IMEKO International Conference on
Metrology for Archaeology and Cultural Heritage
Torino, Italy, October 19-21, 2016

Sub-ablative LQS Nd:YAG laser irradiation effects on cadmium yellow paint layers

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Abstract – **On the wake of recent successful applications of LQS Nd:YAG (1064 nm) laser in conservation of modern easel paintings, here, we focus on the study of undesired side effects of the laser treatment that can occur in photosensitive modern paints. Understanding the phenomenology and nature of their alterations has a crucial importance for extending the laser approach in conservation. In the present work, a measurement methodology for characterising the sub-ablative effects of photosensitive paint layers was developed. The analytical approach was refined by considering the example case of cadmium yellow. CdS-based paint mock-ups using different oily binders were prepared and systematically laser irradiated under an epi-fluorescence microscope coupled to a spectrometer. The latter, image analysis, and ESEM-EDX allowed to collect information on the alteration phenomenology. The method provided underlines the strict dependence of the damage nucleation on the distribution of the pigment within the matrix along with a set of other features of interest for defining and assessing the laser treatments.**

I. INTRODUCTION

The optimisation of non-invasive diagnostic strategies for defining the dosimetry, and monitoring the laser treatment of paintings is a subject of considerable importance for restorers and conservation scientists. The understanding of the nature and extent of laser-induced effects on photosensitive paint layers deserves great attention and it is still under investigation from chemical and physical standpoints.

Although numerous publications have been devoted to study laser interaction with traditional pigments and binders (egg yolk, linseed oil), only a few of them involve artistic materials of the modern paintings [1]. In this regards, the present work is aimed at studying laser-induced alteration features of paint systems containing cadmium yellow pigment (Cdy), which was extensively used in oil and watercolour, after its commercialization in 1840 [2].

In a previous work, 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. Besides, irradiated areas of Cdy-oil paints showed a dotted alteration pattern within which non-fluorescent spots of 2-10 µm size were observed under optical microscope. The nature and the extent of this phenomenon was mostly 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.

Here, sample preparation procedures and irradiation tests were designed in order to understand whether the observed alteration phenomenology depends on the type of binder, dimension and density distribution of pigment particles, or the presence of absorbing impurities. Vis-NIR PL emission and reflection spectroscopies along with ESEM-EDX analysis were used to characterise the samples before and after ageing, as well as during laser irradiation. Optical and epi-fluorescence microscopy, were used to examine particles distribution and to quantify the extent of the laser-induced changes.

II. EXPERIMENTAL

A. Sample preparation

Homemade paint formulations were prepared by mixing binder and Cdy pigment powder using two procedure, as listed in table 1. Manual mixing refers to the use of a flat spatula in order to blend the p/b mixture, while sonication to ultrasound treatment. The latter was used to increase the specific surface area of Cdy particles (i.e. particle-size reduction), thus improving the surface quality of the paint layer. For each homemade formulation, the pigment to binder ratio (p/b) was 50:50 by weight., For comparison purposes, Cdy deep and light produced by Maimeri were selected as commercial oil formulations. With respect to pressed linseed oil, boiled linseed oil with cobalt (Co) driers is characterised by fast curing times. In the early 7-8 hrs, Co^{2+} ions , being primary driers, act during oxidation as catalyst of hydroperoxide decomposition from outside in [3][4]. Polyvinyl alcohol (PVA) was dissolved in water (10 % w/v) and then added to the pigment. PVA-based formulations were prepared for investigating laser induced alterations in a binding medium completely different from oil, in term of physical and chemical properties.

Table 1 List of prepared Cdy-based paint layers.

