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# Laser yellowing

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**Abstract.** Over the past few years there has been an increasing interest in researches related to the application of lasers in conservation, analysis and diagnostics of artwork surfaces. Among the many interesting problems to be tackled, one issue was drawing more interest because of the limitations it can impose on the use of lasers. Laser yellowing is a phenomenon wherein artwork surfaces assume a yellow hue when cleaned with Q-switched Nd:YAG (1064 nm) lasers in particular. Here the effect of yellowing has been studied and quantified for artwork surfaces (marble) using SFR Nd:YAG and LQS Nd:YAG lasers. Colorimetric measurements by employing a spectroradiometer helps to quantify the effect of yellowing by analysing three variables (chromaticity coordinates) of interest.

**Keywords.** Laser; laser yellowing; Mie scattering.

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## 1. Introduction

Lasers are used for the removal of undesired encrustation layers developed during environmental degradation of surfaces. Pulsed lasers are generally used for cleaning artwork surfaces. Nd:YAG lasers are among the most employed systems that are fibre-coupled with versatile hand peices for laser controlling. Nd:YAG lasers are quite effective in cleaning stone artefacts such as marble, dolomite etc., as they absorb contamination very strongly while the underlying substrate is left untouched thus rendering the process self-limiting. It is generally not preferable to remove the whole encrustation as a certain part of the encrustation layer retains information of the authentic underlying surface. The general commitment in laser cleaning is the preservation of stable oxides such as cuprite layers on valuable coatings such as gilded bronzes often called as patina by conservators. Laser yellowing [1–3] a phenomenon wherein artwork surfaces assume a yellow hue following the cleaning of surfaces such as stones, metal, paper, plaster etc. with Q-switched Nd:YAG (1064 nm) lasers, in particular, has been of major interest of late due to the limitation it imposes on the use of Nd:YAG lasers. Several reasons, from pre-existing yellow layers (so called patina) underneath the black encrustation to physiochemical alteration to early signs of substrate damage, have been cited. Laser yellowing is, however, not reported during cleaning with other harmonics and with other cleaning techniques like microsand blasting. In this work, laser yellowing on marble surface contaminated with two different encrustations, using short free running Nd:YAG and long Q-switched Nd:YAG laser systems, is studied and the possible reasons for yellowing have been identified.

The marble artworks ($CaCO_3$), in the presence of reactive $SO_2$-atmosphere, heat and humidity, develops a superficial (few $\mu$m thick) gypsum layer ($CaSO_4 \cdot 2H_2O$) and after many years an outer black layer (some $\mu$m to several 100 $\mu$m-thick rich in pollutants like carbon particles, aluminosilicate particles, Fe etc.) will be formed on gypsum layer (that acts as binder). Cleaning with fundamental of Q-switched Nd:YAG results in the embedded dark particles being selectively vapourized while preserving the gypsum-based layer (maintaining the gypsum-rich layer considered as the patina by many conservators while selectively removing the dark particulates is considered to be the greatest advantage of Q-switched Nd:YAG laser cleaning of stone). The selectivity is due to higher absorptivity (3–4 times) of 1064 nm radiation for black particles than for the gypsum layer or the marble substrate (self-limiting). The undesired after effect however is the final yellowing of the substrate. Yellowing is also noticed during cleaning at higher fluence causing spallation of gypsum besides explosive vapourization of embedded particles. When using the third harmonic of a Q-switched Nd:YAG the removal mechanism is spallation with each pulse removing a certain amount of material without selectivity (i.e. particles and gypsum absorb equally) but no yellowing is observed in this case [4].

## 2. Experimental work

The experiments on laser yellowing were carried out using SFR Nd:YAG and LQS Nd:YAG lasers. Polished white cararra marble slabs of 8 cm × 2 cm × 1 cm dimension was taken. The marble surface was covered with a mask with holes of diameter ∼5 mm to selectively reveal the substrate surface and these uncovered regions were contaminated with black encrustation which was irradiated to study the laser yellowing. Here, two kinds of contamination were used to form encrustation layers that closely resembled the actual contamination found on artwork surfaces. Imitating the contamination found on metal surfaces and paper artworks, was a genuine powdery black encrustation (the black crust was obtained from a naturally aged marble) of a few microns thickness that was smeared under dry conditions. The other encrustation involved a binding medium (gypsum matrix) in which these black particles were mixed (97% gypsum and 3% black encrustation) simulating stone contamination. A fresh region of the sample surface was irradiated each time. The laser yellowing was studied as a function of incident laser fluence and pulse number. The irradiated regions were observed under optical microscope (100×) to find the effect of yellowing and to ascertain and quantify the extent of yellowing, colorimetric analysis of the irradiated surface was carried out. A PR-704 fast spectral scanning system (spectroradiometer) was used for the spectral analysis and thus the colour/luminescence measurement. The CIE-lab system essentially calculates three variables whose values indicate the resulting colour change. The parameter $L^*$ describes brightness, the positive (negative) values of the chromaticity coordinates $a^*$ and $b^*$ signify whether the treated sample is redder (greener) and yellower (bluer) respectively with respect to the reference sample (99% reflective lab sphere white standard). Change of $b^*$ parameter in the CIE $L^*a^*b^*$ colour scale with respect to unsoiled substrates ranges from +4 to +10 units (an indicator of yellowness of the surface). A clean white surface has $b^* \sim 0$. Colorimetric measurements were carried out before and after laser irradiation.

