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
*d.ciofini@ifac.cnr.it

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.

Keywords: Laser, ablation threshold, cadmium yellow, PVA, 3D reconstruction, particle-size

1. Introduction

Within the conservation scientist’s 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][3][4][5][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 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 doted 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) colour 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.

| Sample code | Binder | Producer | Mixing method | Dried film quality |
|-------------|--------|----------|---------------|-------------------|
| Cdy-OilCo[M]| boiled linseed oil (Co salts<0.05%) | Zecchi, Florence | manual | Flat and quite homogeneous |
the use of a flat spatula in order to blend the p/b mixture, while the latter was used to increase the position at 45 °C was exploited in order to collect spectral and 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.

| 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 |

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 hrs, Co²⁺ 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 CaCO₃ 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/100g), 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 50-100 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 hrs, 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 to 100 µs. In the present work 120 ns pulse width was used. In order to simultaneously collect from the same laser irradiated spot, fluorescence, colour and morphology information upon laser irradiation, a setup combining a laser beam aligned to an epifluorescence microscope was built up (Fig.1). This allowed to accurately investigate the nature of alteration phenomenology at sub-ablative fluorences. 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 $F_{\text{sub-ab}}$ sub-ablative threshold,) and at fluences corresponding to ablation threshold ($F_{\text{ab}}$), 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 $F_{\text{ab}}$, was defined by the lowest limit for which ablation (i.e. formation of a micro-hole within the irradiated area) is observed. Once $F_{\text{ab}}$ was determined, changes induced at sub-ablative fluences ($F < F_{\text{ab}}$) were studied as function of laser pulses, 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 [6][16].

2.3 2D image processing

To capture the laser-interaction effects at various irradiation condition, a digital camera was adapted to the eyepiece slot of the microscope (see Fig.1). The measurement of laser-induced defects was carried out according a dedicated image processing procedure, which is step-by-step displayed in Fig. 2.
The recorded optical images were evenly cropped and automatically processed. Firstly, the RGB image acquired on non-irradiated area was subtracted to the corresponding 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 (Fig. 2c). Subtracted images were then converted to 8-bit grey-scale and performed a slight contrast enhancement. At this stage, features of interest were extracted from the background using an iterative selection method of thresholding, in which all gray levels below and above the threshold are mapped into black and white, respectively [17]. All the images were processed using the same threshold value 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 µm². This methodology allowed extracting a series of meaningful information about the laser-interaction process, like counts, average sizes, % area, and Feret diameter. The latter is a common parameter used in the analysis of particle-size and is defined as the longest distance between any two points along the ROI boundary.

2.4 3D reconstructions: background and data processing
Optical microscopy is commonly used for surface inspection in different fields. Due to its limited focus depth, only portions of the surface in the optical plane appear focused in the image, while the others appear defocused. As a result, not all the details of a 3D surface can be observed in a single scene. This problem is generally solved by taking an image sequence of the same scene, corresponding to different object planes. The challenge then becomes to extract, from each image, the pixels that are in focus in order to reconstruct an image projection that is in focus everywhere. A variety of multi-focus fusion methods have been proposed: these deal with creating an image with all the pixels in focus and incorporating their depth information to reconstruct the 3D surface [18]. Among these methods, the wavelet transform based represents one of the better-performing due to its simplicity and its ability to preserve spatial and frequency details of the images to be fused. The wavelet transform decomposes an image into sub-bands that contain details of different sizes. Some useful information can be extracted, for instance, pixels with large wavelet coefficients (W) in some neighborhood can be an indication for sharp details, which is characteristic for the in-focus pixels. In order to extract the pixels in focus in the image sequence, a simple fusion rule can be the selection of the image with the largest absolute value of the wavelet coefficients at each point. These coefficients can be used to anti-transform, in order to obtain a composite image with all the pixel in focus. In the literature [19][20], this simple rule has been widely improved introducing different focus measures. In this paper, the integer wavelet transform (IWT) for image fusion algorithm and the following focus measure (F) have been considered:

\[ F = \frac{\sum_{i=1}^{K} [\sum_{(x,y) \in \Omega_{HHi}} W_{HHi}^2(x,y) + \sum_{(x,y) \in \Omega_{LHi}} W_{LHi}^2(x,y) + \sum_{(x,y) \in \Omega_{HLi}} W_{HLi}^2(x,y)]}{\sum_{(x,y) \in \Omega_{LLi}} W_{LLi}^2(x,y)} \]  

