 300 °C), have been studied in order to evaluate the influence of inorganic pigments in the degradation processes of organic materials such as the formation of metal carboxylates, as described in literature [12–15].

ZnO is a widely diffused white pigment (zinc white or Chinese white) introduced in the second half of the 18th century [16]; it can be easily found also as additive or as co-pigment such in the case of titanium white in order to modify the film-forming properties in particular in presence of drying oils: commercial titanium whites often contain a percentage of ZnO in order to enhance the stiffness of the painting layers [16]. Zinc white is a very active pigment and its ability to easily react with free carboxylic acids present in the oil binding media to form zinc soaps is well assessed [15,16]. Nevertheless, the presence of zinc carboxylates on an easel painting cannot always be associated with a degradation process since commercial formulation may contain zinc stearate as an additive.

To investigate the different ageing and oxidative behaviours of shellac in the presence of zinc oxide FTIR is a particularly suitable technique because of the minimal interference coming from zinc white that does not present significant absorption signals in most of the medium infrared spectral range, with the metal/oxygen band raising only below 600 cm^{-1} .

During the photo-oxidative ageing of zinc white and shellac mixtures, the formation of zinc oxalate has been also detected. This finding was unexpected and clearly indicates that oxidation of natural resin layers can be a suitable source of oxalate patina.

The most common way to find oxalates in the field of Cultural Heritage is on carbonatic stone materials exposed outdoor and on mural paintings (whewellite and weddellite, the monohydrated and dihydrated calcium oxalate form respectively) [17–20] as thin orange yellowish patina. The origin of this decaying process is still unknown even if some hypotheses have been proposed all related to the identification of the oxalic acid source (bioweathering, strong oxidation of organic compounds or the environment itself) [21–25].

All these proposals are mostly suitable and applicable in the case of outdoor exposed artifact; however, calcium and other oxalates are found even in the case of easel paintings or other polychrome artworks reasonably never exposed to outdoor environment or to strong oxidative agents and without any detectable microbiological presence [26–29].

The possibility of formation of oxalates by means of strong oxidative conditions has been experimented only for organic binders, such as linseed oil and egg, on calcium carbonate substrate [30] but never, in our knowledge, in presence of natural resins or other cations and, most important thing, never in weak (xenon lamp filtered for wavelengths below 300 nm) oxidative conditions.

The formation of zinc oxalates has been assessed by means of FTIR transmission measurements and X-ray diffraction on aged laboratory mockups and it has been corroborated with findings on a painting by the futurist artist Giacomo Balla where the painter had used an oleoresinous binder [31].

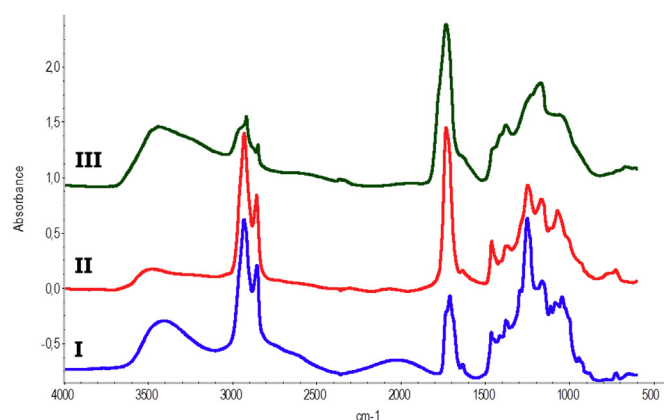


Fig. 1. Spectra of shellac before (spectrum I), after thermal at 300 °C (spectrum II) and solar simulated (spectrum III) ageing, respectively.

The formation of oxalates and the different degradation products from natural resins in presence of pigments is of particular interest considering the way that the different degradation processes (double bond formation, ester formation and polymerisation) and the formation of new chemical species (oxalates, metal soaps, etc) can affect the removability and the cleaning processes, modifying in many cases the boundary between painting layer and varnish, and the aesthetical aspects of the work surfaces.

