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Review Article

Laser Cleaning of Easel Paintings: An Overview

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The application of laser cleaning to paintings is relatively recent despite its use on stone-based materials for over 30 years. The cleaning of paintings is of high importance, because it is the least reversible invasive intervention, as well as the most usual of all conservation treatments. Paintings are multilayer system of heterogeneous nature, often very sensitive and inherent difficult to clean. Being a noncontact method, laser cleaning has advantages compared to alternative techniques. Over the last decade, there have been important research studies and advances. However, they are far from sufficient to study the effects on painting materials and to establish the best parameters for each material under investigation. This paper presents a historical overview of the application of laser technology to the cleaning of paintings giving special emphasis on the research of the last decade. An overview of the current research into the interaction between the radiation and the different painting materials (varnish, pigments, and medium) is also given. The pigment's mechanisms of discoloration and the presence of media as a variable factor in the discoloration of pigments are discussed.

1. THE LASER IN PAINTINGS CONSERVATION

The most widely used traditional techniques employ mechanical or chemical cleaning. The use of solvents applied over the surface may affect the pigments and medium in a nondesirable and nonreversible way because it is difficult to control penetration into the paint layers [1]. Gel formulations to control penetration can lead to problems of clearance from the surface. The integrity of the artwork can be also jeopardised because many layers to be removed are partially or totally insoluble in solvents. Mechanical action typically using a scalpel is another option but it presents an obvious danger by its physical action over the layers which can lead to the damage of the texture. The control of these techniques is in part dependant on the skill of the conservator and there is a border line between optimum cleaning and overcleaning.

Laser technology has great potential in the development of safer procedures for conservation because of its controllability and reproducibility. The application of laser technology to the paintings conservation field started in the earlier 1990s. This technology has always attracted much interest as it became the first technique that did not interact physically with the artwork, and thus was in accordance with the conservation principle of "minimum intervention." Lasers can remove layers that conventional techniques cannot remove safely [2]. For example, in the case of organic polymeric materials, excimer lasers are capable of removing layers with the resolution of 0.1 to 2.0 μm per pulse [3]. However, laser cleaning is an intrusive technique and should be used with good control methodologies. In general, every laser is effective, selective, and safe when used within certain parameters. For painted artworks, laser cleaning is one of the most delicate applications and requires a thorough study of the laser induced thermal, photochemical, and photomechanical effects in order to avoid damage of the paint layer.

1.1. Types of laser used in laser cleaning of paintings

Excimer laser

The term excimer is short for *excited dimer* and refers to the chemical medium of the laser: rare gas-halide mixtures. The excimer laser emits primarily in the UV region, at $\lambda = 193$ nm (ArF), $\lambda = 248$ nm (KrF), $\lambda = 308$ nm (XeCl), and $\lambda = 351$ nm (XeF). Excimer lasers are very effective due to the high absorptivity of materials characteristically employed in paintings causing minimal light penetration on the layers. Research has shown that 248 nm is the most promising wavelength for varnish and over paint layer removal [4–6].

The UV is strongly absorbed by the functional groups of the varnish and its degradation products.

Nd: YAG laser

Nd: YAG is the standard laser system for stone cleaning applications. Nd:YAG is an acronym for *neodymium-doped: yttrium aluminium garnet* (Nd: $Y_3Al_5O_{12}$) and emits typically on the near infrared region (NIR) at $\lambda = 1064\,\text{nm}$ (ω). More recently, this type of lasers have been developed to emit radiation at $\lambda = 532\,\text{nm}$ (2ω), $\lambda = 355\,\text{nm}$ (3ω), $\lambda = 266\,\text{nm}$ (4ω), and $\lambda = 213\,\text{nm}$ (5ω) multiples of the fundamental wavelength [7]. The infrared radiation tends to induce photothermal effects, capable of breaking bonds of inorganic materials. Although it is less efficient with organic materials because its energy is insufficient to break the covalent bonds, this type of lasers can lead to excellent results on the cleaning of painted artworks [8].

