LASER TECHNIQUES FOR CONSERVATION OF ARTWORKS

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Abstract

The potential of laser techniques in conservation has needed a long development period to be fully demonstrated. The possibility to achieve a very precise and selective removal of deteriorated materials was implemented through a series of interdisciplinary studies focussed on laser ablation of specific materials. A suitable choice of the laser types and of the operating parameters could optimise the cleaning results, avoiding side effects while preserving the historical layers behind deposits and encrustation. An extensive validation carried out on a number of renowned masterpieces has definitely spread the interest of the conservation community for laser techniques in many European countries. The paper reviews the development of specific laser cleaning techniques for stone, metals, pigments and organic substances, which require different choices of laser wavelength and pulse width.

KEYWORDS: LASER TECHNOLOGY, CONSERVATION

KULCSSZAVAK: LÉZER TECHNOLÓGIA, RESTAURÁLÁS

Introduction

The remnants of past civilisations are an important part of the historical and cultural identity of the population of each country. The uniqueness of each piece of this treasury justifies the need of the most developed means in order to preserve the material itself against the many sources of deterioration. Because of this, the conservation community has always explored the potential of newly developed science and technology for solving the problems they are everyday facing. Since the opening of a modern meaning of restoration by Brandi (1963), chemistry has been mostly involved, providing reactants, poultices for consolidation and cleaning, coatings for protection. Physics has also given very important contributions for diagnostic methods such as microscopy, optical and X-ray investigations. Laser techniques came in about more than thirty years ago (Lazzerini & Asmus 1973), giving immediately very promising results not only for diagnostic but also for restoration procedures. The potential application for the delicate phase of cleaning was immediately understood but the development of successful laser techniques in conservation took necessarily many years. The aim of this paper is to present a review of laser techniques in conservation, focussing on the most important application in the cleaning phase of a restoration intervention. They have been validated in a significant number of case studies and today have demonstrated to provide advanced solutions for cleaning problems that allow a level of precision and control unreachable by other methods.

Laser cleaning of stone

Stones exposed to urban environments develop on the surface the typical sulphation process, with calcium carbonate turned in a gypsum matrix, enclosing carbon particles deposits, finally leading to a weakening of the material stability and in the worst case to a loss of materials. In this case the restoration intervention becomes often an urgent need, in order to stabilise the state of conservation of the materials. For the delicate phase of the degraded material removal the intervention technique should be able to provide a minimal invasive action, with the possibility to being selective between the encrustation and the historical layers. Traditional cleaning methodologies usually employ mechanical removal or chemical reactions. The erosion of the encrustation by sand-blasting is caused by the kinetic energy and cannot be selective. Chemical perfusion with Ammonium carbonate or other chemical reactants have drawbacks, with scarce control on the effects. Laser cleaning is a good candidate for this task (**Fig. 1**), being potentially very progressive, precise and selective. The physical process involved is laser ablation of inorganic (sometimes also organic) layers composing the deterioration crust. The most important characteristics are:

Laser ablation takes place when a pulse of laser radiation is absorbed at the surface of a material, determining a sudden transition of its solid phase to another phase (gas, vapour, plasma) if the energy density overcomes a certain level defined as the threshold.

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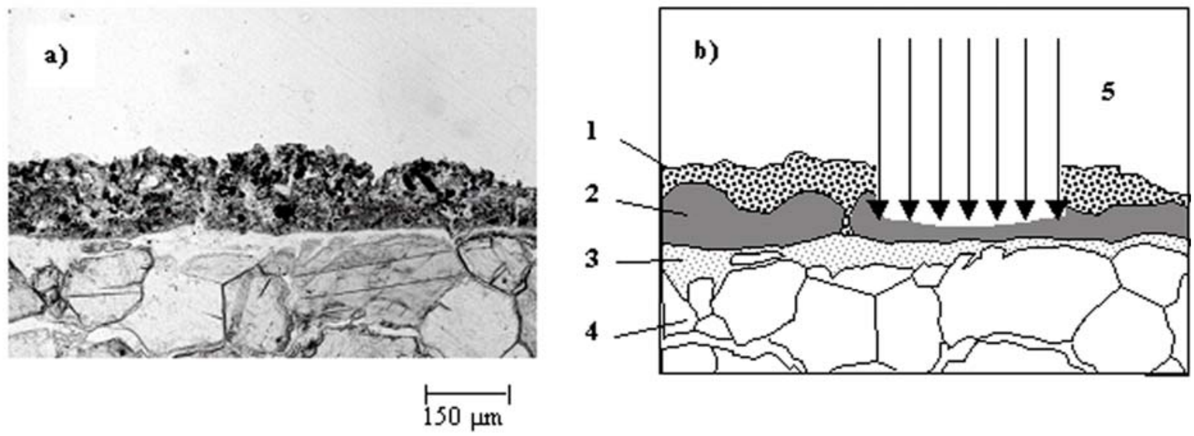

Figure 1.

a) Example of stratigraphy of a deteriorated marble observed by an ultra thin section.

b) Descriptive scheme: 1) black crust, 2) sulphated Ca-oxalates film (showing *craquelure*), 3) surface pseudomorphic sulphation layer i.e. reproducing the shape of the original surface, 4) calcite crystals with intergranular decohesion, 5) laser cleaning proceeds in a controlled way down to the oxalate layer.

