

Optimised pulse duration for the laser cleaning of oil gilding^(*)

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Summary. — The laser cleaning problem of gold leaf gilded surfaces was investigated here. Preliminary irradiation tests carried out on pure gold leaf standards evidenced the crucial importance of the laser pulse duration for avoiding serious damages. Optimised pulse duration providing good cleaning results with negligible side effects was then selected and successfully used in the restoration of three Renaissance masterpieces.

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1. – Introduction

Laser cleaning of artwork was thoroughly investigated along the last decades. The most significant results were achieved for stones where the real effectiveness and advantages of the ablation by Nd:YAG laser systems with respect to conventional techniques were widely demonstrated (see for example the many works published in [1]). Conversely, up to now a few successful studies on metal cleaning were reported [2], along with case studies evidencing unacceptable micro-melting and discoloration effects [3]. Efforts were devoted to overcome these problems by using different harmonics of Q-switching (QS) Nd:YAG lasers (1064, 532, 355, 266 nm) and in some cases excimer lasers [3, 4]. In the present paper we demonstrate a different approach based on the suitable selection of the laser pulse duration [5, 6]. The analysis of preliminary irradiation tests on gold leaf standards allowed selecting the microsecond domain as the best one for cleaning oil (mordant) gilding. This methodological result was successfully applied in the cleaning of gilded decoration of two bronze masterpieces, such as the *David* by Andrea del Verrocchio and the *Attis* by Donatello, and of the marble sculptural group known as the *Santi Quattro Coronati* by Nanni di Banco.

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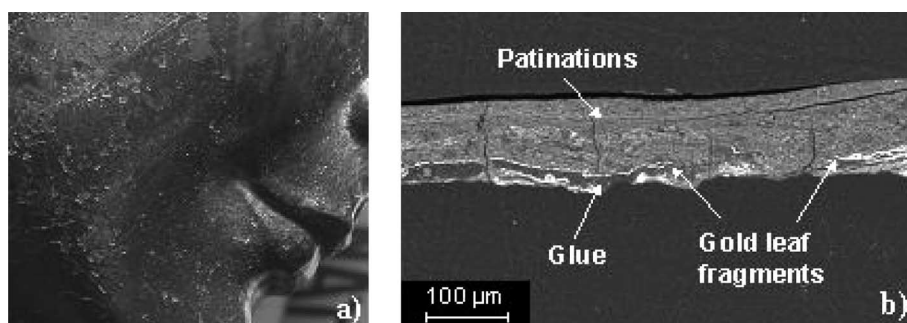


Fig. 1. – David by Andrea del Verrocchio: a) incoherent brown-black patinations on the face, b) BS-SEM stratigraphy of a sample from a gilded zone.

2. – Materials and methods

From a physical standpoint, the cleaning problems encountered in the restoration of the three artworks just mentioned were very similar. For this reason we describe in some details only one of them. Traces of gilded decorations of the *David* by Andrea del Verrocchio were totally covered by a series of coats ranging from brown to black in colour, the so-called bronze-like patinations. In fact, the gilding is not even mentioned in the detailed nineteenth-century descriptions of the statue, as well as in more recent works. The state of conservation was investigated using optical and SEM-EDX microscopy for stratigraphic characterisation, FT-IR to analyse stratified compounds, and gas chromatography for a clear identification of the binders and protective treatments. Bronze-like patinations were realised with earths, ochres and carbon black pigments in a linseed oil matrix (binder). They also include dispersed copper minerals produced by corrosion of the metal substrate.

Figure 1 displays a surface detail with irregular distribution of the stratified patinations (see also fig. 3 and fig. 4a showing the similar situation of the *Attis*) and a cross-section of a sample taken in a gilded area, as observed by back-scattered electrons SEM microscopy. Figure 1b along with EDX elemental analysis clearly revealed pure gold-leaf gilding applied with linseed glue and completely covered by relatively thick coats. The thickness of the gold leaf was measured directly on micro-fragments, *i.e.* without any preparation of the samples, which provides more reliable values. We took measures on various fragments similar to those of fig. 2.

