

## Two new mechanisms for laser cleaning using Nd:YAG sources

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### Abstract

Two new methods for the laser cleaning using a Q-switched Nd:YAG laser have been developed and investigated. These offer increased efficiency and reduction in possible substrate damage for a wide range of substrate/encrustation combinations. In angular laser cleaning, it is shown that by controlling the angle of incidence of the cleaning laser, significant improvement in the efficiency of cleaning can be achieved when compared with conventional cleaning with a normal angle of incidence. A model is proposed to explain this effect. In laser shock cleaning, a completely different approach is presented. By aligning the incoming laser beam to be horizontal to the surface to be cleaned but close to it and selecting operating parameters that lead to a breakdown of the air above the object to be cleaned, a laser-induced shock wave is produced that is very much more effective than conventional normal incidence cleaning in removing surface pollutants. However, because the laser does not come into contact with the substrate, this method significantly minimises the potential for substrate damage. Again, a model for the cleaning process is presented. The results for the operation of both methods on polluted marble are presented. © 2003 Éditions scientifiques et médicales Elsevier SAS. All rights reserved.

*Keywords:* Laser cleaning mechanisms; Angular cleaning; Shock cleaning; Cleaning of marble

### 1. Introduction

Laser cleaning utilises the versatile, controllable, selective and environmentally friendly nature of the laser system to optimum effect [1,2]. Its effect can be highly localised allowing specific areas of contamination to be targeted. These unique characteristics of laser cleaning have been demonstrated effectively in the surface treatment of many types of works of art [3–9].

Traditional conservation techniques include the use of solvents and mechanical removal methods [3,10], which have, in the past, caused lasting damage. Therefore there is a need for an alternative technique that will not only successfully clean artefacts but also avoid any permanent damage.

Recently lasers have proved to be very successful in the removal of sub-micron particles in the semiconductor industry [11–17]. Industries have been motivated by cost savings, yield enhancement and environmental concerns. The successes of such techniques in this industry have brought about increased interest in the art world for using a laser as another tool.

However, utilisation of a laser for such cleaning purposes has its own disadvantages particularly where larger areas require treatment. Care is needed in avoiding damage to the underlying substrate when removing contaminants. Therefore there is a great need to continue the investigation of cleaning techniques that will not only improve the cleaning efficiency of artworks but also minimise damage to critical surfaces during the cleaning process.

In this paper, two alternative laser cleaning methods have been used for the removal of encrustations from marble [18,19]. The first technique is called “angular laser cleaning” in which the laser irradiates a surface at a glancing angle in contrast with typical cleaning using a perpendicular angle of incidence and the second technique is called “shock laser cleaning” in which airborne plasma shock waves are used to remove contaminants from the stone surface. The relative advantages of these methods over conventional normal incident laser cleaning are outlined.

### 2. Experimental

An investigation into the removal of black encrustation from a large section of marble was carried out using a Paragon 2XL Q-switched Nd:YAG laser operating in its

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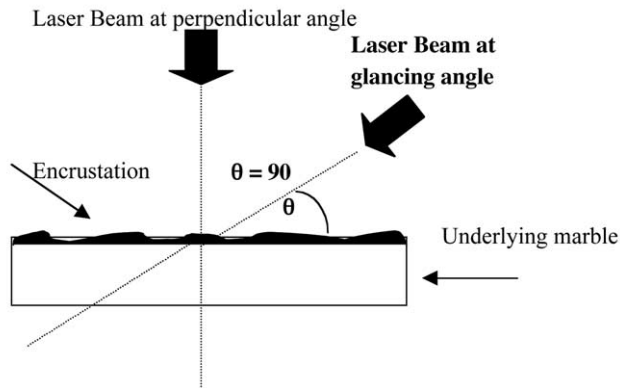


Fig. 1. Schematic diagram of angular laser cleaning.

fundamental frequency (1064 nm). The marble had accumulated the typical black patina associated with exposure in an industrially polluted environment. Both new laser cleaning methods outlined below were used and compared with that of conventional laser cleaning. The main objectives were to determine the optimum operating parameters to successfully clean the artefact in terms of number of pulses, fluence, gap distance and angle of beam incidence. The cleaning efficiency (defined as the percentage of the pollution layer removed) was determined by using optical grey-scale monitoring (Optimas) of the surface before and after irradiation.

### 2.1. Angular laser cleaning

This technique irradiates the stone surface at a glancing angle in contrast with conventional laser cleaning in which the laser beam is directed at a perpendicular angle of incidence to the target material, as shown in Fig. 1. The beam is directed to the surface at different angles, one is perpendicular to the surface (angle  $\theta = 90^\circ$ ) as for conventional laser cleaning and the rest at reduced angles (angle  $\theta < 90^\circ$ ).