Er: YAG laser

This is the most recent laser tested for the cleaning of paints with successful results [9]. Er: YAG is an acronym for *erbium-doped: yttrium-aluminium-garnet* (Er: $Y_3Al_5O_{12}$). It generates a wavelength of 2.94 μm in the midinfrared region which is highly absorbed by OH bonds (in aqueous liquids). Consequently, the laser beam is quickly absorbed achieving very superficial ablation depths. Theoretically, the efficiency of the laser ablation is directly proportional to the amount of OH groups present in the materials. These OH bonds, when not present on the original material, can be obtained by the addition of hydroxylated liquids, which can also help to limit the radiation and heat penetration.

1.2. Historical overview into laser cleaning of paintings

Following their pioneering work with laser cleaning of stone, Asmus et al. studied the possibility of using laser technology to remove lime layers to uncover a mural painting by Leonardo da Vinci [10]. Although not published, the first paper reported about the potential application of the laser technology to the cleaning of easel paintings dates from 1981 [11]. It consisted in a preliminary study of the removal of varnish and dirt using two lasers working at 308 nm. Several undesirable consequences thought to be caused by the irradiation, nevertheless it was concluded that there was potential for laser technology with the need of further research. In 1986, some cleaning of mural paintings was attempted [12]. It was only in 1992 that the first paper was published reporting a scientific study about the use of excimer laser on easel paintings [13]. The investigation was based on the applicability of UV radiation on the ablation of varnishes and other deposits from painted surfaces. It was stated that the composition of both paint layer and dirt or over paint layers were of the most importance in order to determine the best laser parameters. It was also advanced, for the first time, the necessity to develop a database for a generalisation of the cleaning process due to the direct dependence of the laser parameters on the surface layer characteristics.

Since 1993, the Foundation for Research and Technology Hellas (FORTH) has conducted studies about laser development in order to assess their potentialities and limits on artwork cleaning applications. These studies included laser cleaning of surface layers and over paint, analysis of medium and pigments, imaging techniques for structural diagnostics, and authentication techniques.

In 1995, the first edition of the international workshop LACONA (lasers in the conservation of artworks) was organised to discuss the emergent application of laser technology to conservation. Its success turned this workshop into an international biannual conference in this field of research. Since then, lasers became better known to conservators and it consolidated the interest by the establishment of several research groups in Europe with several different material interests.

Cooper [14] published the first book entirely dedicated to laser cleaning of artworks in general. It includes an explanation of the laser principles and of the laser types. Despite the fact of being focused on sculpture on its several supports, mainly stone and metal, it includes a chapter especially dedicated to the developing laser cleaning of paintings [4]. Since then, and as the best of the author's knowledge, there was no newer published review of the literature concerning the laser application to paintings.

So far the only equipment built specifically for laser cleaning of paintings is a excimer laser, developed by a European consortium under an EU project between 1999 and 2001, which was one of the most relevant and comprehensive studies ever made [15, 16]. However, portable and flexible lasers for the cleaning of painted artworks are still not commercially available to the restorers. The main focus of the EU research project was the interaction of UV radiation on varnish and pigments in egg tempera medium and on the molecular changes to these materials by the UV radiation was investigated.

Over the last decade, several studies have been focused on the effect of UV radiation and also of infrared light and other regions of the electromagnetic spectrum on pigments and other paint materials [4, 7, 8, 17–21].

2. THE LASER RADIATION EFFECT IN PAINTING MATERIALS

A representative painting consists of a support or substrate (canvas, wood, or stone), a ground layer and several paint layers, each one of approximately 20 to 50 μm thickness, deposited over the former. The paint layer is a mixture of pigments and a medium to aggregate the pigments. Traditionally, the media is either egg tempera or oil (commonly linseed, walnut, and poppyseed). Furthermore, varnish used to be applied over the painting to serve as a protective layer and to provide colour saturation. A typical layer of varnish is about 50 to 80 μm thickness. During the aging process, two processes occur at the same time: three-dimension polymerisation and natural oxidation [22].

Several paint materials samples have been prepared by different authors to be tested by laser radiation, which range from pigments compressed into pellets to real paintings. In order to proceed with the cleaning, the laser radiation is fired into the layer to ablate, and once the protection layer has been removed (if present) the radiation will penetrate the paint layer if not prevented or controlled. This penetration into the paint layer can induce discoloration of the paint depending on the pigment material affected by the laser radiation. Discoloration of pigments is a serious problem; it can affect polychromies after laser irradiation depending on factors such as the nature of the material and the type and intensity of the laser used. It was suggested that photochemical modifications could occur from the radicals, and ions originated from the ablation could produce photo-oxidation products [23].