The sudden phase transition is mainly due to photo-thermal effects rising the temperature of the material up to a hot vapour that expands quickly in the surroundings, producing a material removal.

Laser cleaning is essentially a surface treatment, where only a thin layer limited to a few microns or less than a micron is directly involved by absorption of light, while chemical methods usually perfuse with solvents internal layers without control;

The ablation threshold of high absorption materials (black encrustation for example) is lower than low absorption materials (light colour stone for example), so that a selective removal is possible without problems to preserve historical layers, as it is shown in **Fig. 2**.

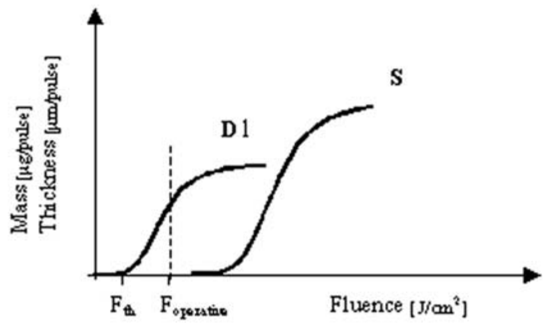

Figure 2.

Typical laser ablation curves for deposit (D) and substrate (S). They describe the dependence of the mass or thickness removed by the laser ablation process by varying the fluence or energy density. Setting the laser irradiation at the fluence value $F_{operative}$ an effective removal of deposit takes place, while no removal of the substrate is possible.

Accurate control of the treated volume is possible, due to the very progressive action of the laser, removing the encrustation pulse after pulse.

The applications of laser cleaning to stone materials are certainly the most advanced ones. For this problem is now recognised that laser cleaning represents the best possible technique, resulting selective and progressive. Nevertheless many studies and experimentation were needed to arrive at the present point after the first pioneering test by Lazzerini & Asmus in Venice in the 1972 (using ruby lasers). Since then the most practical Nd:YAG lasers emitting in the infrared spectrum (IR) at 1.06 μm, operating in Q-switch mode with very short (about 5-10 nS) and intense pulses have been employed if the following experiments. In Italy several laser cleaning tests were carried out in the '70s and in the '80s in Venice, Padua, Cremona by Calcagno (1987). The interest in laser cleaning started again in the '90s in France by Orial (1989) with these lasers employed for the restoration of the portals of cathedrals in Amiens, Mantes-La Jolie, Paris, Chartres, Saint Denis etc. Another group (Cooper et al. 1995) was studying laser cleaning of artefacts in Liverpool using Nd:YAG lasers, while in Crete Fotakis (1995) began to consider also the category of excimer laser (a gas laser emitting in the ultraviolet spectrum) for icons and paintings, and in Germany Olainek et al. (1997) considered also the problems of medieval glass as candidates for excimer laser cleaning.

In Vienna Calcagno, Nimmrichter et al. (1997) could use laser cleaning on a large scale at the restoration of the St. Stephan cathedral, producing another important step in the validation of the laser technique.

Nevertheless these investigations remained somehow isolated without a real spread of laser techniques for the conservation of stone. This was partially due to side effects shown after laser cleaning such as yellowing or discoloration of the stone. This phenomenon observed by several authors has had different interpretations and perception. In Greece using the term discoloration is underlined that the original colour of the historical patina is modified. In France the yellowing (Labourè et al 2000) shown by cleaning of limestone with Q-switch Nd:YAG laser was simply softened by washing gently the surface, demonstrating that it was due to a superficial fall of micro particles after the ablation. In Germany SEM analysis has shown Fe nanoparticles after ablation that could justify the yellowing.

In order to overcome the limits shown by Q-switch mode operation, a special Nd:YAG laser operating with long and less intense pulses in the microsecond range was developed by Siano et al. (1997) in Florence. This new laser avoids yellowing effects and has been successfully employed in the restoration yard of the church of San Frediano in Pisa, at the *Porta della Mandorla* by Nanni di Banco, the north door of the Santa Maria del Fiore Cathedral in Florence, at the *Porta di San Ranieri* at the Duomo of Pisa, on many fragments of the original *Fonte Gaia* by Jacopo della Quercia, formerly set in *Piazza del Campo* a Siena. In all these restoration activity the microsecond laser technique has allowed to discriminate the proper layers removal in very complex stratigraphy overimposing various layers of pigmentation, sulphation, oxalate and so on.