Sample code	**Binder**	**Mixing method**
Homemade formulations		
Cdy-OilCo[M]	boiled linseed oil (Co salts<0.05%)	manual mixing
Cdy-OilCo[S]	boiled linseed oil (Co salts<0.05%)	sonication at 40°C-45 min.
Cdy-Oil[M]	cold-pressed linseed oil	manual Mixing
Cdy-Oil[S]	cold-pressed linseed oil	sonication at 40°C-45 min.
Cdy-PVA[M]	polyvinyl alcohol	manual mixing
Cdy-PVA[S]	polyvinyl alcohol	sonication at 40°C-45 min.
Commercial formulations		
M081-Oil	oil colour tubes	applied as it is
M084-Oil	oil colour tubes	applied as it is

Once thoroughly blended, both the formulations were applied on glass slides by flat spatula without any further processing and left to dry under controlled laboratory conditions protected from dust. 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 [5]. As the presence of CdS does not have a great influence on the drying of the oil [6], 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 hrs corresponds to about 3.3 years of natural ageing.

B. Laser testing methodology

Laser irradiation tests were performed using a multiple temporal regime Nd:YAG (1064 nm) laser emitting pulses from about 100 ns to 100 µs. The present work was carried out using 120 ns pulse width. In order to simultaneously collect in the same laser irradiated spot, fluorescence, colour 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.

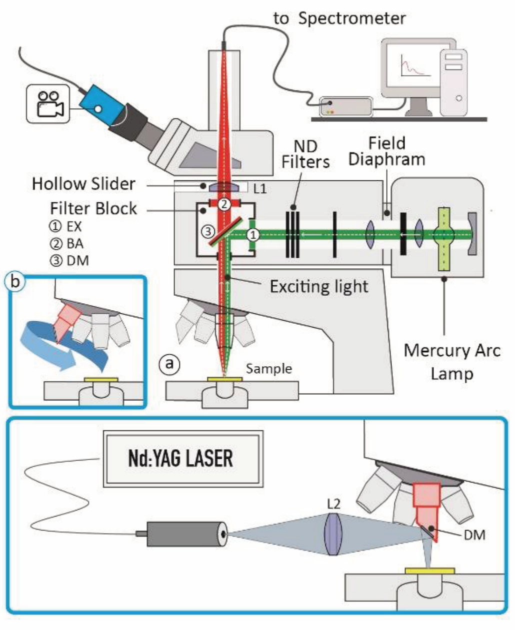

Figure 1 Versatile setup for measuring laser sub-threshold induced effects. A dichroic mirror (DM) mounted at 45° in place of the microscope's objective lens allows to switch from the acquisition (a) to laser irradiation line (b).

To make laser tests more easily comparable each other, irradiation conditions were defined according to the single shot ablation threshold, F_{ab}. Anyway, it was not possible to define easily the latter in a general way since the ablation phenomenology observed was markedly inhomogeneous. F_{ab} hence represents a sort of empirical irradiation limit corresponding to a unequivocal and predominantly ablative alteration.

Once F_{ab} was determined, three-four fluences below F_{ab} were tested. At each of these sub-ablative fluences a fixed number of laser pulses was delivered, which ranged between 5 (highest fluences)-100 (lowest fluences), according to a well-established dependence of the alteration threshold on fluence and number of pulses reported elsewhere [1][7].

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. To capture the fingerprint of laser beam at various irradiation condition, a digital camera was adapted to the eyepiece slot of the microscope (see Fig.1). The recorded optical images were evenly cut and automatically processed (i.e. batch processing) through the execution of simple operations. Firstly, the RGB image acquired on non-irradiated area was subtracted to the respective image sequence taken after the laser treatment. This allowed to obtain exactly the mark left by the laser beam excluding any unwanted intrinsic features, such as paint film inhomogeneities and porosities. Subtracted images were then converted to 8-bit grey-scale and slightly contrast enhanced. At this stage, features of interest were extracted from the background using an iterative selection method of thresholding, in which all gray levels below the threshold are mapped into black, those levels above are mapped into white [8]. Obviously, all the images were processed using the same thresholds in order to get quantitatively comparable results. To avoid shortcomings ascribed to pixels having gray levels in the region of interest, threshold was decided on the basis to maximize counts in the irradiated areas and to reduce as much as possible the value before irradiation. The best spatial resolution achieved during particles analysis was 6 μm^2.