In order to prevent pigment discoloration, it has been proposed in [6, 24] that a thin layer of varnish should be left to avoid the radiation penetration into the paint layer. The study included several kinds of varnishes normally used and the energy transmitted by the laser was measured in relation to the ablation depth with an excimer laser at 308 nm. It was verified that fresh varnish is more transparent to UV light than older varnish. It was also suggested in the same study that for fresh varnish, after the first laser incidence, the surface suffers some modification and changes its absorption properties; the second incidence is more strongly absorbed and the material is ablated; furthermore, shots will irradiate fresh varnish. It was shown that freshly prepared varnish could not be representative of artificially or naturally aged varnish because of its different ablation/absorption behaviour.

On direct irradiation over paint material without protective varnish, several oxidation products were found and are explained due to a photodissociation of the pigments and that the radicals reacts with the oxygen present on the atmosphere or with the medium [25]. Although some studies suggested that the mechanism responsible for the discoloration of pigments was oxidation [26], latter studies suggested reduction as responsible for the blackening [27]. This process could be explained by a punctual scarcity of oxygen caused by the dense plasma which could lead to some compound's decomposition. Oxidation was also suggested as possible to occur after the irradiation is over and the heat dispersed.

2.1. The laser radiation effect on varnishes

Chemically, varnishes are normally tetracyclic or pentacyclic organic compounds with carbonyl or hydroxyl groups [22]. The UV radiation is strongly absorbed by the several varnish functional groups and its degradation products. Thus, general studies of UV laser effects on polymers/organic compounds have been used as starting point to the study of varnishes. Following these studies, Georgiou et al. [28] states that photochemical effects could be expected for the ions and radicals produced by the ablation process to be reactive and that photooxidation could take place during irradiation or in the long term. The same authors found chemical differences when comparing dammar and mastic varnishes under irradiation of 248 nm wavelength. The fact that dammar is characteristically a much weaker absorber to 248 nm than mastic seems to justify the related differences. It was also stated that depolymerization or cross-linking could occur. On a preliminary work, performed by Madden et al. [29], a set of 35 different materials, including varnishes, was studied. It was demonstrated that the reaction of both polymers and oligomers to laser radiation depends on their chemistry and preparation.

A study performed by Zafiropulos et al. [26] made some important findings on varnish irradiation. It was experimentally demonstrated that when the fluence increases the efficiency also increases until a maximum is achieved [15, 26]. This point is referred as the saturation point in the light absorption on the most superficial layers; at higher fluence the irradiation is transformed into thermal energy. Other important work on excimer laser ablation of varnishes (dammar, mastic, and copal oil) was performed by Theodorakopoulos [30]. His study focused on the organic chemistry of the aged coatings as a function of depth. It was demonstrated that the removal of 10–15 μm from the degraded surface layer of varnish causes no damage to the remaining film as was proven by the decreasing gradients in degrees of condensation, oxidation, and polarity [30].

2.2. Laser radiation effect on binding media

Although the interaction between traditional binding media and laser radiation has been the focus of some research, the amount of this work when compared with the research of pigment discoloration is small. The involved mechanism on the deterioration of the medium by laser radiation has not yet been full understood even though several theories have been proposed.

2.2.1. Laser radiation effect on egg tempera

The interaction of the radiation on egg tempera has been investigated by Teule et al. [17]. Chemical changes or physical effects such as discoloration have been observed when using an excimer-based laser ($\lambda = 248$ nm). The main problem found was the oxidation of the binding media although it was limited to the surface of the samples (<2 μm). The same conclusion was reached by Castillejo et al. [31] during a laser cleaning tests with KrF laser. The oxidation seems to be influenced by the presence of certain inorganic pigments. The analyses showed that unpigmented egg tempera samples after irradiation presented a low degree of chemical change. Comparison of the results between the organic and the inorganic samples on the same binding medium showed that in the presence of inorganic pigments there are alterations of the pigment and degradation and charring of the binding medium. The authors concluded that this can be attributed to oxidation and cross-link phenomena.