Important applications of the laser techniques have been carried out on marble statues severely degraded by exposition for centuries to the sulphation process. Several masterpieces by Donatello such as the *Prophet Habacuc*, shown in **Fig. 3**. during the restoration, the *Pulpit* in the Prato Cathedral and Nanni di Banco's *Santi Quattro Coronati* have been successfully restored using laser cleaning especially when other traditional techniques such as micro sandblasting or chemical treatment could not ensure the achievement of the result. This has been the case of gilding traces, left by the action of time in the dresses borders and in the hair. Only the delicate calibration possible with the microsecond pulses laser cleaning has allowed preserving them at best.

In Greece, archaeological pieces such as a marble statue of *Hermes*, and recently a panel of the west frieze of the *Parthenon* were cleaned using a Q-switch Nd:YAG laser and combining the emissions at both the fundamental wavelength 1.06 (IR) and at the third harmonic (UV).

Figure 3.

The marble statue of the *Prophet Habacuc* during laser cleaning at the *Opificio delle Pietre Dure* in Florence. The restorer employs the hand piece as a tool on the statue.

The combination of IR and UV radiation could avoid yellowing of the cleaned surface, which was observed using IR emission alone.

Detailed descriptions of these case studies are reported in the proceedings of the International Conference LACONA (Lasers in the Conservation of Artworks) edited by Salimbeni R. & Bonsanti G. (2000), Verges-Belmin V. (2003), Dickmann K., Fotakis C. & Asmus J.F. (2005). The COST Action G7 provides a reference site on the web for this topic at http://alpha1.infim.ro/cost/.

The two regimes (Q-switch and Short Free Running) have also different features in respect of the beam delivery:

Laser systems emitting Q-switch high intensity pulses employ typically articulated arms (with mirrors at each turning joint) to propagate the beam to a hand-piece, because optical fibres could be damaged by the beam energy density higher than the damage threshold of silica fibres. Consequently Q-switch lasers may give a maximum pulse energy in the order of 300 mJ out of 1 mm diameter fibre, or higher pulse energy (up to 1 J) using an articulated arm. The use of a laser equipped with an articulated arm is practical only in a laboratory

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condition, where the relative positioning of the laser in respect of the artwork is easy. For outdoor use on scaffoldings the use of Q-switch lasers have given problems for the weight, the positioning and for the possibility of heavy environmental conditions such as rain, humidity and dust.

Short Free Running Lasers emitting microsecond pulses may couple easily 2 J in a silica fibre, without risks of damage, consequently they are equipped with optical cables of various lengths, to operate on the scaffoldings keeping the laser instrument in a safe place against the environmental danger, as shown in **Fig. 4** for the restoration of the Mausoleum of Theodoric in Ravenna. Using the fibre the hand-piece provides a quite homogeneous spot, which is a premise of a well controlled material removal all over the irradiated area.

Nowadays all the spread use of lasers in conservation of stone is based on the clear task to provide a very precise cleaning where the highly valuable decorations (statues, relieves, friezes, columns capitols, coats of arms, labels etc.) are worth of the best possible treatments.

Figure 4.

The restoration of the *Mausoleum of Theodoric* in Ravenna. A 50 m long optical fibre delivers the laser radiation from the laser system at ground to the hand piece held by the restorer.

Figure 5. A frieze of the *Porta del Paradiso* by Lorenzo Ghiberti during the laser cleaning intervention. The gold film behind the dark deposit of soot, carbon particles and salts is perfectly preserved.

Laser cleaning of metals

Metals artefacts experience the action of corrosion and oxidation processes due to the many reactive agents present in the air, in the water and in the ground where these objects were kept for centuries. These are the cases of archaeological metals when they are recovered from the excavation sites, or the case of archaeological metals found under the sea. Today as well metal artefacts host in polluted environments develop typical oxidation and corrosion layers. To stabilise the state of conservation these layers have to be removed in order to apply protective coatings. Tests of laser cleaning have been reported by Pini et al. (2000) concerning Roman coins and artefacts completely covered by a thick encrustation of calcareous concretions, with oxides and salts of copper and silver. Also other bronze objects, silver objects and iron objects have been submitted to laser cleaning in many trials. Using Nd:YAG lasers in both Q-switch and microsecond mode a suitable choice of laser fluence and pulse-width could discriminate case by case the removal of the encrustations, avoiding side effects as local melting and preserving stable oxide coatings where they were present.