2. Materials and methods

Shellac and zinc white, a pure zinc oxide pigment, were supplied by Kremer GmbH & Co. Methanol (Aldrich) solutions of Shellac and of the mixture shellac/zinc white (1:1 in weight) have been applied by brush on polished silicon wafers.

Four sets of samples have been aged in the following ways:

- 2 years at room condition with no direct sunlight exposition
- 1000 h in oven at 60 °C
- 3 min at 300 °C on a heating plate
- 1000 h of simulated solar irradiation in an UV solar box Hereus Suntest CPS equipped with a filtered (Coated quartz glass simulating a 3 mm window glass, cutting $\lambda < 300$ nm) Xenon lamp and with an average irradiation of 750 W/m^2 and an internal temperature of about 50 °C.

FT-IR transmission spectra (64 scans) recorded using a diamond anvil cell (High Pressure Diamond Optics, Inc.) were obtained on a Bruker Vertex 70 spectrophotometer coupled with a Bruker Hyperion 3000 IR microscope equipped with an MCT detector (Infrared Associates Inc.), working in the spectral range from 4000 to 600 cm^{-1} with an average spectral resolution of 4 cm^{-1} .

X-ray diffractometry analyses have been carried out on a Panalytical X'Pert PRO X-ray powder diffractometer (XRPD) equipped with an X'Celeator detector PW3015/20 and diffraction patterns have been collected from 5° to 60° 2θ , scan speed 0.21° s^{-1} , with a $\text{CuK}\alpha$ -radiation source, working conditions 40 kV and 40 mA. Powdered samples have been spread on an amorphous silicon holder and then analyzed.

3. Results and discussion

The composition and degradation behaviour of pure shellac under the applied ageing conditions is described and discussed, in the following, starting from concordant results reported in the

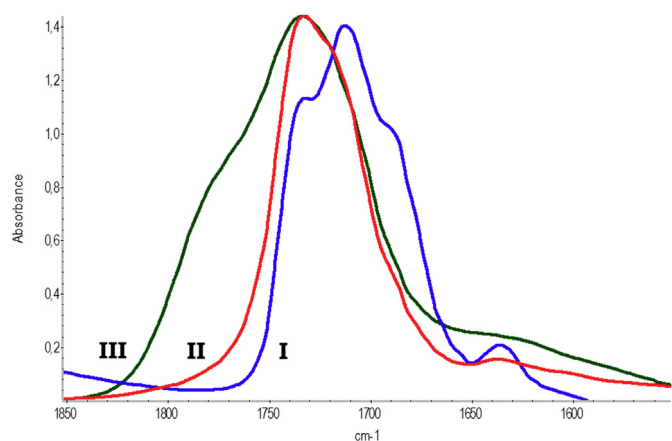


Fig. 2. Carbonyl bands detail. Spectra of shellac before (spectrum I), after thermal at 300 °C (spectrum II) and solar simulated (spectrum III) ageing, respectively.

literature [4,6,7,10,32–38]. The infrared spectrum of shellac is shown in Fig. 1 (spectrum I) where it is compared with the spectra of the same resin after photo-oxidative (1000 h) and after thermal (3 min at 300 °C) ageing.

The carbonyl absorptions from 1650 to 1800 cm^{-1} , the OH related broad band around 3400 cm^{-1} and the band at 1252 cm^{-1} are clearly affected by the different ageings.

The unaged shellac shows a triple carbonyl stretching signal (Fig. 2, spectrum I), with maxima at 1688, 1711 and 1734 cm^{-1} attributable to the alicyclic sesquiterpene free acids, the aliphatic hydroxy acids (mostly aleuritic acid) and the complex mixture of mono and polyesters respectively.

After the strong (3 min at 300 °C) thermal ageing (Fig. 1, spectrum II) there is a rising of the esteric signal while the signal of acids decreases, in particular the one at 1688 cm^{-1} seems to disappear (Fig. 2, spectrum II). This behaviour is consistent with the decrease of the OH bands at 1252 cm^{-1} and around 3400 cm^{-1} : the high temperature promotes the inter-esterification of acid function with the OH groups of aleuritic acid and similar hydroxy acids, and eventually with remains of alcohol used as solvent.