where \( S \) represents a selected window, the pixel \((x,y)\) the window center, the wavelet coefficients in the level \( i \) for the \( HHi, LHi, HLi, LLi \) bands are \( W_{HHi}, W_{LHi}, W_{HLi}, W_{LLi} \). For each pixel \((x,y)\) in the image sequence, the calculated focus measure (F) can be fitted with a Gaussian function. Its peak position represents the focus position and can be related to the height at which the image was recorded. Hence,
two data sets can be extracted: the height map and the corresponding RGB value for color rendering. The first was used to measure the height, and the second to measure the area of each laser-induced alteration. We used four levels Haar wavelet, and a 50x50 pixel window to process the image sequence. The optical system comprised a digital camera and a standard microscope. Using a 100 X objective (Depth of Field: 0.19 µm) a scene of 154x115 microns (images 1280x960) at 0.5 micron step was imaged. The best capturing condition was achieved with bright-field pushed in, polarizer and analyzer in parallel position, field diaphragm fully open and aperture diaphragm closed. Within each irradiated spot were recorded 10 3D scans covering overall around 1.2x1.2 mm².

3 Results

Samples manually mixed were characterized, at any PVC, by visible coarse CaCO₃ extender particles (80-120 µm² as average size), which cover around between 0.1 and 1% of the analyzed area (1.2x1.2 mm²). Other features as craters, pinholes, and small cracks were also observed, especially in PVA-based coatings. In contrast, the sonication treatment produced different properties of the paint layer. In particular, Cdy-OilCo [S] samples showed the best film surface quality. Most probably, the presence of Co driers as additives had a positive influence on the wetting of pigment particles and film formation. On the contrary, Cdy-Oil and Cdy-PVA mixtures were decidedly worst. This suggested that sonication treatments did not have a dramatic influence on the size-reduction of CaCO₃ extender particles. Instead, due to the presence of additives (i.e. zinc oxide), paint layers obtained by commercial formulations M081 and M084 resulted very fine and flat.

3.1 Dependence of threshold fluence on PVC

The dependence of laser discoloration/ablation threshold fluences on PVC between the two categories of samples (linseed oil vs. PVA) is shown in Fig.3.

![Graph](image)

Figure 3 Threshold fluences for PVA and oil Cdy paint films (dried samples) as function of PVC. Tests carried out with single pulse a) and multiple laser pulses b). Data corresponding to 30 PVC for oil samples were extrapolated from a previous publication [11].

An exponential decrease of threshold fluence with increasing PVC was observed, either after exposure to single (F_ab ) and multiple laser pulses (F_s-ab). F_s-ab resulted lower than single pulse F_ab, mostly due to the accumulation of defects within the irradiated spot. Instead, no significant difference in threshold
fluences was measured between manually mixed and sonicated samples, as well as in those exposed to thermal aging. The most prominent and appreciable variation was found to be dependent on the type of binding medium. As shown, PVA-based films exhibited higher F\text{ab} than oil ones. Generally, irradiation effects occurring at F< F\text{ab} at various PVC, resulted in permanent changes of surface morphology, which were slightly different in the kinetic of damage nucleation among oil and PVA mixtures, but both underwent accumulation of microstructures and defects followed by ablation/depletion of material at fluence close to F\text{ab}.

At 20 PVC, Cdy-Oil, Cdy-OilCo, either sonicated or not, M081-Oil and M084-Oil films showed the formation of micro-holes at around 300 mJ/cm\textsuperscript{2}, whereas for Cdy-PVA this occurred at about 800 mJ/cm\textsuperscript{2}. This latter represented an empirical estimations of F\text{ab}. Contrarily to PVA, irradiation at F_{s\text{-ab}} of oil samples was characterized by accumulation of dark micro-dots which grew in number and in size with fluence until ablation at F\text{ab} occurred. Although morphologically slightly different, the type of microstructures observed for M081-Oil and M084-Oil paint films can be always associated with the nature of Cdy particles. Nucleation, density distribution and size of damaged spots were remarkably different at lower PVC. At 10 PVC, in [M] and [S] oil samples, micro damaged spots increased in the center of the spot but were more isolated in comparison to those observed at 20 PVC. Under UV-induced fluorescence, non-fluorescent inclusions of calcium carbonate were visible, and the occurrence of laser interactions (discoloration and ablation) seemed to occur both in correspondence of these large extender particles and in the nearby, thus indicating that the latter were not the main cause of alteration. However, at low PVC, the intensity of damage where present extender particles, was the most impactful. This result was even more evident at 2.5 PVC, where the Cdy particles can be considered evenly spaced. In fact, at 2.5 PVC and with increasing fluences, in Cdy-oil and PVA samples cracks and ablation craters were formed starting from extender particles. However, where the Cdy particles were more packed, a sort of darkening is appreciable, especially for oil films.