The measured thickness in the present case was between 0.18–0.55 μm . Anyway, lower values cannot be ruled out since it is well known the Renaissance gold leaf can reach minimum values around 0.1 μm . Preliminary irradiation tests have been performed on 0.1 μm thick gold leaf standards whose surface reflectance at 1064 nm was 93%, as directly measured using an integrating sphere. Despite it was not possible to measure the reflectivity of the genuine gilding, because of the small sizes and strong incoherence of the gold fragments under investigation, it is expected to be very close to this latter value. In fact, the standards were handicraft products realised by a very similar technique as during the Renaissance. Damage thresholds of the standards under laser irradiation were measured both in thermally insulated condition and with the standard glued to a silicone substrate with known thermal properties ($K_s = 0.29 \text{ W/mC}$, $D_s = 1.08 \times 10^{-7} \text{ m}^2/\text{s}$). Commercial QS, Long Q-Switching (LQS) and Short Free Running (SFR) Nd:YAG (1064 nm) laser systems providing pulse duration $t = 8 \text{ ns}$, 120 ns, and 50 μs , respectively, have been employed throughout preliminary trials and cleaning tests on artworks.

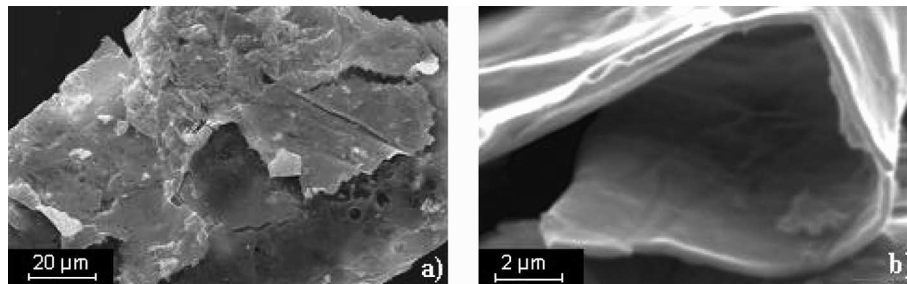


Fig. 2. – SEM details of gilding remains found on the David by Andrea del Verrocchio: a) surface view showing the fragility of the gold leaf because of the fragmentation (see also fig. 1b) and weak adhesion to the substrate; b) cross view of the gold leaf showing the sub-micron thickness.

3. – Results

QS-Nd:YAG produced ablation of the gold leaf at the absorption fluence $F_{\text{ath}} = 63 \text{ mJ/cm}^2$ ($F_{\text{th}} = 906 \text{ mJ}$), without any dependence on boundary conditions. For SFR the ablation (damage) threshold for insulated and glued gold leaf were 69 mJ/cm^2 and 291 mJ/cm^2 with an uncertainty of about 20%, as estimated through a number of measurements. The corresponding threshold values for LQS Nd:YAG laser ($t = 120 \text{ ns}$) were 40 and 60 mJ/cm^2 , respectively. The cleaning tests on the genuine gold leaf decorations, covered with organic binder patinations, revealed no possibility to safeguard the fragile gold leaf fragments when using QS and LQS lasers. The removal of the patinations was very efficient at operative fluences around 700 mJ/cm^2 ($F_a = 49 \text{ mJ/cm}^2$) but at this irradiation level also the gilding fragments were removed. Conversely, a safe cleaning was achieved using SFR laser with pulse duration of $50\text{--}70 \mu\text{s}$ in water-assisted condition, *i.e.* by spraying water on the surface under irradiation. Figure 3 displays the corresponding two tests performed on the gilded belt of the *Attis* by Donatello. It is worth noting that the degree of safeguard shown in fig. 3b would be not achievable using any chemical and mechanical approaches.