III. RESULTS AND DISCUSSION

The type of Cdy used is CdS (Se, Zn) with the addition of about 3.3 % of $CaCO_3$. Under ESEM, calcite crystals having a diameter ranging in size between 5 and 25 μm were clearly visible since they were much more larger than the tiny Cdy particles (≤ 1 μm). However, this component is expected to provide a scattering rather than an absorption contribution, thus its influence on the alteration threshold can be reasonably neglected.

As regards paint samples, those manually mixed were characterised by visible coarse agglomerates, 80-120 μm^2 as average area, which cover around 1% of the analyzed area (1.2x1.2 mm^2). Other features as craters, pinholes, and small cracks were also observed, especially in PVA-based coatings. In turn, the sonication treatment produced different properties of the paint layer. In particular, Cdy-OilCo[S] samples showed the best film surface quality, whereas that of the linseed oil and PVA mixtures was decidedly worst. This shows the presence of Co driers as additives had a positive influence on the wetting of pigment particles and film formation. However, above a given thickness, the paint layer exhibited the formation of shrinkage and wrinkling. These defects were not observed when using M081 and M084 oil color tubes, which contain several additives.

Irradiation at rising fluences between 100-1000 mJ allowed estimating the parameter F_{ab} corresponding to the occurrence of evident ablative effects by single pulse. Cdy-Oil, Cdy-OilCo, either sonicated or not, M081 and M084 showed the formation of microcraters around 300 mJ/cm^2, whereas for Cdy-PVA this occurred at about 800 mJ/cm^2, which represent empirical estimations of F_{ab}

Image analysis allowed extracting meaningful quantitative information about the surface modifications. The results achieved on thermally aged Cdy paint films, which were the most similar to the real paint layers in term of physical and chemical properties, using five pulses at F_{ab} are shown in Fig. 2. As shown, alteration patterns remarkably different among the various paint mixtures were observed. In particular, the influence of the binding medium was unexpectedly greater than that due to the different blending methods (manual vs. sonication). The density of the induced modifications within the laser spot differed significantly and evidenced the most intensive damage was that induced on Cdy-Oil [M] and Cdy-Oil [S]. Conversely, Cdy-OilCo films were less prone to change, most likely due to the presence of Co driers that improved the binder's thermal stability.

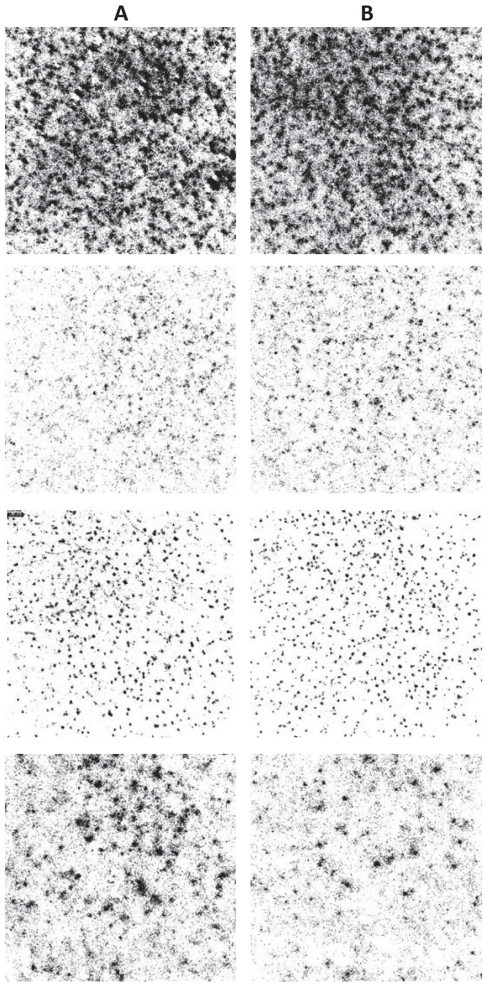

Figure 2 Comparative image analysis of thermally aged Cdy paint samples irradiated at F_{ab} with 5 laser pulses. Manually mixed samples are displayed on left column (A) whilst those sonicated on the right one (B). From the top to bottom: Cdy-Oil (300 mJ/cm^2) Cdy-OilCo (300 mJ/cm^2), Cdy-PVA (800 mJ/cm^2), M081-Oil and M084-

Oil (300 mJ/cm^2, similar features were observed for both samples). Image sizes: 1.2x1.2 mm^2.

