ARTICLE IN PRESS

Measurement xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Measurement

journal homepage: www.elsevier.com/locate/measurement

Multi-pulse laser irradiation of cadmium yellow paint films: The influence of binding medium and particle aggregates

D. Ciofini*, I. Cacciari, S. Siano

Istituto di Fisica Applicata "Nello Carrara" (IFAC), Consiglio Nazionale delle Ricerche (CNR), Florence, Italy

ARTICLE INFO

Keywords:
Laser
Ablation threshold
Cadmium yellow
PVA
3D reconstruction
Particle-size

ABSTRACT

The present work is focused on the study of laser-induced effects that can occur in cadmium yellow paint films. To this aim, samples were prepared with different binders (linseed oil and polyvinylalcohol), mixing methods (manual vs. sonication) and pigment volume concentration (PVC). Laser experiments were performed under a microscope-based setup coupled to a spectrometer, which allowed to study surface and in-depth changes thanks to 2D image processing and 3D reconstructions. The present methodology revealed effective for studying the role that binder, particle-size and density distribution have upon laser irradiation. Results showed the threshold fluences strictly depend on the type of binder and PVC. The damage nucleation is size-dependent with fluence and PVC, and the micro-damaged sites can be ascribed to non-linear absorption of CdS aggregates, whose size is of the order of the incident wavelength. These conclusions were further corroborated by Vis-NIR PL emission and reflection and ESEM-EDX.

1. Introduction

Within the conservation scientist' community, the understanding of the nature and the extent of alterations induced by intense radiation sources (i.e. synchrotrons, ion-beam accelerators and lasers) and related mitigations strategies are issues of considerable importance for improving diagnostic techniques and conservation practices of valuable cultural heritage artifacts [1]. Among these, the optimisation of non-invasive diagnostic strategies for defining the dosimetry, and monitoring the laser cleaning treatment of paintings deserves great attention. Since the mid-1990s, numerous publications have been devoted to study laser interaction with art pigments and various pigment-binder mixtures. In particular, many types of lasers operating in different spectral regions and pulse durations, including UV excimers, Nd:YAG and Er:YAG lasers, have been tested. Results have shown that, regardless to the laser wavelength used, discoloration (darkening and/or bleaching) of a thin surface layer of pigment particles and/or binders may occur in various extents and differently according to laser parameters (wavelength, fluence, pulse duration, pulse repetition frequency and number of pulses) and physico-chemical properties of paint layers (type of binder and pigment, pigment to binder ratio, pigment-binder interactions, ageing and presence of film defects) [2–6]. In the ns range, these modifications are usually ascribed to changes in the pigment chemistry (i.e. reduction mechanisms and crystalline phase changes), and in the organic matrix as well (oxidation, photo-dissociation, charring). Basically, in case of low absorption, laser-induced effects occur first on pigments and then are possibly transferred to the organic matrix, whereas in the UV range due to the higher absorption of most materials, they can take place concurrently. However, at the present state-of-art, laser-interaction mechanisms with paint layers have been always characterized more by a chemical standpoint than a physical one. Therefore, systematic investigation in this regards are needed in order to extend laser treatments in conservation. Bearing this in mind, the present work was aimed at developing and testing, for the first time, a non-invasive strategy for the accurate measurement of surface and in-depth sub-ablative effects. This analytical approach was applied on paint films containing cadmium yellow (Cdy), a semiconductor material which was extensively used as artistic pigment in oil and watercolour, after its commercialization in 1840 [7]. Among the studies of laser interaction with artistic pigments, Cdy received undoubtedly marginal attention. It was demonstrated that cadmium red-oil paints turned dark upon laser irradiation with QS Nd:YAG (1064 nm) laser, whereas Cdy showed higher color and structural stability [8,9]. Careful measurements by XRD diffraction and TEM microscopy proved that the crystallite mean size of the red pigment decreases upon laser irradiation and the lattice expands due to sulphur elimination. Although less pronounced, a similar behavior was observed also for Cdy paint films. Contrarily, Athanassiou et al. [10] have shown that the intensity of the fluorescence emission in UV laser-treated Cdy oil paints decreased considerably due to the alteration both of pigment and binder. In a

* Corresponding author.
E-mail address: d.ciofini@ifac.cnr.it (D. Ciofini).

http://dx.doi.org/10.1016/j.measurement.2017.07.046
Received 28 February 2017; Received in revised form 20 July 2017; Accepted 24 July 2017

recent work [11], Vis-NIR steady-state photoluminescence (PL) emission and Vis-NIR reflection were used in order to investigate the effects induced on modern paint layers by LQS Nd:YAG (1064 nm, 120 ns) laser at sub-ablative fluences. In particular, Cdy, lithopone white (Liw) and chromium oxide green (Crg) pigments with and without oil matrix were investigated. Although no detrimental effects were pointed out on pure pigment pellets as well as on Liw and Crg oil paints, laser tests carried out at sub-ablative fluences showed that PL emission and color variation in Cdy-oil paints depended drastically on the number of laser pulses. This behavior was due to the formation of a dotted alteration pattern within the laser-irradiated spot, where non-fluorescent spots of 2–10 µm size were observed under optical microscope. The nature and the extent of this phenomenon, being mostly a surface morphological change, was associated with the degree of polymerization of oil binder, the presence of paint film defects (i.e. coarse pigment particles) and/or absorbing impurities within the crystal lattice of CdS.

To get more insights on the present alteration phenomenology, here, a novel measurement methodology based on 2D and 3D optical microscopy was used to comparatively assess sub-ablative photo-physical changes induced on Cdy paint films. In particular, the measurement of counts, average size, % area, Feret diameter, shape and depth of the etched region allowed extracting qualitative and quantitative information about the laser-interaction mechanisms. Vis-NIR PL emission and reflection spectroscopies and ESEM-EDX analysis were used as further analytical confirmation.