### 2.2. Laser shock cleaning

This technique uses a plasma shock wave produced by a breakdown of air due to an intense laser pulse to remove the encrustations from the underlying marble substrate (Fig. 2). The beam is directed parallel to the surface in order to avoid direct laser interaction with the target material and is tightly focused a few millimetres above the area to be cleaned. The power density of the beam at the focal point is around  $10^{12} \text{ W cm}^{-2}$ . The gaseous ambient constituents begin to break down and ionise and as a result a shock wave is produced which has an audible snapping sound. In air, the typical peak pressure of the shock front for a spherically expanding plasma is estimated to be in the order of hundreds of millipascal [20,21]. However, the precise value depends on the laser power density and the distance from the shock wave. This new approach has unique character-

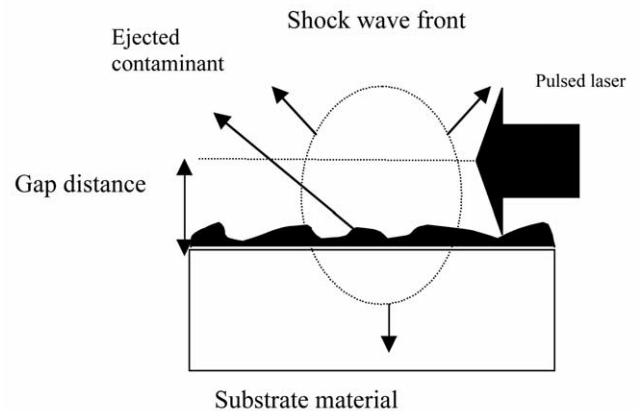


Fig. 2. Schematic diagram of laser shock cleaning.

istics, as it is independent of physical properties of the contaminants (for example it does not depend on the absorptivity of the surface contaminant and hence may be useful in removing low absorptivity materials). Also, the risk of damage to the underlying substrate is much reduced, as the incident beam does not come directly into contact with the work piece. (However, the effect of the laser-induced shock wave itself must be considered).

## 3. Results

The cleaning efficiency of marble as a function of fluence using the conventional laser cleaning technique and angular technique is shown in Figs. 3 and 4, respectively. Five single pulses were used with a repetition rate of 0.63 Hz. It can be clearly seen that the efficiency is a maximum at  $\sim 1 \text{ J cm}^{-2}$  for the conventional case but a reduced laser fluence is required for the surface when it has been cleaned with the incident beam at  $10^\circ$  to the surface. The laser energy per pulse used for complete removal of the pollution layer in both cases is roughly the same ( $\sim 1 \text{ J}$ ); however, if we consider the total area cleaned by each technique, we discover that the angular technique cleans over a much larger area ( $8 \text{ cm}^2$  compared with  $1 \text{ cm}^2$  for the conventional case). Hence the cleaning threshold fluence for the angular technique is smaller by a factor of 8. Moreover the rate at which the marble is cleaned is dramatically increased as shown in Fig. 5.

It is shown in Fig. 6 that there exists a minimum beam incident angle ( $30^\circ$ ) at which maximum cleaning rates are achieved. At angles  $> 30^\circ$ , the cleaning rates are reduced significantly.

Fig. 7 shows that for the case of laser shock cleaning, the cleaning efficiency is dependent upon the "gap distance" which is the distance between the laser focus position and the target material. Using a laser pulse energy of 2 J, a gap distance of 2 mm and three laser shots, an area of  $3 \text{ cm}^2$  was cleaned. The cleaning rates achieved using this particular

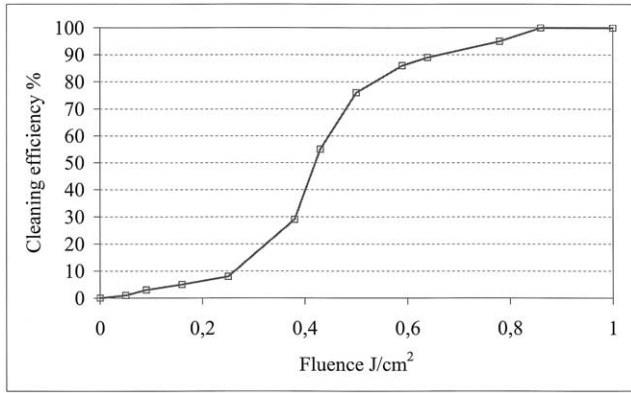


Fig. 3. The cleaning efficiency of marble as a function of fluence using Nd:YAG laser at 1064 nm. Five shots at a repetition rate of 0.63 Hz. Laser incident at 90°.