On the other hand the thermal ageing at 60 °C does not affect significantly the shellac: the spectrum (not here reported) is very similar to the unaged one.

After the photo-oxidative ageing, a carbonyl band trend similar to the thermal aged (300 °C) one is observed but the important shoulder at 1770 cm^{-1} suggests that also an intra-molecular

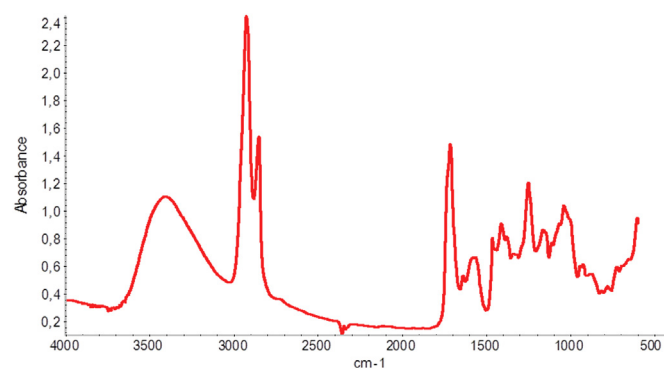


Fig. 4. Spectrum of shellac and zinc white mixture aged 2 years at room conditions.

esterification has taken place with the formation of lactone compounds (Fig. 2, spectrum III).

Chromatographic studies suggest that the amount of aliphatic hydroxy acids, consumed by esterification and lactonisation, should be definitely lower but the acid carbonyl signal only slightly decreases because a partial de-esterification of the polymeric backbone takes place and previously bonded acids become available [10].

This new available hydroxy acids participate to the creation of a three-dimensional structure responsible of the resin solubility reduction. In the spectrum of the UV aged shellac (Fig. 1, spectrum III) it is also possible to note the appearing of a sharp signal at 2850 and 2920 cm^{-1} due to the wax component (shellac contains around 5–10% of waxy fraction), only partially deducible from the other spectra. It is important to highlight that after the photo-oxidative ageing the mockups of shellac layers lost their yellowish-orange shade to became transparent as confirmed by the disappearing of the conjugated double bond signal at 1636 cm^{-1} (Fig. 2, spectrum III). Conjugated double bonds are related to dyestuff presence in the resin and to the double bond conjugated with carbonyl groups.

The addition of zinc white significantly modified the behaviour of shellac submitted to the different ageing conditions. The main differences are clearly seen in the spectral range between 1500 and 1650 cm^{-1} .

After the strong thermal ageing, while the main spectral response appears almost unaltered, two new strong bands appear at 1420 and 1590 cm^{-1} (Fig. 3, spectrum II). These are the bands related to the formation of zinc metal soaps coming from the reaction between the pigment and the resinous acids.

The recorded wavenumbers values and the shape of the two bands are perfectly comparable to the ones known for the zinc metal soap formed from drying oils [14]: this coincidence seems to indicate that aliphatic hydroxy acids are more prone to give the metal soaps than the alicyclic sesquiterpene free acids.

As in the case of pure shellac, ageing at the high temperature favours the formation of esteric structures, as shown by the strong carbonyl band centred at 1734 cm^{-1} . At the high wavenumbers the OH stretching band appears split in two: the usual OH band of shellac at 3420 cm^{-1} and a new band at 3268 cm^{-1} that could be attributed to OH groups interacting with the ZnO centres.