2.2.2. Laser radiation effect on oil

In preliminary work, Schnell et al. [32] prepared linseed oil samples containing different pigments. The authors irradiated samples containing pigments with low discoloration threshold with radiation at 1064 nm wavelength using $\sim$0.6 J/cm^2. The reaction products were analysed by nuclear magnetic resonance (NMR) spectroscopy. Glycerin, alkenes, alkanes, and aldehydes were detected in the gas phase and other nonidentified low-molecular products. It was suggest that the emitted gases were cooled down very fast due to adiabatic expansion induced by short pulses and therefore oxidation was prevented by the reducing atmosphere [32].

Bracco et al. [18] investigated the use of Er: YAG lasers on mock-up paintings. The gas chromatography-mass spectrometry (GC-MS) analysis revealed that between the ablated material and the untreated surfaces only minor alterations in the composition were noticeable. These alterations consisted basically in the decrease of the oleic acid content on the resinous and oil-resinous varnishes and a slight decrease of the hydroxylic components of the ablated materials. Fourier transform infrared spectroscopy (FTIR) analysis showed no change of composition before and after the irradiation, except some minor variations in the amounts of several polar substances and some small wavelength shifts of the absorption bands of esters from the ablated materials from resin and oil-resin varnishes [18, 33]. Zafiropulos et al. [26] looked at the possibility of cross-linking of oil. The authors found that after a successful partial removal of a varnish there was cross-linking of the underlying oil medium.

2.2.3. Laser radiation effect on acrylics

Acrylics are synthetic resins made by polymerising esters of acrylic acids. Real et al. [34] performed tests to remove over paints and other materials from acrylic substrates with 248 nm excimer laser, although his study did not cover the laser effect on acrylic paint. Using a fluence of 1.3 J/cm^2, the over paints were removed and also some of the acrylic layer, inducing a greyish discoloration. With a fluence of 0.21 J/cm^2, the over paints were removed but the acrylic layer appeared undamaged under the microscope.

2.3. Laser radiation effect on the pigments

The first study to consider the effect of laser radiation (Nd: YAG, excimer and dye) on pigments was done by Shekede [35–37]. It was essentially a qualitative study focused on the visual effects and how they were assessed. It was found that the removal of a coating produced changes on the underlying layer independently of the media type, coating material, or wavelength used. Generally, the studies made up to 1999 were not able to determine the physical/chemical changes that pigment discoloration introduced. Since then, some studies have been performed to assess this issue although a detailed comprehension of the discoloration has not been yet achieved. Some authors attribute pigment discoloration to chemical decomposition, phase changes [27, 38–40], or physical effects, such as melting [32].

Recent research using X-ray diffraction (XRD) on pigments attempted to understand pigment discoloration process [39]. The results showed crystalline phase and chemical composition changes and the authors suggested a structural modification within the volume of the pigment's particles near to the ablation threshold (i.e., minimum energy required for ablation). Pouli and Emmony [20] studied the reaction of some pigments to Nd: YAG radiation by the application of X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) to the altered surfaces and XRD to irradiated pigment pellets and compared the obtained results with heated samples. XRD curves did not yield new peaks which were explained by the amorphous nature of the reaction products or by the superficial alteration. Although there was discoloration of the pigment, the surface analysis showed similar results before and after laser irradiation [20].

It is known that the presence of a medium does affect the degree of discoloration of some pigments [19, 41]. The influence of the binding media nature on the discoloration of the paint layer is clearly evident in a study performed by Gordon Sobott et al. [38] which prepared samples of several pigments in different binding media. It has also been reported that binders are less sensitive than inorganic pigments when irradiated with 1064 nm radiation [32].