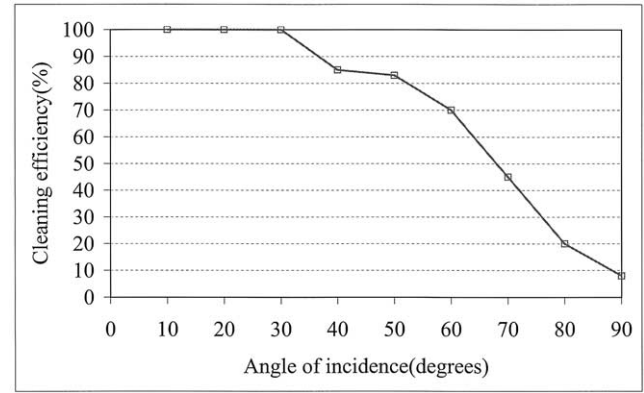


Fig. 6. Variation of cleaning efficiency with angle of incidence for laser cleaning of polluted marble.

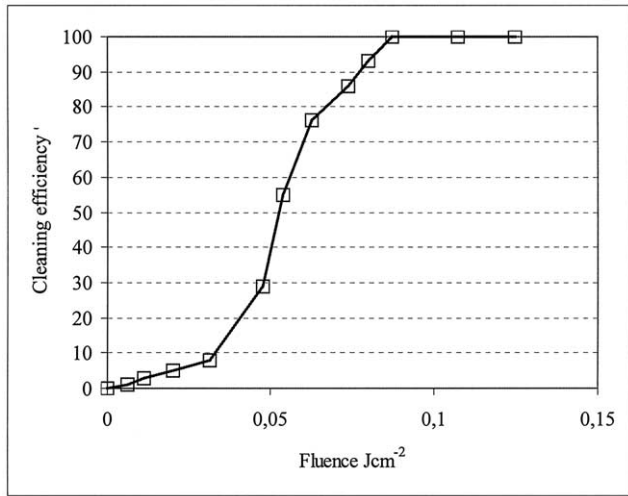


Fig. 4. The cleaning efficiency of marble as a function of fluence using Nd:YAG laser at 1064 nm. Five shots at a repetition rate of 0.63 Hz. Laser incident at 10°.

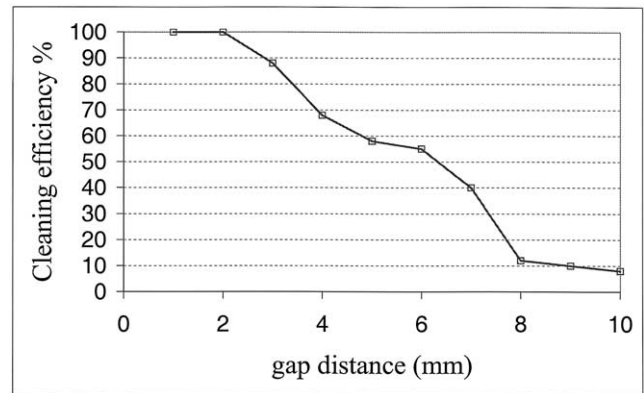


Fig. 7. The cleaning efficiency of marble as a function of gap distance for laser shock cleaning using Nd:YAG laser at 1064 nm, three single shots parallel to the surface at a repetition rate of 0.63 Hz.

method are intermediate between conventional laser cleaning and angular laser cleaning as shown in Fig. 5.

#### 4. Mechanisms

##### 4.1. Angular cleaning

A heat conduction analysis is presented to characterise the removal of encrustation from marble by means of Q-switched Nd:YAG laser radiation.

A one-dimensional thermal model is considered.

Let us suppose that:

A uniform heat flux ( $I_0$ ) impinges on a planar semi-infinite surface during time  $t$ ;

The heat is conducted inward into the material so that the temperature varies with depth ( $z$ );

The thermal properties of the material are constant and do not vary with temperature;

The beam diameter is much larger than the encrustation thickness and thermal diffusion distance ( $(2kt)^{1/2}$ ).