3.2 Quantitative assessment of surface laser interaction

Quantitative results of 2D image analysis upon multiple laser pulses irradiation tests are shown in Fig. 4. As the percentage area of laser-induced modifications at lower PVC (2.5 and 10) involved less than 1 % (i.e. quantitatively similar to sample defects), only those referred to samples prepared at 20 PVC allowed to be thoroughly analyzed.
Figure 4 Histograms illustrating changes in average size ($\mu m^2$) and percentage area ratio (%) induced by laser irradiation on dried and thermally aged Cdy samples (PVC=20) at sub-ablative fluences. Error is less than 5%. From the top to bottom: Cdy-Oil, Cdy-OilCo, Cdy-PVA, M081-Oil and M084-Oil. Inset images (1.2x1.2 mm$^2$) show the microstructures induced by laser at $F_{ab}$ with 5 laser pulses.

As shown, the density of the induced modifications within the laser spot differed significantly among the various prepared samples and evidenced the most intensive interaction was that induced on Cdy-Oil [M] and [S]. It is noteworthy that average size and area of the micro-dotted alterations grew almost linearly as function of laser fluence in most of paint samples studied, underlying that damage nucleation is size-dependent with fluence. As shown in Fig. 4, at the maximum fluence ($\approx F_{ab}$) the altered area fractions varied between 10 and 20 % for Cdy-Oil, M084-Oil aged, and between 3 and 6 % for Cdy-OilCo, Cdy-PVA and dried commercial paints (M081-Oil M084-Oil).

As mentioned above, M081 and M084 coatings generated a slightly different 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, similar alteration phenomena but less pronounced were observed.

On the opposite, average size and counts suggest that in PVA the ablative dynamics can be mostly
associated with the removal of coarser particle clusters with fluence, but without inducing significant darkening. The trend observed in oil-based coatings was instead the result of the average between large and very small damaged dots (lower than the measuring resolution of 6 µm²), in agreement with the sub-micron domain of the tiny CdS particles. 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 described before, 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.

Deeper information can be argued by the analysis of Feret diameter distribution displayed in Fig. 5.

![Figure 5](image)

**Figure 5** Comparison of Feret diameter distribution obtained for [M] and [S] dried Cdy paint films at F_{ab} and 5 pulses.

Apart to be similar in shape, all the distributions have a common feature, a characteristic mode value of about 5 µm (FWHM: ≈3 µm). Commercial formulations (M081 and M084) were characterized by distribution frequently peaked between 4.5 and 6 µm, thus suggesting a similar particles-size distribution. The double distribution observed in Cdy-PVA is mostly related to the larger extender particles, whose ablation occurred at 800 mJ/cm². This effect was not so evident in oil matrix because of the lower threshold fluences. Aging does not have an appreciable influence or it may be considered negligible in the present laser-induced mechanism. However, the characteristic mode value of about 5 µm (FWHM: ≈3 µm) gives a clear explanation on the nature of damage precursor. This result allows to state that particles with diameter lower than the mode value could be associated with agglomerates/ aggregates having a characteristic dimension of the order of incident wavelength.

### 3.3 3D reconstructions and heights distribution of ablated sites

An essential step towards the understanding of laser-irradiated effects is the depth characterization of defects, as depicted in 3D reconstructions and heights distribution of Fig. 6.
Figure 6 Examples of 3D reconstructions of manually mixed Cdy-OilCo a) and Cy-PVA b) paint films irradiated at $F_{ab}$ with 5 laser pulses. Plots showing heights (c-d) and effective radius to height ratio distributions (e-f).

The higher density of accumulated defects (i.e. darkening) and the low number of ablated sites in the irradiated spot did not make possible to accurately measure heights of holes in Cdy-Oil, M081-Oil and M084-Oil paint films. Instead, thanks to the limited darkening, 3D reconstructions in Cdy-OilCo and PVA samples revealed the morphology of laser-generated micro-holes, as well as their areas and density within the captured scene (Fig. 6 a-b).