In a recent study, Chappé et al. [8] compared the influence of several laser wavelengths on ten inorganic and one organic pigments. It was concluded that in general the highest discoloration threshold occurs at 1064 nm. Nevertheless, it was also found that the samples show as well a high sensitivity to laser radiation at 355 nm and 266 nm. It was also concluded that the chemical reaction which by the pigments suffer the discoloration was due to laser induced heat. Sansonetti and Realini [19] studied Nd: YAG laser irradiation over samples prepared with six inorganic pigments and with linseed oil and gypsum as binders. It was observed that for the pigmented oil samples the lower fluence (0.1 J/cm^2) preserved the surface morphology while at the intermediate fluence (1 J/cm^2) some variation was observed and at the higher fluence (3 J/cm^2) the layers were ablated. Regarding the chromatic analysis, a change was observed for the low and intermediate fluences, although the low fluence only produced minor variation in lightness ($\Delta L < 1$). At the intermediate fluence, chromatic changes were always produced according the total colour variation ($\Delta E > 5$). It was shown by the authors that the chromatic changes are not directly proportional to the used fluences.

As confirmed by several sources [17], the intensity of fluorescence emission is considerably decreased after UV laser irradiation, which can be evidence of the binding medium degradation or due to the presence of impurities. The degradation of the medium may induce an alteration to the optical properties and contribute to pigment discoloration.

2.3.1. Lead pigments

Lead white ($2PbCO_3 \cdot Pb(OH)_2$)

Its darkening upon laser radiation has been attributed to the formation of plattnerite (PbO_2) as an alteration product

resulting from oxidation [42, 43], but more recently it has been attributed also to reduction phenomena [40]. Pouli and Emmony [20] demonstrated that under laser irradiation the pigment suffered only from a temporary blackening. The reduction assumption is supported by AES analysis which indicated the presence of elemental carbon after laser incidence [20] and by XPS analysis which revealed an increase of the amount of lead relatively to oxygen [40]. The temporary blackening [27] could be explained by the exposure to the air humidity and to CO_2 which induces the formation of carbonate-hydroxide complex above the PbO surface [27, 40, 44]. A study by Cooper et al. [41] suggested that presence of binding media affects the discoloration degree of the pigment, which was attributed to the conversion of basic lead carbonate into elemental lead on the surface.

Red lead or minium (Pb_3O_4)

This pigment is naturally unstable inducing a blackening mainly due to the transformation into Plattnerite (PbO_2) or galena (PbS) [45, 46]. Pouli and Emmony [20] performed heat tests of red lead, which showed to transform into yellow lead. As similarly with lead white, the incidence of laser radiation induced temporary darkening. Chappé et al. [8] refers that under laser irradiation the colour change occurs first to metallic-grey and with increasing energy density it changes back into orange probably due to a photochemical interaction. Like lead white, it has been found that graphite (C) and pure metal (Pb) [34] regained its original colour over one week. Gordon Sobott et al. [38] studied the pigment behaviour with different binding media and wavelengths and it was concluded that the discoloration could be attributed to the formation of lead oxides.

Yellow lead or massicot (PbO)

Pouli and Emmony [20] addressed laser induced discoloration of this pigment. They have showed that the pigment has a high decomposition temperature of over 1000°C. Although XRD analysis indicates no change on the direct heating tests, it was suggested that the observed blackening induced by laser radiation could be explained by the reduction of PbO to metallic lead.

Lead chromate or red chrome ($Pb(OH)_2 \cdot PbCrO_4)_2$

Gordon Sobott et al. [38] verified that under 248 nm wavelength radiation lead chromate became black up to 0.25 J/cm^2, and above 0.375 J/cm^2 pigment particles were removed.

Naples yellow ($BiVO_4$, $Pb(SbO_3)_2$ or $Pb(SbO_4)_2$)

Chappé et al. [8] studied this pigment (lead antimonate) showing that the discoloration is most evident at 355 nm and the colour change is probably due to a photochemical interaction. Pigment reduction seems to be typical of this pigment [31].

Chrome yellow (PbCrO4)

It has been suggested [31] that pigment reduction is typical of this pigment the same way as for the Naples yellow. Gordon Sobott et al. [38] verified that with 1064 nm wavelength the pigment reacted only slightly while with 248 nm it turned black.

2.3.2. Cobalt pigments

Cobalt blue ($CoO \cdot Al_2O_3$)

Chappé et al. [8] reported colour changes with the four harmonics of Nd: YAG laser, although it was concluded that this pigment is relatively stable under laser radiation. The measured discoloration thresholds were $\sim$0.5 J/cm^2 at $\lambda = 1064$ and 532 nm and 0.1 J/cm^2 at $\lambda = 355$ and 255 nm.