2. Material and methods

2.1. Sample preparation

Homemade paint formulations were prepared by mixing commercial Cdy pigment powder with different types of binders (purchased by Zecchi, Florence), as listed in Table 1. Cdy pigment powder is a commercial CdS (Se, Zn) containing about 8–10% of small and large $CaCO_3$ extender particles. Under ESEM, calcite crystals range in size between 2 and 25 µm, while the distribution for the tiny Cdy particles is peaked between 0.6 and 1 µm. For comparison purposes, Cdy deep (M084-Oil) and light (M081-Oil) color tubes produced by Maimeri were selected as commercial oil formulations. Both contain calcium and zinc-based extender particles, even if M081-Oil is lighter due to major amounts of Zn.

In addition to cold-pressed linseed oil binder, boiled linseed oil with cobalt (Co) driers was selected due to its fast curing times. In the early 7–8 h, Co^{2+} ions act as catalyst for hydroperoxide decomposition from outside towards the inside of the film [12,13]. Polyvinyl alcohol (PVA) was dissolved in water (10% w/v) and then added to the pigment. PVA-based formulations were prepared for investigating laser interactions in a binding medium physically and chemically different with respect to linseed oil. Particle loading, quantified by Pigment Volume Concentration (PVC) including $CaCO_3$ extender particles, was equal to 20, 10, and 2.5. Since linseed oil absorption (OA) value on a non-flocculated dispersion of CdS is approximately 37.5 (g/100 g), it can be estimated a CPVC (Critical PVC) of about 55, which in turn allows to state that, in the homemade formulations, no air voids are present and binder fills interstices between the tightly packed particles.

Manual mixing method refers to the use of a flat spatula in order to blend the p/b mixture, while sonication to ultrasound treatment performed at 40 °C for 45 min. The latter was used to increase the specific surface area of Cdy particles (i.e. particle-size reduction) and avoid flocculation, thus improving the surface and bulk qualities of the dried paint layer.

Once thoroughly blended, both the formulations were evenly distributed on glass slides by flat spatula without any further processing and dried out under controlled laboratory conditions for one-month before laser irradiation. Film thickness as measured by optical microscope ranged between 50 and 100 µm. In order to speed up the natural processes of drying and degradation, a set of samples was subjected to thermal treatment at 80 °C, with air ventilation in absence of ambient light [14]. As the presence of CdS does not have a great influence on the drying of the oil [15], a rough estimation of ageing time can be done by considering that at 80 °C, the accelerating factor was calculated to be approximately 40 times. Therefore, our treatment extended to 720 h, corresponds to about 3.3 years of natural ageing.

2.2. Laser testing methodology

Laser irradiation tests were performed using a multiple temporal regime Nd:YAG (1064 nm) laser emitting pulses ranging from about 100 ns–100 µs. In the present work 120 ns pulse width was used. In order to simultaneously collect from the same laser irradiated spot, fluorescence, color and morphology information upon laser irradiation, a setup combining a laser beam aligned to an epi-fluorescence microscope was built up (Fig. 1). This allowed to accurately investigate the nature of alteration phenomenology at sub-ablative fluences. To collect spectroscopic information a high-sensitivity Avantes CCD spectrophotometer (200–1100 nm, grating 300 lines/mm) was coupled via optical fiber to the microscope. HBO mercury short-arc lamp (emission above 295 nm) and suitable filters cubes were used to excite and collect PL emission. An external light source (illuminant A) positioned at 45 °C was exploited in order to collect spectral and color information. A more detailed description about the setup is reported here [11]. Surface morphology was also examined with ESEM by using 23–25 kV and 1 torr pressure.

Laser interactions were investigated below threshold (indicated in the text as $F_{s\text{-}ab}$ sub-ablative threshold,) and at fluences corresponding to ablation threshold (F_{ab}), according to single and multiple laser pulse experiments. Spot diameter was kept at 3 mm and pulse repetition frequency at 1 Hz. Since the ablative response observed was markedly inhomogeneous, here, the threshold fluence F_{ab}, was defined by the lowest limit for which ablation (i.e. formation of a micro-hole within the irradiated area) is observed. Once F_{ab} was determined, changes induced at sub-ablative fluences ($F < F_{ab}$) were studied as function of laser pulses, which ranged between 5 (highest fluences) and 100

Table 1
List of prepared Cdy-based paint layers together with comments to their surface quality.

Sample code	Binder	Producer	Mixing method	Dried film quality
Homemade formulations				
Cdy-OilCo[M]	Boiled linseed oil (Co salts < 0.05%)	Zecchi, Florence	Manual	Flat and quite homogeneous
Cdy-OilCo[S]	Boiled linseed oil (Co salts < 0.05%)	Zecchi, Florence	Sonication	No defects
Cdy-Oil[M]	Cold-pressed linseed oil	Zecchi, Florence	Manual	Presence of coarse grains and cratering
Cdy-Oil[S]	Cold-pressed linseed oil	Zecchi, Florence	Sonication	Less coarse grains, cratering still visible
Cdy-PVA[M]	Polyvinyl alcohol, 99+% hydrolyzed	Aldrich	Manual	Coarse grains, cratering and small cracks
Cdy-PVA[S]	Polyvinyl alcohol, 99+% hydrolyzed	Aldrich	Sonication	Improved quality but defects are still present
Commercial formulations				
M081-Oil	Linseed oil	Maimeri Classic	Applied as it is	Flat, homogeneous
M084-Oil	Linseed oil	Maimeri Classic	Applied as it is	Flat, homogeneous