M081 and M084 coatings generated a distinct alteration pathway with respect to homemade paints, where round cratering on large scale and a well-distributed greyish halo were observed over the irradiated spot. In the naturally dried films (one-month ageing), similar alteration phenomena were observed. The only exception was found for the commercial formulations, which underwent less pronounced changes.

Cdy-PVA presented a clean alteration morphology within the irradiated area, where any single feature was easily recognizable. Considering that Cdy-PVA films did not produce high quality coatings, the observed behavior is indubitably due to the superior thermal stability of PVA.

As well known, besides being used as capping agent and stabilizer for the synthesis of CdS-PVA nanocomposites, PVA is highly crystalline with a crystalline melting point of ~218 ◦C, has a high dielectric strength (>1000 kV/mm), good charge storage capacity, and dopant dependent electrical and optical properties. Furthermore, it has a glass transition temperature of 75-85 °C and does not undergo relevant thermal discoloration up to 100°C. It was also been demonstrated that the presence of CdS causes a decrease in the decomposition temperature of the PVA by ~20 ◦C, thus confirming a strong interaction between PVA and CdS [9].

A quantitative comparison of the above-mentioned phenomenological features is displayed in Fig. 3. It is worth noting that average size and area of the micro-dotted alterations grew almost linearly as function of laser fluence in most of paint samples studied. As shown in Fig. 3, at the maximum fluence (F_{ab}) the altered area fractions varied between 10-30 % for Cdy-Oil, M081-Oil and M084-Oil, and between 3 and 6 % for Cdy-OilCo and Cdy-PVA.

The increase of average size observed may be easily explained through an accurate analysis of all the features of the sub-ablative alteration morphology. As stated above, in Cdy-PVA films the area surrounding the altered dots was not affected by laser irradiation. As a consequence, the calculated average size is higher than in oil films and corresponds exactly to that of the dotted region, as no contributions ascribable to smaller features nearby were introduced in the calculation.

A further consideration concerns the counts of the dots, which for Cdy-PVA were lower than 1000 at 800 mJ/cm^2 and less of 100 at 600 mJ/cm^2. Average size and counts suggest that in PVA the ablative dynamics can be mostly associated with the removal of coarse fragments. In contrast, the trend observed in oil-based coatings was the result of the average between large and very small damage dots. The latter were even much smaller than the present measuring resolution (6 µm^2), in agreement with the nanoscale size of the tiny CdS particles. This suggests that cumulative heating of CdS particles in oil could be greater than in PVA. However, taking into account that CdS is a weakly absorbing material at 1064 nm (reflectance, R=85 %; optical penetration, δ= 70 µm), it can be argued that at sub-ablative fluences (range in oil 100-300 mJ/cm^2) the onset of the dotted darkening effect is triggered by the oil matrix decomposition around the Cdy particles.

Therefore, the type of binder along with its thermal properties, determines the extent of laser-heated region, which strictly depends on the pigment particle size distribution and fluence applied.