## 3. Results and discussion

Experiments carried out with SFR Nd:YAG laser has revealed yellowing even when the contaminated surface was exposed with a single pulse for incident fluence varying from ~12 to 24 J/cm$^2$. This resulted in the value of $b^*$ to vary from 6.4 to 7. Pulses of varying duration (20–40 $\mu$s) with pulse energies varying from 200 to 400 mJ focussed to a spot of 1.4 mm size were used in the study. In another experiment, when the contamination, applied under dry conditions, was undone by dabbing and then thoroughly cleaned with alcohol, the subsequent laser irradiation did not result in yellowing ($b^* \sim 0.1$) showing that yellowing occurs during the laser cleaning of contamination. The presence of soiling residues formed by laser radiation is a possible reason for laser yellowing.

The laser yellowing was also noticeable during cleaning with LQS Nd:YAG (75 mJ, 100 ns) laser. Pulses of varying fluence (0.8–1.8 J/cm$^2$) were used to see the effect. Irradiation with a single pulse did not result in yellowing ($b^* \sim 1.342$) as the energy of the laser beam was absorbed mostly in the contamination and only resulted in scattered melt comprising coarse and micron-sized particles on the surface. Cleaning the substrate with alcohol (to wipe off the residues) here resulted in the retrieval of the clean surface without any yellowing ($b^* \sim -0.11$). However, multiple irradiation without cleaning the substrate (containing the scattered melt material formed during initial exposure) resulted in yellowing at all the fluences ($b^* \sim 4.5$–$7.0$). The yellowing of the surface increases with the number of pulses and thereafter saturates quickly at $b^* \sim 4.11$ (studied at ~0.93 J/cm$^2$). Also, the coarse particles tend to get finer with each irradiation. Hence the resulting moderately clean surface now consisting of micron and sub-micron particulates gave it the yellow hue ($b^* \sim 4.11$). Here, a thorough wiping of the surface with alcohol resulted in reduced yellowing ($b^* \sim 2.64$) leading to the conclusion that the presence of micron particles can give rise to yellowing due to Mie scattering. A particle is a Mie scatterer if $D > \lambda$, $D < \lambda$ or $D \sim \lambda$ and a Rayleigh scatterer if $D \ll \lambda$, where $D$ is the scatterer size and $\lambda$ is the wavelength used. A higher irradiating fluence of ~1.8 J/cm$^2$ at this stage results in the sudden increase in yellowing of the surface as vindicated by the change in the $b^*$ parameter from 2.64 to 12. The sub-micron particles (the melt redeposit too) that were otherwise difficult to be cleaned with the low fluence (~0.93 J/cm$^2$) could now be removed or transformed by the incident higher fluence (~1.8 J/cm$^2$). The optical microscopy also revealed that the irradiated surface with particulates and re-deposited melt, shrunk in size but the effective area over which these particulates/redeposited melt were spread was large. These submicron size particles were scattered on the surface and were difficult to be removed due to their size resulting in the yellow hue.

From the studies, it can be surmised that yellowing is observed in both SFR and LQS Nd:YAG laser cleaning of black encrustation on marble. Also, from the experiments it can be concluded that the yellowing is neither due to any natural cause nor due to the pre-existing patina but it is due to laser cleaning. The presence of soiling residues and deposited/re-deposited laser ablated products that have become more difficult to be cleaned because of the laser treatment can be the reasons for yellowing. Also, the light scattering resulting from void formed by the selective removal in the case of contamination embedded in gypsum matrix can be emphasized [5]. Further experiments with a different encrustation together with SEM analysis can also help in detecting any compositional change of residues resulting in laser yellowing.

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