The effect of ZnO on the photo-oxidation of shellac is particularly interesting (Fig. 3, spectrum III) since some photo-oxidative protection effect was expected. Beside the formation of the zinc metal soap (in a definitely smaller amount than in the case of the 300 °C thermal ageing) a growth of the band at 1636 cm^{-1} due to carbon-carbon conjugated double bonds takes place. This absorption is probably responsible for the “pink” colouration that mockups assumed after the photo-oxidative ageing. In the carbonyl

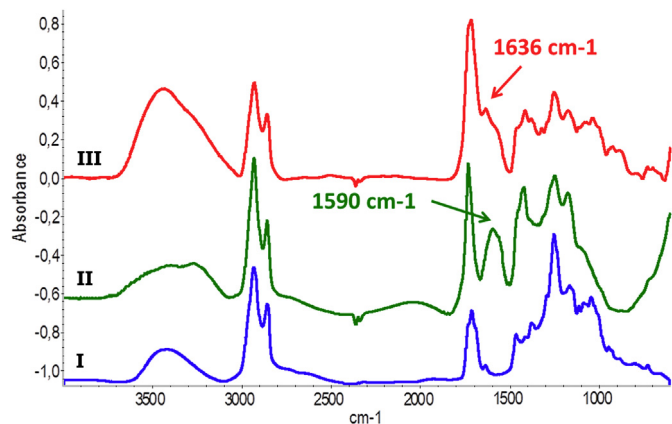


Fig. 3. Spectra of shellac and zinc white mixture before (spectrum I), after thermal at 300 °C (spectrum II) and solar simulated (spectrum III) ageing, respectively.