The laser beam diameter is of the order of 0.3 cm and a typical encrustation is in the range 0.1–1 mm in thickness

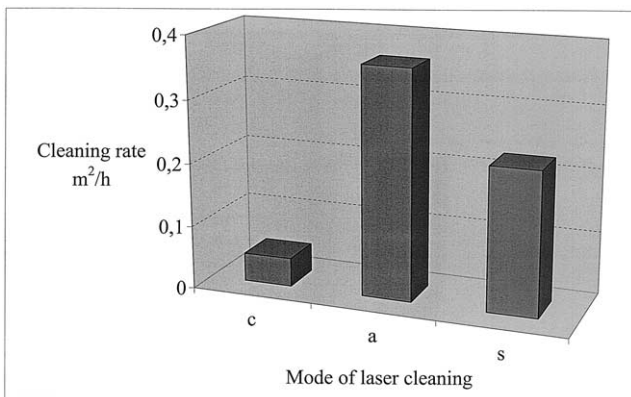


Fig. 5. The cleaning rates for three different laser cleaning techniques: c-conventional (perpendicular irradiation), a-angular technique, s-shock technique.

(1). The second condition requires consideration of the thermal diffusivity  $k$  for the material and the laser pulse duration  $t$ . The thermal diffusivity is given by:

$$k = \frac{K}{\rho C_v} \quad (1)$$

where  $K$  is the thermal conductivity,  $\rho$  is the density and  $C_v$  is the specific heat. For typical minerals:

$$k = 10^{-2} \text{ cm}^2 \text{ s}^{-1}$$

Consequently the distance  $d$  that the thermal wave will advance into the material during normal pulse duration of  $10^{-9}$  s will be

$$d = (2(kt)^{1/2}) \quad (2)$$

$$d = 63.2 \times 10^{-6} \text{ cm} \approx 0.63 \text{ } \mu\text{m}$$

which easily satisfies the condition of being much less than the beam diameter of 0.3 cm and the thermal effect might be strongly localised on the surface.

For a stationary system and heat flow in one dimension, the temperature is given by:

$$\nabla^2 T(z,t) - \frac{1}{k} \frac{\partial T(z,t)}{\partial t} = - \frac{A(z,t)}{K}, \quad (3)$$

where  $T(z,t)$  is the temperature at distance  $z$  after time  $t$ ,  $A(z,t)$  is the heat produced per unit volume and per unit time as a function of position and time,  $K$  is the thermal conductivity and  $k$  is the thermal diffusivity.

If a constant flux  $I_0$  is absorbed at the surface ( $z = 0$ ) and there is no phase change in the material, the solution of the above equation is:

$$T(z,t) = \frac{2\alpha I_0}{K} \sqrt{kt} \text{ierfc} \left( \frac{z}{2\sqrt{kt}} \right), \quad (4)$$

where  $\text{ierfc}$  is the integral of the complimentary error function.

At the surface ( $z = 0$ )

$$T(0,t) = \frac{2\alpha I_0}{K} \sqrt{\frac{kt}{\pi}}, \quad (5)$$

where  $\alpha$  is the absorptance ( $= 1$ , reflectance) and  $I_0$  is the incident flux.

Three scenarios will be considered for the removal of black encrustation from marble, i.e. three possible temperature rises:

- Temperature rise as a result of conventional laser cleaning (perpendicular to the surface);
- Temperature rise as a result of angular laser cleaning (reduction of angle of incidence of laser radiation);
- Temperature rise if the surface considered is rough; therefore for the angular case, multiple reflections will

occur when the laser radiation comes into contact with the surface.

There exists an angle at which the absorptivity is at its maximum, the Brewster angle. This angle is found from the refractive index of the material  $n = \tan$  (Brewster angle).

It is possible to predict the temperature rises for the three cases mentioned by determining the absorptivity at various angles and using the one-dimensional heat equation.

For the perpendicular case, a temperature of 1793 °C was calculated. For the angular case, at the Brewster angle, the temperature rise was 346 °C. Finally for the case if the surface was rough, multiple reflections would take place and so the laser absorptivity would increase further and hence this in turn would produce a slightly higher temperature rise than if the surface was even which is proven from the calculated value of 386 °C.

#### 4.2. Shock cleaning

If we assumed that the encrustation on the marble was made up of spherical particles, then we can determine the adhesion forces of the particles at the surface and determine the thermo-elastic force required to detach them from the underlying substrate.