First, comparison of heights distribution for Cdy-OilCo [M], Cdy-OilCo [S] and Cdy-PVA samples have indicated that micro-hole depths are evenly distributed in a 2-12 µm range, even if some dissimilarities were pointed out (Fig. 6c-d). In Cdy-OilCo [M] the 93 % of counts was between 2-8 µm with a predominant frequency of 25% peaked at 7 µm. Instead, Cdy-OilCo [S] seemed characterized by two different distributions, one in the 2-5 µm range and the other one between 6-9 µm, which cover the 46% and 44% of heights, respectively. This suggests heights are more evenly distributed in sonicated samples.
Heights distribution of Cdy-PVA \([M]\) and \([S]\) samples were more similar each other and differed markedly with respect to those of oil films. More than 90% of heights in Cdy-PVA films were between 2-8 \(\mu m\). However, as mentioned before, the effect of sonication may be barely appreciated, although it seems to take place with a different efficiency between the two binding media.

For a better comparison, \(R_{\text{eff}}/H\) distributions, where \(R_{\text{eff}} = \sqrt{A/\pi}\) and \(A\) is the area of the ablated crater, were calculated, as displayed in Fig. 6 (e-f). Cdy-OilCo \([M]\) and \([S]\) films showed \(R_{\text{eff}}/H\) distributions fairly different, whereas Cdy-PVA ones quite identical: a \(R_{\text{eff}}/H\) ratio of 5 and 3 was found for manually-mixed and sonicated oil films, respectively, and for both the PVA films instead it was 3, thus indicating a superior attitude of PVA as dispersant.

Most important, heights and \(R_{\text{eff}}/H\) distributions underlined that the observed laser-induced cratering effect took place in a well-confined depth range and is driven by a common mechanism, regardless to the type of binder. In addition, \(R_{\text{eff}}/H\) ratio is the evidence that etching depth is practically three times lower than the effective radius of the ablated area.

3.4 Vis-NIR PL emission and reflection

The above-discussed irradiation phenomenology is in good agreement with the changes observed in steady-state PL emission and reflection spectra shown in Fig. 7.

![Vis-NIR PL and reflection spectra](image)

*Figure 7 Vis-NIR PL and reflection spectra of aged Cdy-OilCo \([S]\) films (20 PVC) showing laser-induced changes occurring at 140 mJ/cm\(^2\) as function of delivered laser pulses.*

The response to multiple laser pulses in Cdy-OilCo paint films produced an overall decrease of 15-20% in the PL band of linseed oil component at 545 nm and in the broader emission of Cdy in the 700-900 nm range [21]. PL band at 790 nm (1.57 eV) assigned to deep-level emission of hexagonal-CdS was not affected in shape, as well as the other shoulders assigned to impurity ions and lattice defects. Likewise, it was detected a decrease of Vis-NIR reflection of about 15-20%, which is mostly related to the accumulation of laser initiating sites for damage (darkening). With the same fashion, no evidence of laser-induced chemical modifications were appreciated in PVA mixtures, where no PL contribution by the matrix was detected. The decrease of PL signals is only due to darkening of oil and removal of material, which affects the intensity of the backscattered light.
4. Discussion

The results achieved have shown that the lower is PVC and the greater the damage threshold fluence. The size of micro-damaged sites decreased with increasing PVC, while the number density increased and vice versa. At lower PVC the main contribution to alteration comes, at high thresholds fluences, from film defects, like the coarser extender particles, while Cdy particles resulted less involved. This was the first evidence that for high PVC (particles tightly packed) plays a crucial role on the occurrence of alteration the small-sized Cdy particles.

2D and 3D Image analysis carried out at 20 PVC allowed extracting meaningful quantitative information about the surface modifications induced by laser radiation at various exposure conditions. As shown, average size and number density distribution of alteration patterns were remarkably different among the various paint mixtures. The influence of the binding medium was unexpectedly greater than that due to the different blending methods (manual vs. sonication). Results suggests that cumulative heating of CdS particles in oil matrix are greater than in PVA. 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, film defects and fluence applied. For instance, Cdy-OilCo samples, irrespectively to any treatment (manual vs. sonication), showed an improved thermal stability in comparison to Cdy-Oil films, most likely due to the presence of Co-driers. Cdy-PVA presented a clean alteration morphology (darkening negligible) within the irradiated area, where any single feature was easily recognizable under microscope. Considering that Cdy-PVA films did not produce high quality coatings, the observed behavior it is likely 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 $\sim 218 \, ^\circ C$, 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 $^\circ C$ and does not undergo relevant thermal discoloration up to 100$^\circ C$. It was also been demonstrated that the presence of CdS causes a decrease in the decomposition temperature of the PVA by $\sim 20 \, ^\circ C$, thus confirming a strong interaction between PVA and CdS [22].