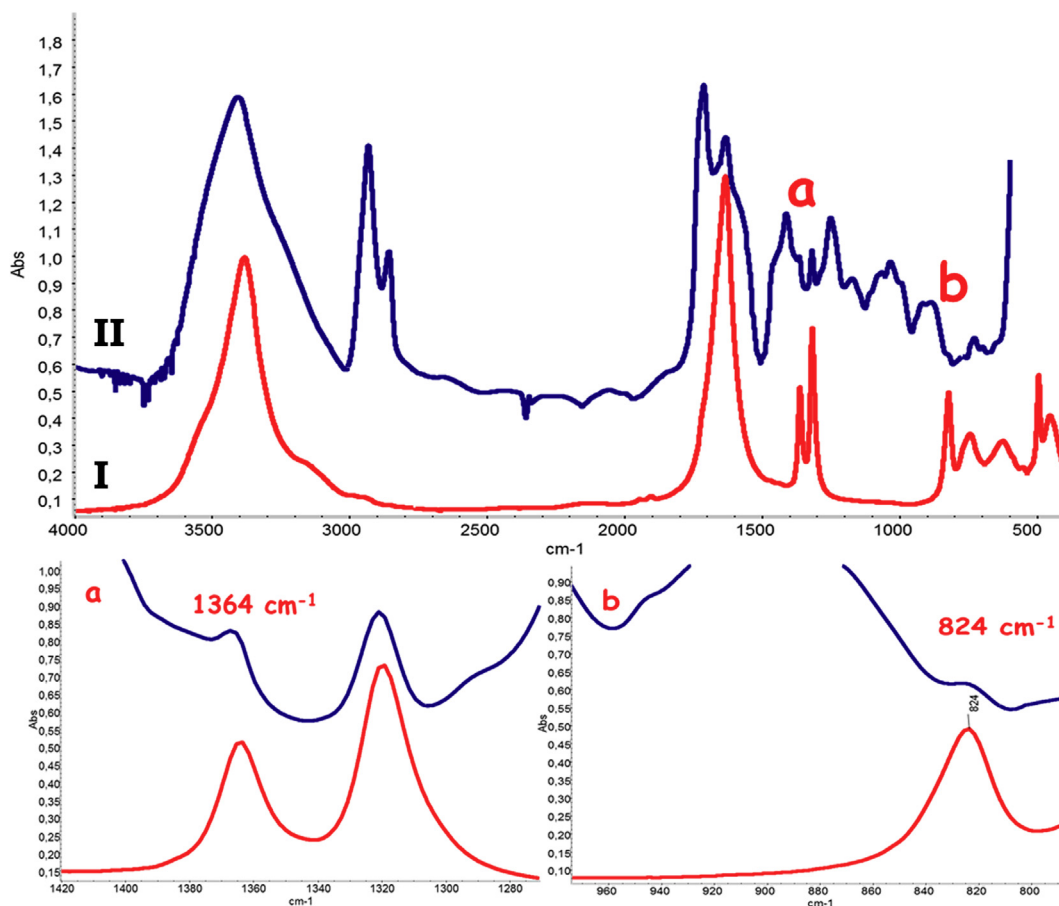


Fig. 5. Reference spectrum of Zn oxalate (spectrum I) vs spectrum of zinc white/shellac mixture (spectrum II) after the solar simulated ageing.

spectral range the strongest band remains the one at 1711 cm^{-1} related to the aliphatic hydroxy acids (mainly aleuritic acid). This feature, together with the strong carbonyl signal at 1734 cm^{-1} , due to mono and polyesters, and with the metal soaps formation (all reactions that subtract free acids), seems to confirm that even in

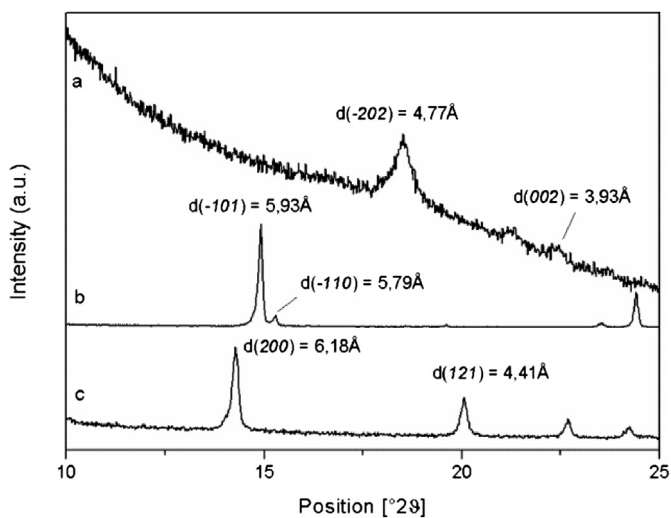


Fig. 6. X-ray diffraction spectra of sample (a), whewellite (b) and weddellite (c) in the $10^\circ\text{--}25^\circ\ 2\theta$ range. Miller indices, calculated from ICSD (1997), and interplanar distances (d) are reported.



Fig. 7. Giacomo Balla, «Grido dimostrazione in piazza del Quirinale» (1915).