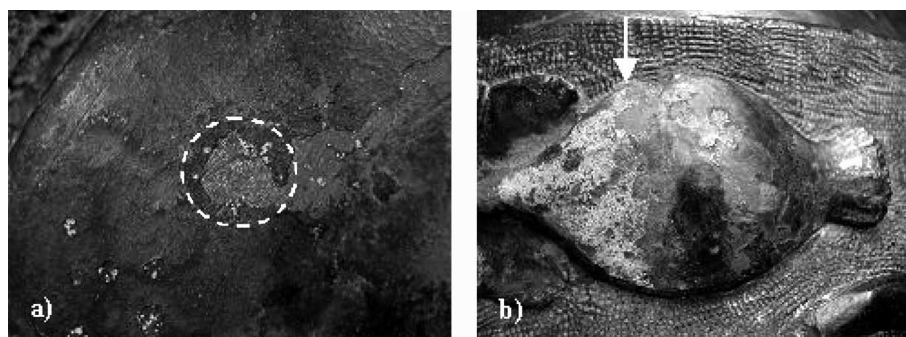


Fig. 3. – Cleaning test on the gilded belt of the *Attis* by Donatello: a) lack of discrimination by QS-Nd:YAG laser; the circle indicates the irradiated area where the gilding was completely removed by a single laser shot; b) effective and safe cleaning by SFR-Nd:YAG laser; the arrow shows the transition between cleaned (left) and not cleaned (right) zones.

The operative fluences for the *David* and *Attis* were between 1.5–2 J/cm² and about 3.5–4 J/cm² for the *Santi Quattro Coronati*. The damage thresholds were slightly above the operative fluence: 2.5–3 J/cm² and 5–6 J/cm², respectively, as assessed while irradiating gilded areas under stereomicroscope observation. The wetting of the surface during the irradiation resulted to be very important for avoiding serious damages, especially for gilded bronzes because of the high absorbance of copper minerals surrounding and covering the gold leaf fragments.

4. – Discussion and conclusions

The results of the irradiation and cleaning tests summarized above evidence the crucial importance of the transient heating induced by direct laser irradiation of the metal surface and the need to control it by a suitable selection of the laser pulse duration. The critical fluence for melting F_{am} and vaporisation (boiling) F_{ab} of a gold leaf of thickness l in insulated condition is provided by the following equations:

$$(1) \quad F_{am} = \rho_g \times l \times (C_g \times \Delta T_m + H_m),$$

$$(2) \quad F_{ab} = \rho_g \times l \times (C_g \times \Delta T_b + H_m + H_g),$$

where ρ_g is the density of gold, C_g its specific heat capacity, H_m and H_b its latent heat of melting and vaporisation, respectively. By substituting the parameters, we find $F_{am} = 40.7$ and $F_{ab} = 358$ mJ/cm². The comparison with the experimental damage thresholds associate with LQS Nd:YAG laser irradiation in insulated condition (40 mJ/cm²) suggests it is mostly determined by melting of the gold leaf (thermal interaction regime). This holds also for SFR laser. The higher threshold in this latter case (69 mJ/cm²) can mainly be attributed to possible thickness fluctuations, being the losses due to the lateral thermal conduction, convection thermal transfer, and defocusing effect produced by air turbulence negligible. Actually, the corresponding values of the thermal diffusion length ($\delta_{\text{ther}} = 205$ μm), convection transfer coefficient (1–100 W/m²C), and the refractive index modulations are really low to provide relevant contributions. Despite also the damage threshold of QS laser ($F_{\text{ath}} = 63$ mJ/cm²) is not far from the estimated melting threshold, its higher value with respect to LQS laser and the corresponding high intensity suggest an important role could be played by ionisation and optical breakdown. In fact, the damage intensity $I_{\text{ath}} = 1.1 \times 10^8$ W/cm² is relatively close to the breakdown threshold for gold mirrors reported in the literature. Thus for example in [7] $I_{\text{th}} = 6.6 \times 10^8$ W/cm² that corresponds to $I_{\text{ath}} = 1.6 \times 10^8$ W/cm² whether considering roughly the present absorption scale factor (7/1.5).