Most important, 2D image analysis suggested that laser-induced defects with diameter lower than 5 µm could be associated with Cdy agglomerates/ aggregates having a characteristic dimension of the order of incident wavelength. Likewise, 3D Image analysis has shown that the extension in depth of the laser-induced cratering is confined to 2-8 µm with a costant $R_{eff}/H$ ratio of about 3, which suggests a similar surface interaction mechanism regardless to the type of binder.

Further insights were assessed through ESEM-EDX analysis of Cdy-OilCo paint films and hard pellets without oil matrix (see Fig.8). First, rough estimation of particle-size distribution under ESEM confirmed that CdS particles have a characteristic size of 0.8-1 µm and are evenly distributed and embedded in the oil matrix over the whole painted surface. Furthermore, CdS particles aggregates up to 3-5 µm diameter were also observed. ESEM-EDX examinations clarified even more that the smallest craters had a diameter comprised between 2 and 5 µm (Fig.8 a). This size fits well with the explosion of initiating sites for damage of the order of incident wavelength, as the scattering cross-sectional area is usually greater than the physical cross-sectional area.
In combination to this mechanism a further contribution of different nature (i.e. defect-driven) was provided by the ablation of Cdy layers covering coarser extender particles (see Fig. 8 b), which occurs at higher threshold fluences. Therefore, their influence on the onset of sub-ablative effects may be reasonably neglected, as it is expected that CaCO₃ extender particles provide a scattering rather than an absorption contribution. Irradiation of pigment pellets confirmed what above described. At single-pulse threshold fluence of 450 mJ/cm², CdS particles showed a surface morphology more similar to a sublimation rather than melting (Fig. 8 c). The former occurs at 980 °C while the latter at 1380 °C [23]. As for PVA, darkening was absent in pellet. The onset for the partial ablation of Cdy in the sites occupied by CaCO₃ extender particles was observed after 20 pulses (Fig.8 d).

Furthermore, taking into account that CdS is a weakly absorbing material at 1064 nm (R in oil 85 %; optical penetration, δ= 70 μm), it can be argued that at sub-ablative fluences (range in oil 100-300 mJ/cm²), the absorbed energy will not be sufficient to generate temperature rises for inducing vaporization or melting. Therefore, localized darkening of oil matrix and cratering are triggered by a nonlinear change in the absorption of Cdy clusters with a critical size of the order of incident wavelength. One possible explanation to this type of laser initiated-damage is provided by the impurity theory, rather than avalanche and multiphoton ionization processes [23][24]. Basically, well-dispersed particles, being smaller than aggregates, absorb less total energy and hence is required additional energy for material removal to occur and be visually recorded as damage. As seen, this implied an exponential increase of the damage threshold fluences at low PVC. In contrast, in more packed systems (high PVC), aggregates with critical size absorb much more incident radiation and its temperature rises producing melting, vaporization, or stress fractures.

Conclusions

In this work, we have 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 draw the following conclusions:
• the lower is PVC and the greater the threshold fluence
• the size of micro-damaged sites decreases with increasing PVC, while the number density increase and vice versa
• at low PVC (2.5) the main contribution to alteration comes from film defects (coarse extender particles), while Cdy particles resulted less involved
• at certain PVC, the damage nucleation is size-dependent and density-dependent with fluence
• the effect of sonication is negligible both in threshold fluence and in the extent of laser-induced cratering effect. The same drawback was observed in commercial formulations, thus suggesting that particle aggregation is reasonably challenging to avoid (i.e. flocculation due to Van der Waals attractions).
• thermal aging of paint film did not have any influence on the extent of this mechanism
• the entity of the laser-induced damage is strictly dependent on the type of binding medium, and its thermal properties. Single-pulse threshold fluences were two-three times higher in PVA than in linseed oil.
• No darkening or negligible in PVA-mixtures
• the laser etching depth (2-8 μm) is almost independent from the type of binder
• laser-induced defects with diameter lower than 5 μm can be ascribed to Cdy aggregates with a critical size of the order of incident wavelength.

Finally, understanding the scattering phenomena and physical interactions between light and pigment particles is an essential step in understanding and controlling ablation effects of a paint film. In this regards, further studies will be devoted to study the pulse-width and wavelength dependence of the damage threshold and its relation with film thickness.

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