INTRODUCTION

Twentieth-century paintings made with industrial paints have often been restored without a thorough knowledge of their chemical and physical properties (Learner, 2004). In particular, contemporary paintings have often been retouched using materials rather similar to the originals, thus compromising the actual reversibility of the overpainting. Therefore, the selective removal of overpaints is a challenging task in these cases (Meles-sanaki et al., 2006) as the use of organic solvents may often be limited because of their lack of selectivity (Bordalo et al., 2006; Ormsby and Smithen, 2006–2009). Lasers may offer a viable solution for the selective removal of overpaints without compromising the underlying original layers (Fotakis et al., 2006).

LASER CLEANING TESTING

To test both effectiveness and limitations of laser cleaning in contemporary paintings, an integrated study was carried out on painting mock-ups, which were irradiated with different laser parameters (wavelength, energy density, number of pulses, etc.) and then analyzed by optical microscopy, micro–Fourier transform infrared spectroscopy (FTIR), and micro–Raman spectroscopy.

Six mock-ups (cotton canvases on stretchers) were prepared by respectively applying six different binders (commercial tube formulations) with titanium white. Then a second layer was applied on each of the six canvases. This second layer was applied in 11 squares, leaving 1 square of the first layer exposed. Five of the 11 squares were the other five commercial binders with titanium white. Six squares were with the six commercial tube formulations with either ultramarine blue or phthalocyanine blue. The binders used were acrylic emulsion resin (for artists), vinyl emulsion resin (for artists), acrylic in solvent, oil-modified alkyd (for artists), oil-modified alkyd (household), and alkyd with nitrocellulose (for artists). For the blue paints, the ones for artists contained ultramarine blue, whereas the others (acrylic in solvent and household oil-modified alkyd) contained phthalocyanine blue.
The cleaning procedures tested were based on different laser systems with wavelengths ranging from the ultraviolet (248 nm) up to near infrared (1064 nm), with various pulse lengths $t_p$. In all cases the objective was to remove the outer layer without affecting the white ground layer. Preliminary cleaning tests were performed mainly on a spot basis in order to define the optimum parameters for effective and safe removal of the overpaint and to establish the methodology of this method. This was followed by scanning tests in order to develop the appropriate cleaning methodology.

The effectiveness of laser cleaning to remove the outer layer without affecting the ground paint was evaluated using different physical and spectrophotometric tools. In particular, optical microscopy, micro-FTIR, and micro-Raman spectroscopy were employed to evaluate the irradiation tests (cleaning efficiency, color homogeneity, and surface morphology; De Cesare et al., 2008) and to perform a chemical analysis of the irradiated surfaces, whereas laser-induced fluorescence was used to monitor the cleaning process.

RESULTS

A very strong gray discoloration was evident on titanium white paint upon irradiation for all the laser parameters tested, even using single-pulse irradiation at very low energy densities. Still, no laser-induced discoloration (which is a well-known issue in laser cleaning applications) was observed on the blue paints. Using the UV wavelengths, it was possible to remove the unwanted overlayers in a stratigraphic (layer by layer) manner.

The most efficient cleaning results in our tests were obtained using the 355 nm laser in the nanosecond range at rather high energy densities and several pulses (~10). On the other hand, the KrF Excimer emitting at 248 nm ($t_p = 30$ ns) required higher flux values and a significant number of pulses in order to produce an efficient cleaning level (flux $F > 3$ J/cm² and 10–50 pulses).

The Nd:YAG laser was not very satisfactory at either 532 or 1064 nm (10 ns). In particular, the 532 nm wavelength did not result in a good cleaning level except in certain areas, and even in those cases the removal was never homogeneous, mainly because of the inhomogeneities of the beam profile. Similarly, IR radiation at 1064 nm had an apparent abrasive effect without any control. Furthermore, strong photochemical effects (visible as crack formation around the irradiation craters) were recorded.

Parallel tests were performed to investigate the conditions that would eliminate the white ground with minimal disruption to the canvas (i.e., without discoloration and damage to the fibers). The best results were obtained on the white alkyd ground using the 355 nm ($t_p = 150$ ps, $F = 1.4$ J/cm², and 20 pulses). The spectrophotometric analysis of the irradiated surfaces by micro-FTIR and micro-Raman spectroscopy revealed residues of the outer-layer materials as well as the presence of alteration phases responsible for color changes.

DISCUSSION AND CONCLUSIONS

A systematic study, integrated with the physical and chemical analysis of the paints, confirmed that ultraviolet wavelengths (at 248 nm and, in certain cases, at 355 nm) were the most appropriate ones for an effective and safe removal of unwanted retouches on contemporary paintings. Tests with IR laser radiation (at 1064 nm) were found to be particularly aggressive, resulting mostly in ground damage but also inducing photomechanical effects visible as cracks around the irradiation craters and with a limited selectivity option. On the other hand, the visible radiation (at 532 nm) could not reach an acceptable cleaning level at the tested energies, and further studies are being conducted in this regime in order to exploit all the possibilities (i.e., lower fluxes).

The discoloration phenomena observed upon irradiation of titanium white, which is a strong UV absorber and a redox catalyst, could be related to traces of carbon detected on the irradiated surfaces, most probably because of the degradation of the organic medium. The removal of white overpaints appears to be far more demanding than the blue ones, which generally were removed more easily and effectively. An important issue that should also be addressed when developing the cleaning methodology is the appearance of a dark “halo” that was visible around the irradiation spots and was attributed to redeposition of alteration products upon laser ablation. The fine-tuning of the operational parameters toward the development of the optimum laser cleaning methodology for every individual material tested is currently being researched.

REFERENCES