Smalt (potassium glass with cobalt oxide)

Gordon Sobott et al. [38] studied the effect of Nd: YAG laser on smalt mixed with several binding media (lime, casein, and linseed oil). It was demonstrated that smalt did not reveal any discoloration but suffers mechanical damage [35, 38].

2.3.3. Iron pigments

Yellow ochre (goethite, $Fe_2O_3 \cdot H_2O$)

Athanassiou et al. [47] has noticed that after UV laser irradiation the composition of this pigment changed from goethite to haematite (Fe_2O_3). Gaetani and Santamaria [48] have not verified any transition from yellow to red ochre (red ochre is prepared by heating yellow ochre). Sansonetti and Realini [19] reported that under low fluence at 1064 nm there was colour change although no morphological alteration was observed. The author also verified that at an intermediate fluence the oil layer was damaged. XRD showed that after laser irradiation there was a decrease of goethite [FeO(OH)] and an increase of Fe_2O_3, among other nonspecified variety of components [39].

Brown ochre (Fe_2O_3, $Fe_2O_3 \cdot nH2O$)

Chappé et al. [8] reported some colour changes into black. This pigment revealed to be very unstable and it was classified as suitable only for laser cleaning at 532 and 1064 nm wavelengths.

Raw sienna (goethite, FeO(OH))

Raw sienna is an iron-oxide pigment and it is quite transparent being easily affected by changes of the binder. Pouli and Emmony [20] found that it has a similar behaviour when compared with yellow ochre. Heat testing revealed that they transformed into red iron oxide (haematite).

Burnt sienna (haematite, Fe_2O_3)

This pigment was briefly studied by Pouli and Emmony [20] which performed laser testing with Nd: YAG at 1064 nm wavelength. The pigment revealed a slight darkening after 3 pulses with 0.3 J/cm^2 of fluence.

Red ochre (Fe_2O_3)

Sansonetti and Realini [19] prepared red ochre samples with linseed oil and gypsum as binders. It was observed that under a low fluence the oil samples suffered a colour change although no corresponding morphological alterations were observed and that the intermediate fluence caused total ablation. It was observed a strong discoloration and morphological alterations in the gypsum sample using the lowest fluence.

Green earth (complex aluminosilicate minerals)

Gordon Sobott et al. [38] verified the reaction threshold for green earth at 81.9 J/cm^2 when mixed with linseed oil and a severe ablation of the paint layer at 135.4 J/cm^2. The same study determined the absorption minimum of green earth at 536 nm.

2.3.4. Copper pigments

Malachite ($CuCO_3 \cdot Cu(OH)_2$)

Chappé et al. [8] defined it as highly sensitive to laser radiation changing its colour from green to black upon irradiation. Discoloration was attributed to the formation of oxides of copper. XRD analysis revealed the formation of $Cu_2CO_3(OH)_2$ and CuO [20]. Pouli et al. [27] suggested that the discoloration is due to the decomposition of copper carbonate and copper hydroxide components into copper oxide (black). Gordon Sobott et al. [38] indicates decomposition into copper oxide, carbon oxide, and water upon laser irradiation above the reaction threshold. As suggested by Teule et al. [17], the colour change of malachite can be due to the alteration to tenorite (CuO) and cuprite (Cu_2O).

Verdigris ($Cu(C_2H_3O_2)H_2O$)

Laser irradiation tests revealed that this pigment did not suffer any discoloration [20, 27]. Furthermore, the increase of fluence or pulse number resulted in spallation rather then discoloration [28]. XPS was reported as not being able to find chemical changes. It was suggested to try other approaches in order to certify that no changes are occurring.

Azurite ($2CuCO_3 \cdot Cu(OH)_2$)

Gordon Sobott et al. [38] verified the appearance of cuprite which indicates decomposition into copper oxide and carbon oxide upon laser irradiation above the reaction threshold. A similar reaction was verified on malachite.

