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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.

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 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].

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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.

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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 weddelite, 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].

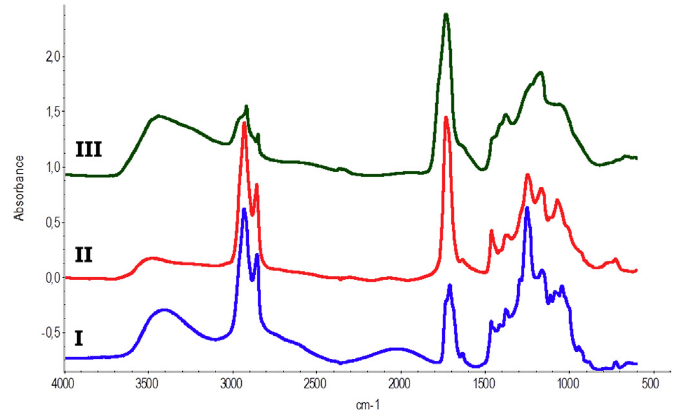

Fig. 1. Spectra of shellac before (spectrum I), after thermal at 300 °C (spectrum II) and solar simulated (spectrum III) ageing, respectively.

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'Celetator detector PW3015/20 and diffraction patterns have been collected from 5° to 60° 2θ, scan speed 0.21° s^{-1}, with a CuKα-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