The principal forces responsible for particle adhesion on a solid surface are Van der Waals force, capillary force and electrostatic force [22]. Van der Waals force,  $F_v$ , is the predominant adhesion force for small particles less than 50  $\mu\text{m}$  in diameter on a dry surface. This force is due to dipole-to-dipole attraction between a spontaneous dipole in a body and the induced dipole in an adjacent body. The attraction force between a spherical particle and a flat substrate is given by:

$$F_v = \frac{hr}{8\pi Z^2}, \quad (6)$$

where  $h$  is the material-dependent Lifshitz–Van der Waals constant,  $r$  is the particle radius and  $Z$  is the atomic separation between the substrate surface and the bottom surface of the particle, respectively. The constant  $h$ , ranges from about 0.6 eV for polymers to about 9 eV for metals. From Eq. (6), the Van der Waals force can range from about 19 mdyn for a 1  $\mu\text{m}$  particle with 9 eV to about 120 mdyn for a 100  $\mu\text{m}$  particle with 0.6 eV. These correspond to forces per unit area approximately from  $2.3 \times 10^5$  Pa ( $= \text{N/m}^2$ ) for a 1  $\mu\text{m}$  particle to  $1.5 \times 10^2$  Pa for a 100  $\mu\text{m}$  particle. These are tremendous forces, i.e. the adhesion force for a 1  $\mu\text{m}$  particle is greater than the gravitational forces acting on the particle by a factor of  $10^7$ .

The second significant adhesion force is a capillary force,  $F_c$ , due to high humidity or capillary action where a thin layer of liquid such as atmospheric moisture is condensed in the microscopic gap between the particle and the substrate, which is given by:

$$F_c = 4\pi r\gamma, \quad (7)$$

where  $\gamma$  is the liquid surface tension.

Electrostatic force is the predominant adhesion force for particles larger than 50  $\mu\text{m}$  in diameter. Two types of electrostatic forces may act to hold particles to the surfaces. The first force is an electrostatic image force,  $F_i$ , due to bulk excess charges present on the surface of the particle, which produce a classical Coulombic attraction, which is given by:

$$F_i = \frac{q^2}{4\pi\epsilon\epsilon l^2}, \quad (8)$$

where  $q$  is the charge,  $\epsilon$  is the permittivity of free space,  $\epsilon$  is the dielectric constant of the medium between the particle and surface and  $l$  is the distance between charge centres. If two different materials are in contact, the force operating is an electrostatic double layer force,  $F_d$ , resulting from a contact potential difference caused by differences in the local energy states and work functions, which is given by:

$$F_d = \frac{\pi\epsilon r U^2}{Z}, \quad (9)$$

where  $U$  is the potential in volt.

Phipps and Turner [23] suggested a laser-target scaling model, which allows approximate prediction of the shock pressure during laser ablation. The resulting equation is given by:

$$P_a = bI^{0.7} \lambda^{-0.3} \tau^{-0.15}, \quad (10)$$

where  $P_a$  is the shock pressure (kbar),  $b$  is the material-dependent coefficient (for example 3.9 for copper and 6.5 for C–H materials),  $I$  is the laser intensity ( $\text{GW}/\text{cm}^2$ ),  $\lambda$  is the laser wavelength ( $\mu\text{m}$ ) and  $\tau$  is the pulse length (ns) used. From this equation, the variation of shock pressure with laser intensity during laser ablation can be understood. As  $2.0 \text{ J}/\text{cm}^2$  corresponds approximately to  $200 \text{ MW}/\text{cm}^2$  at the pulse duration of 10 ns, the shock pressure thus induced on the surface is about 2200 bar ( $= 2.2 \times 10^8 \text{ Pa}$ ). This is very large (by a factor of  $10^3$ ) when compared to the adhesion force estimated from Eq. (6) for small particles (1  $\mu\text{m}$  in diameter) on the surface, i.e. higher by a two-order magnitude. As a result, the shock pressure generated by rapid expansion of plasma plume and rapid evaporation of the material can remove even the small and strongly adhered particles from the surfaces.

## 5. Conclusions

There are many advantages of using angular laser cleaning as an alternative to conventional perpendicular laser cleaning including significant improvement in cleaning efficiency. It was found that, for the same laser input energy, the cleaned area irradiated at a glancing angle was up to eight times larger than the typical laser cleaned area using normal incidence. Hence the speed at which contaminated areas are cleaned for the same incident laser energy is

greatly increased. Moreover cleaning threshold fluence is reduced at glancing angles therefore reducing the risk of surface damage considerably in comparison with normal incidence laser cleaning. It was also evident that the temperature at the surface was greatly reduced for the angular case, therefore reducing the risk of damage to the marble even further.

It was found that as with angular laser cleaning, an increased cleaning efficiency is observed in terms of the area cleaned for a given input of laser energy for the shock cleaning technique. It was discovered that the gap distance between the surface to be cleaned and the laser focus is critical in terms of successful cleaning as this distance alters the pressure of the shock wave striking the surface. In terms of practical application, there may be limitation in usefulness of the technique to the cleaning of flat surfaces.

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