The gluing to the silicone substrate produces an increase of the damage threshold because of the thermal conduction. For SFR laser the effect is more pronounced than for LQS laser, which allows a larger cleaning operative range in the former case. Temperature estimations can be achieved by considering the film as a surface layer [8]:

$$(3) \quad \Delta T = \frac{I_a}{bK_i} \left[2b \sqrt{\frac{D_i \times t}{\pi}} \times e^{-\eta^2} - (1 + bz) \operatorname{erfc} \eta + e^{b(z + D_i \times b \times t)} \operatorname{erfc}(\eta + \sqrt{D_i \times t}) \right],$$

where the index i stays for insulating substrate, $\eta = z/2(D_i t)^{1/2}$, $b = r_i C_i / C_{g1}$, with C_{g1} thermal capacity per unit area of the gold layer. For pulses of tens of microseconds the temperature provided by eq. (3) only slightly lower than the one of the semi-infinite solid solution:

$$(4) \quad \Delta T = \frac{2I_a}{K_i} \sqrt{\frac{D_i \times t}{\pi}}.$$

Here, at the SFR laser threshold ($F_{\text{ath}} = 291 \text{ mJ/cm}^2$) the two equations provide $\Delta T = 506$ and $527 \text{ }^\circ\text{C}$, respectively. Such a damage temperature is compatible with the pyrolysis of the silicone rather than with the melting of the gold leaf. Conversely, for LQS laser the situation is more complex. The temperature values provided by eqs. (3) and (4) are significantly higher and very different (1160 and $2217 \text{ }^\circ\text{C}$) because the thermal diffusion length of silicone is short (228 nm) and it is of the same order of magnitude as the gold leaf thickness. No ablation is observed well above the thermal decomposition threshold of silicone since the damage is likely very localised within possible microporosities and other irregularities in close proximity of the gold leaf. Thus the ablation starts at higher temperature values were both the direct melting of the leaf and the explosive phase change of a thin silicone layer can provide significant contributions. The operative fluences of SFR laser ($50 \mu\text{s}$) to clean gilded decoration of the *David*, *Attis* ($1.5\text{--}2 \text{ J/cm}^2$), and the *Santi Quattro Coronati* ($3.5\text{--}4 \text{ J/cm}^2$) correspond to absorption fluences of $105\text{--}140 \text{ mJ/cm}^2$ and $245\text{--}280 \text{ mJ/cm}^2$, which are lower than the damage threshold of glued standards. Conversely, the damage threshold measured for the gilding of the *Santi Quattro Coronati* was higher than the one of the glued standards likely thank to the favourable thermal properties of the substrate. In particular, the mineralisation processes of the linseed layer could result in a significant increase of thermal conductivity, up to a factor of ten for Ca-oxalates layer, which is the typical mineralisation result on carbonatic stones. On the basis of the present optimisation study, gilded decorations found on the *David*, *Attis* and *Santi Quattro Coronati* were completely cleaned using a SFR Nd:YAG laser with a pulse duration around $50\text{--}70 \mu\text{s}$. A detail of the fine result achieved on the gilded belt of the *Attis* by Donatello is shown in fig. 4.

In conclusion, the present work demonstrates the best laser solution for cleaning mordant gilding is represented by SFR Nd:YAG lasers, whereas nanoseconds laser (QS and LQS Nd:YAG lasers) should be avoided. Such a conclusion becomes even stronger whether considering that in cleaning conditions a relevant damage contribution to the fragile and incoherent gold leaf is also expected from the strong photomechanical effect

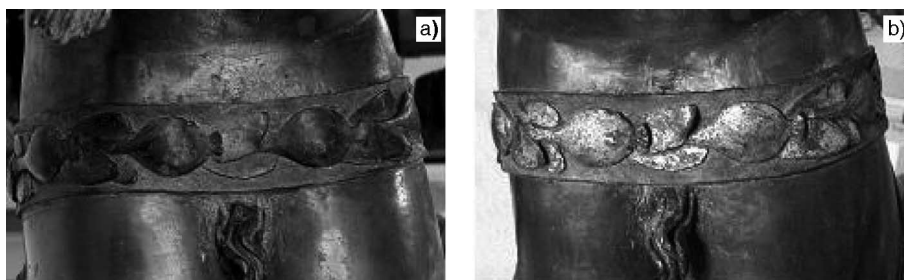


Fig. 4. – Gilded belt of the *Attis* by Donatello: a) before laser cleaning; b) after laser cleaning.

associated with nanosecond pulses. LQS and QS lasers could be suitable only in rare situations where very low operative fluences can provide an effective cleaning and for some modern artefacts where the gilding layer has a good thermal contact with a metal substrate.

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