An important example of the laser parameter adjustment was demonstrated for gold-coated bronze renaissance artworks, where the gilding was suffering a complex deterioration process due to environmental pollution, leading to micro blistering and loss of the gilding layer. This has been the case of the *Porta del Paradiso*, a famous masterpiece by Lorenzo Ghiberti, and the main door of the Baptistery in front of the cathedral in Florence. Many years of analysis and diagnostic studies begun in the 1980 leaded to a chemical approach based on washing with Potassium tartrate, in order to clean the outer deposits laying over the gilding layer. Unfortunately the complete washing determined a long term flourishing of salts. A laser cleaning approach could avoid the complete washing and provide an ideal cleaning if the heating of the gold film could be controlled. This case study made possible to clarify that only laser pulses ranging between 70-100 ns and a few microsecond would allow minimum transient heating to the few microns gold layer, avoiding local melting. This possibility was demonstrated by Siano & Salimbeni (2003) and now the restoration of this piece of art is going to be completed by means of laser cleaning for the last 48 freezes, one of them shown in **Fig. 5**.

Laser cleaning of paintings, paper and polychromes

For artefacts composed by materials involving organic fibres and compounds the laser approach encounters the problem of low thermal damage threshold. Furthermore the valuable historical materials have often micro dimensional structure with features of sub micron thickness, and this characteristic adds another factor of difficulty to achieve the same selectivity, precision and control well demonstrated for other inorganic materials. The situation here described is the case of paintings, paper and parchment, where the laser cleaning approach has been necessarily different from stone or metals. For the problems encountered in paintings restoration a special category of gas lasers (excimer) emitting in the ultraviolet spectrum was proposed in Greece by Fotakis (1995), to achieve sub micron removal of deteriorated varnish and also for repainting removal. In fact the ultraviolet laser radiation is absorbed in less that one micron thickness by the varnish, resulting in an adequate ablation precision.. Unfortunately most of inorganic or organic pigments react with very low thresholds to laser radiation producing an unacceptable change in the colour. In order to avoid this limit the technique developed by Scholten et al. (2000) was controlled on-line by a spectroscopic sensor (LIBS, Laser Induced Breakdown Spectroscopy) in order to detect any beginning of irradiation of the pigments layer and avoid the direct irradiation of pigments.

For the cleaning of deteriorated varnishes on paintings De Cruz at al. (2000) in USA and Italy have proposed the use of Erbium lasers at 2.9 µm, in the medium infrared spectrum. In fact molecules bearing O-H bond have an extremely high optical absorption at the Erbium laser wavelength and the radiation remains absorbed in a few microns, which is the condition for a very fine ablation control.

The application of laser techniques for the cleaning of paper and parchment has followed different solutions. For them the organic collagen structure of fibres represents the material to be preserved, besides inks and pigments constituting the graphics or the drawing. Ancient documents on paper or parchment may have problems of readability or conservation, because of accumulated dirt and dust, or fungi and other organic stains. A laser cleaning system (shown in **Fig. 6**) for high-precision cleaning of flat large area substrates has been developed by Kautek et al (1997). It allows restoration of artefacts of organic materials such as paper, parchment, leather, textiles, wood and also inorganic materials such as metals, alloys and ceramics. The laser spot is scanned over the objects through a remote computer control system. A high energy diode-pumped Q-switched Nd:YAG laser operating at 1.06 µm and 0.532 µm was installed. The authors of this system discovered that the green line at 0.532 µm was minimally absorbed by the collagen fibres, thus eliminating the occasional damage observed using the 1.06 µm line. One of the major challenges of precision cleaning was to avoid areas where ink or pigments were present. This was accomplished very precisely by image processing of the paper, verifying the ink presence and controlling the laser firing to avoid the ink irradiation.

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Figure 6.

The laser system developed for the cleaning of paper and parchment is organised in a closed box, providing maximum safety of operation. The set-up includes besides the laser imaging systems and a positioning table.

Conclusions

Laser techniques in conservation are presently a very interesting scientific issue, with significant successful applications and many challenges offering promising fields of research. After more than thirty years of studies and validation they are today a well accepted and appreciated professional tool in the hands of restorers. The advantages in respect with other techniques are now demonstrated, and the improvement in the precision and control of the cleaning is actually crucial especially when delicate historical layers have to be preserved. Examples are calcium oxalate on marble, gilding on bronze, paintings, fresco (wall) paintings, antique documents, antique textiles and so on. A number of well renowned masterpieces have been treated by a laser cleaning system in many countries and today the national public institutions of conservation have accepted the innovation determined by lasers in conservation. The use of the laser cleaning systems of course has to be necessarily restricted to trained restorers. The last generation of laser systems has improved the comprehension of their effects and their engineering. They allow proper settings of the emission parameters for a cleaning free of side effects, and an easy use of the hand-piece that make them to be employed as a new advanced tool.

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