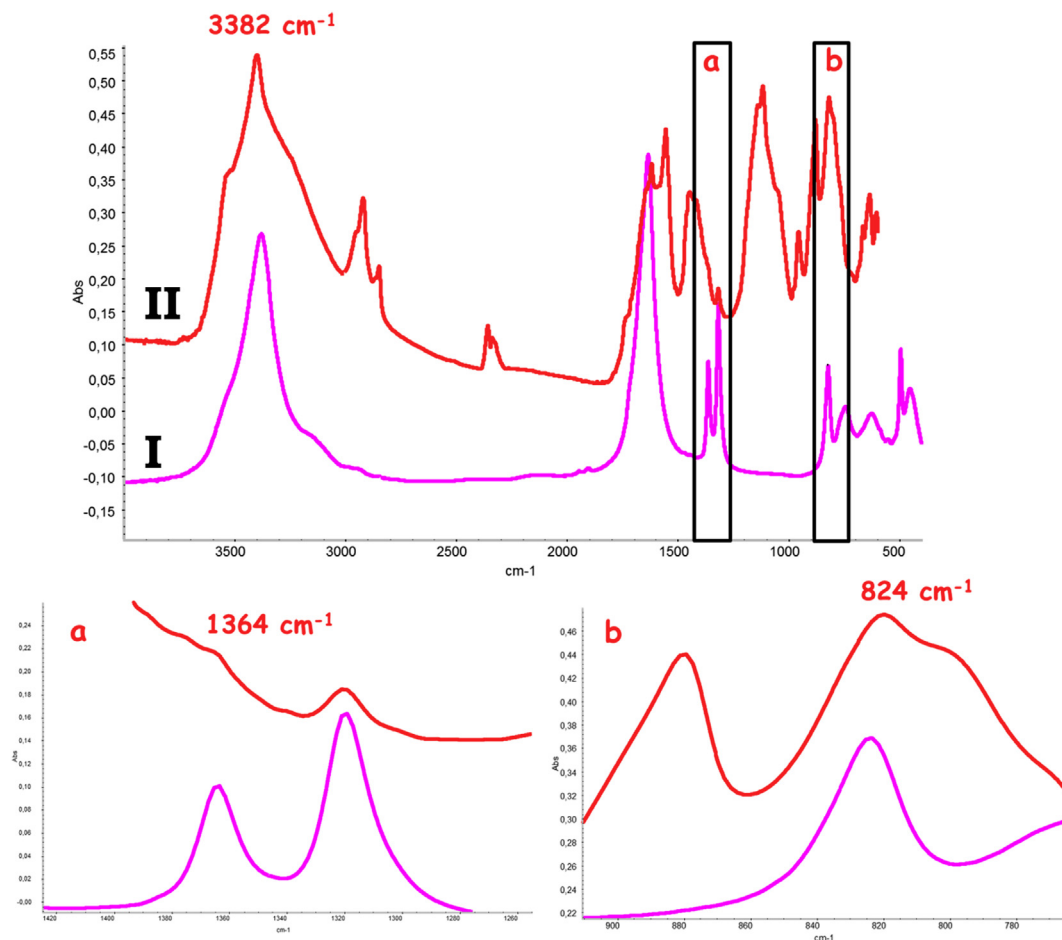


Fig. 8. Reference spectrum of Zn oxalate (spectrum I) vs spectrum coming from a green layer of the Giacomo Balla painting (spectrum II).

presence of ZnO the photo-oxidation promotes a new acid formation through hydrolysis of the backbone polymer, as suggested by Coelho et al. [10]. Moreover the signal of intra-molecular esterification, related to the formation of lactones, around 1770 cm^{-1} , clearly detectable in the UV aged pure shellac, is not present here: the pigment promotes the other degradation patterns.

At the high wavenumbers the OH stretching band at 3420 cm^{-1} presents an increased intensity confirming the presence of larger number of hydroxy functions, moreover the band seems to be intensified also by the presence of another signal at slightly lower wavenumbers. The other absorption, appearing as a shoulder at 3268 cm^{-1} , could be assigned to OH groups influenced by the presence of the oxide.

The spectrum of shellac mixed with ZnO aged 2 years at room conditions (Fig. 4) shows an intermediate situation. Obviously, the degradation is lower but both double bonds and metal soaps formation are developing. The photo-oxidative ageing drives the system to the double bond formation and backbone hydrolysis while thermal ageing favours the formation of metal soaps and the esterification without double bond formation. The kinetic, and in many cases also the chemistry of these reaction is not clear and should be related to the catalyst/coordinative behaviour of the ZnO under the different thermodynamic conditions. The complexity of the natural resin composition prevents a clearly comprehension of the involved phenomena. More in depth studies should be carried out on simpler systems such as single alicyclic sesquiterpenic and aliphatic hydroxy acids mixed with pigments.

The FTIR spectra of the photochemically aged mixture also reveal the formation of oxalates, in particular of Zn oxalates. The signals of the etheric band at 1320 cm^{-1} common to many oxalates, the second etheric band at 1364 cm^{-1} and the bending at 824 cm^{-1} typical of the Zn oxalate are present in all the recorded spectra and in the spectrum presented in Fig. 5, where the spectral zones of interest are shown in the enlargements, the presence of the new compound is particularly evident.