2.3.5. Other metal oxide pigments

Chromium oxide (Cr_2O_3)

Sansonetti and Realini [19] refers to colour change under low fluence (<0.1 J/cm^2) but no morphological alteration was observed. Under intermediate level of fluence it was observed loss of material. Chappé et al. [8] found the pigment as stable under the four harmonics of Nd: YAG laser although discoloration was verified from a dark-green into grey. The measured discoloration threshold was 0.17 J/cm^2 for $\lambda = 1064$ nm and $\sim$0.1 J/cm^2 for $\lambda = 532$, 355, and 266 nm.

Zinc white (ZnO)

Chappé et al. [8] reported colour changes into grey upon laser irradiation due to the reduction of ZnO into Zn, according the authors. It is also reported that the discoloration reverses to white after a week. After laser irradiation at 0.6 J/cm^2 (at 1064 nm) discoloration into brown/grey was reported [32]. Environmental scanning electron microscope (ESEM) analysis revealed melting points of 1 micron thick or less, being the melting point of ZnO 1975°C.

Titanium white (TiO_2)

This pigment turned into a bluish grey tone using 0.6 J/cm^2 (at 1064 nm) of fluence [32]. Although the melting point of TiO_2 is 1855°C, ESEM revealed melting points on the incidence area. It was advanced that the discoloration could be caused either by physical effects through the increase of the particle size, or by the chemical decomposition of the metal oxides [32].

2.3.6. Other pigments

White gypsum ($CaSO_4 \cdot 2H_2O$)

It was studied by Sansonetti and Realini [19] who refers to white gypsum as very stable showing no chromatic or morphologic changes until 3 J/cm^2 of fluence is used.

Black bone (C)

Sansonetti and Realini [19] reported Nd: YAG laser irradiation of 0.1 and 1 J/cm^2 on bone black pigment with oil and gypsum medium. On the oil samples, the low fluence induced no morphological or chromatic alteration while some changes were observed (grooves with corroded edges on the surface) with intermediate fluence.

Vermilion or cinnabar (HgS)

Vermilion is in a metastable equilibrium of two isometric phases, red hexagonal cinnabar (α-HgS), and black cubic (α'-HgS) metacinnabar [20]. This pigment changes its red colour to black by a light-induced phenomenon probably due to a

photochemical interaction [49]. Although these phases have the same chemical composition and molecular weight, they have different properties. Pouli and Emmony [20] reported that its discoloration is permanent when using laser irradiation at 0.3–0.5 J/cm^2. AES and XPS showed an increase of carbon and of the Hg/S ratio. It was suggested that this was explained by the formation of black mercuric sulphide (Hg_2S). Abraham et al. [50] advanced the possibility that the discoloration was due to conversion to meta-cinnabar which was confirmed when it was found that under laser radiation cinnabar changed from a red hexagonal crystal structure into a grey-black metacinabar cubic structure [8, 39]. This modification is almost independent of the wavelength. However, XPS analysis suggested the presence of Hg_2S and Hg after irradiation and that this chemistry change contradicts the previous hypothesis justified by the fact that such modification would not affect the Hg/S ratio and would not introduce new species of Hg [27]. Furthermore, scanning transmission electron microscopy (STEM) analysis confirmed no change in the crystal shape. However, Schnell et al. [32] revealed in their study that cinnabar was the only pigment to suffer a phase change, which was detected by XRD.

Ultramarine ($Na_{8-10}Al_6Si_6O_{24}S_4$)

Sansonetti and Realini [19] refer a discoloration (on oil samples) at a low fluence (0.1 J/cm^2), which is stable until an intermediate fluence (1 J/cm^2) is used. No morphological changes were observed by the authors with this range of fluence when using a microscope. The same author observed a good morphological resistance under laser irradiation independently of the used fluence on gypsum samples. However, it was observed a strong colour change under the lowest fluence although it was not proportional to the used fluence. It was verified by Chappé et al. [8] that ultramarine pigment is a highly stable pigment. The pigment, upon laser irradiation, only showed some degree of discoloration (from dark blue into white) after some high threshold is reached. Thus, it was classified as suitable for laser cleaning with each of the four Nd: YAG laser wavelengths. It was advanced the possibility that the observed discoloration could be motivated by the presence of a mineral (Nosean) although its presence could not be definitively proved.