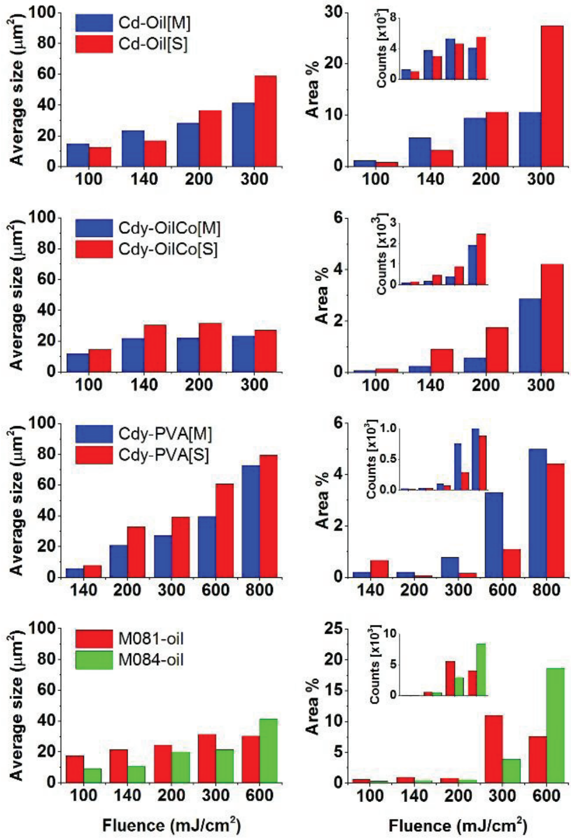

Figure 3 Histograms illustrating changes in average size (µm^2) and percentage area ratio (%) induced by laser irradiation on thermally aged Cdy samples at sub-ablative fluences (calculations carrid out on a 1.2x1.2 mm^2 area). Inset graphs report the number of alteration microspots. Error is less than 5%.

The above-discussed irradiation phenomenologies are perfectly in agreement with the changes observed in PL and reflection spectra shown in Fig. 4. Laser irradiation produces a decrease of PL emission and reflection as function of laser fluence and number of delivered pulses. In the specific, PL emission spectra showed an overall decreasing of 15-20% in the band at 545 nm attributable to the linseed oil component. Likewise, the darkening effect was also detected both by NIR-Vis PL emission and reflection. Once the matrix starts to decompose with increasing pulses, the process proceeds until a small cluster of Cdy particles is ejected away.

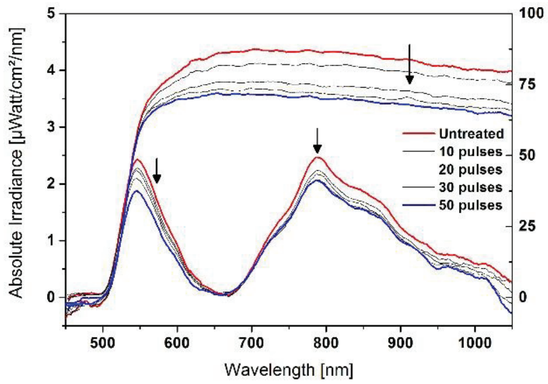

Figure 4 Vis-NIR PL and reflection spectra showing laser-induced changes at 140 mJ/cm^2 in aged Cdy-OilCo [S] films.

As assessed through ESEM-EDX examinations, such ablation microcraters, had a roundish shape and an average diameter of about 5 µm, which fits well with the early average area values estimated through the image analysis shown in Fig. 3, which was around 20 µm^2.

IV. CONCLUSIONS

In this work, we studied the laser-induced sub-ablative effects of various Cdy-mixtures under different laser exposure conditions, by discriminating different alteration pathways. The results achieved led to clearly demonstrate that the presence of film defects, like coarse grains, cracks and craters does not have any influence on the onset of sub-ablative effects occurring at 100 mJ/cm^2. The influence of the binding medium was unexpectedly greater than the differences between the two blending methods investigated (manual vs. sonication). The alteration morphology seems indeed strictly dependent on the type of binder, degree of polymerization and especially on its thermal properties. Cdy-PVA films showed ablation thresholds significantly higher than those of oil-mixtures, in agreement with the lower glass transition temperature of the latter.

The present multianalytical method will be soon exploited for investigating the statistical distribution of the alteration patterns associated with different binding media, as well as the dependence on the particle density distribution. This approach will be extended to a set of paint layers in order to explore the potential of the laser ablation in restoration of modern and contemporaneous paintings and define the most suitable application methodologies.

ACKNOWLEDGEMENTS

The present study was carried out in the framework of the European Project IPERION CH – Integrated Platform for the European Research Infrastructure on Cultural Heritage (H2020-INFRAIA-2014-2015, Grant Agreement n. 654028).

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