In addition to the above spectroscopic evidences, the nature of the compound has been confirmed by XRD diffraction analysis (Fig. 6) showing the typical inter-planar distance (d) of hydrated Zn oxalate. In Fig. 6 the comparison with calcium oxalates is reported. The presence of oxalates allows a clearer comprehension of the infrared spectrum of the aged mixture in photo-oxidative conditions: the hydroxy groups band at 3420 cm^{-1} and the double bond band at 1636 cm^{-1} are increased by the Zn oxalate absorption bands at 3382 cm^{-1} (OH stretching of the coordinated water) and at 1624 cm^{-1} (carbonyl stretching) respectively.

The measurements reported in this work show that the formation of oxalates can occur even under simulated “light” oxidative environmental conditions (xenon lamp filtered for wavelengths below 300 nm) and that natural resins in particular shellac have to be considered as substrates promoter of the oxalates patina formation on paintings once in contact with an active pigment that can work as catalyst [39]. This phenomenon indeed may occur also in real artworks under natural ageing conditions. We have in fact detected the presence of zinc oxalate

in a 1915 Giacomo Balla painting “Grido dimostrazione in piazza del Quirinale” (Fig. 7), one of the first works of his futurist period, which we have studied in the occasion of a restoration intervention [31].

The analyses on this painting (FT-IR) showed a wide employ of zinc white and the use of an oleo-resinous binder in some areas. The same characteristic signals of the hydrated zinc oxalate, the etheric band at 1364 cm^{-1} and the bending at 824 cm^{-1} , have been detected (Fig. 8) on samples coming from the light green layer. In this case the painting was not varnished but recently the presence of different oxalates under the varnish layer, has been reported [27]. This confirms that the oxalate formation can occur even in sheltered areas, surely not microbiologically active and not directly exposed to the environmental hazards such as direct sunlight or aerial pollutants. The reaction is probably catalyzed by pigments that favour the degradation of painting binders and varnishes to reactive oxalic acid [40] or promote the coordination of active ionomeric complexes that lead directly to the formation of oxalates [41].

4. Conclusions

The complex degradation processes occurring during thermal and photo-oxidative ageing of shellac resin in presence of zinc white (pure ZnO) have been studied and characterized. The paper brings the attention on the importance of natural resin reactivity with pigments from the point of view of the conservation of paintings whose decaying paths may be dramatically affected. It has been shown that photo-oxidative ageing (xenon lamp filtered for wavelengths below 300 nm), in presence of ZnO, forces the system to formation of un-saturations and to backbone hydrolysis, partially altering the saponification and reticulation processes, while thermal ageing favours the formation of metal soaps and the esterification of the acid functions. Intra-esterification reactions, that lead to the formation of lactones, clearly observed during the photo oxidative ageing of the pure resin, are inhibited or limited by the presence of the zinc oxide. Moreover, during the photo-oxidative ageing of the shellac and zinc white mixtures, the formation of zinc oxalates has been obtained in particularly “weak” oxidative conditions (xenon lamp filtered for wavelengths below 300 nm). The kinetic, and in many cases also the chemistry, of these reaction is not clear and probably related to the catalyst/coordinative behaviour of the ZnO under the different thermodynamic conditions. The complexity of the natural resin composition prevents a clear comprehension of the involved phenomena.

All these results suggest that in the evaluation of the conservation conditions of a varnish layer at the two interfaces (air and painting layer) not only a different exposure to temperature, radiation and pollutants but a different chemistry must be considered.

Natural resins, and in particular shellac, can be responsible of the formation of metal soaps and other by-products such as oxalates, suggesting that in many paintings at the painting/varnish layer interface a competition between carboxylic acids from drying oil and resin acids is active.

The formation of oxalates and the different degradation of natural resins in presence of pigments is particularly interesting considering the way that the different degradation processes can affect the varnish removability in the cleaning processes, modifying, in many cases, the boundary between painting layer and varnish, and the aesthetical aspects.

The study of the influence of pigments on the oxidative degradation process of artistic organic materials (binders and varnishes) with particular attention to the natural resins behaviour is proceeding with examination of other resin/pigment combinations and particularly the effect of resins mixtures.

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