2.3.7. Organic pigments

The samples that have been presently studied have shown a high degree of stability under intense laser treatment [31]. The ablation of organic material leads to the formation of a thin layer of char that covers the paint surface. Castillejo et al. [31] have demonstrated that this layer is not produced in the absence of inorganic materials in the paint. This seems to indicate that the pigment particles mediate the char formation through an energy transfer mechanism.

Madder lake (Al-Ca complex salt of alizarin)

Under laser irradiation, this organic material changes its red colour to white. This discoloration was observed in all the Nd: YAG laser wavelengths tested with the exception of 1064 nm where the threshold was higher. No chemical explanation could be given.

Curcumin ($C_{21}H_{20}O_6$)

Castillejo et al. [31] determined that the colour of this organic pigment remained practically unaltered under UV excimer laser radiation (248 nm) using low fluence of irradiation (0.11 J/cm^2). However, at higher fluence (0.4 J/cm^2) the pigment reveals a slight discoloration.

3. REAL EASEL PAINTING TESTS

Apart from the tests in samples and mock-ups, real paintings have been used to test laser cleaning. Teule et al. [2] performed the study of the treatment of two oil paintings severely damaged in a fire using an excimer laser. Both paintings presented several hard problems that were not possible to treat by conventional techniques. The first painting had suffered discoloration due to high temperatures and soot that was located on the top of the paint layer, while on the second painting heat caused detachment of the paint from the support and hard and brittle blisters were formed. Tests with solvents were performed but none was able to remove the layer successfully without damage on the paint layer. Furthermore, it would also result on the penetration of soot particles into the painting. Physical contact was not advisable as it would cause delamination of the paint layer as well. In the first case, a moderate fluence of 0.38 J/cm^2 was applied while the second painting was irradiated at 0.41 J/cm^2. No discoloration of the paint layer was visible and the surface texture remained intact as well. Similar work on another painting was also described by Teule et al. [17]. The main problem in this case was a yellowed varnish. The painting presented also some burnt retouching due to past interventions. In order to proceed to a relining, it was required the removal of these interventions as well of the varnish. The use of solvents was not desirable as it would have deeply penetrated the dry paint layers. An energy fluence of 0.43 J/cm^2 was then used to remove successfully the retouchings and fillings. During the process, the original paint layer was irradiated with a 248 nm excimer laser and no discoloration or change was detected. However, the lead white that had been used on the retouch turned grey, although it is mentioned that it did regenerate. In order to prevent pigment discoloration, it has been proposed [24, 28] that a thin layer of varnish should be left in order to avoid the radiation penetration into the paint layer. As mentioned by Hill et al. [24], this layer should have a thickness of the order, or greater than, of the optical penetration depth.

An Nd: YAG laser was also already used to clean an icon covered by candle soot and dirt over sensitive silver layer and an uncharacterized yellow layer [7]. It was found that the wavelength of 355 nm was the most efficient wavelength to the removal of the soot and dirt without damaging the underlying layers.

It has also been reported [18] that several real easel paintings were cleaned using Er: YAG laser. The laser was used to

gradually remove an egg-tempera over paint which showed to be of difficult removal by both solvent and mechanical cleanings. It was stated that the layer was removed with success without affecting the original layer despite no online characterisation technique is mentioned.

The potential of the laser to remove overpaintings from a contemporary painting was assessed by McGlinchey et al. [51]. On this study, it was used mock-up samples for a first assessment and later the real painting with Nd:YAG and excimer lasers. The overcleaning removal was successful and it was concluded that the laser irradiation were viable for small areas.

4. CONCLUSION

Laser research is nowadays focused on the development and enhancement of the controllable removal of layers, either protective layers, such as varnishes, or over paint layers. The direct incidence of laser radiation into the paint layer usually induces discoloration of the paint materials, which depends on factors such as the nature of the material and type and intensity of the used laser. The discoloration mechanism has been studied and it has been concluded that it is due to oxidation and reduction phenomena depending from the irradiated material. A complete knowledge of the interaction between the laser radiation and pigments, binding medium and varnish involved is necessary before the actual cleaning procedure. Further research on samples is necessary in order to fully understand the interaction laser material.

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