

Journal of Cultural Heritage 4 (2003) 163s-164s

Journal of Cultural Heritage

www.elsevier.com/locate/culher

Report on session "Cleaning of organic materials: paper, parchment, textile, wood"

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The general development in laser conservation has led to the observation that scientific approaches and diagnostics have been introduced as never before in this traditional discipline. The contributions of the laser cleaning on organic materials comprised cellulose- and protein-based fibrous matter. These materials represent the most sensitive objects which laser cleaning has to deal with. Therefore, the highest input of scientific knowledge and advanced diagnostic tools are required from all disciplines of laser cleaning.

The most important and ubiquitous artefact in this context is certainly paper. Consequently, most of the contributions were concerned with it. The research groups in Ljubljana, Slovenia (J. Kolar et al.) and Berlin, Germany (Kautek et al. "Interaction of laser light with soiled paper") gave insight into a joint systematic investigation in the problem of laser interaction with soiled paper, which led to discoloration, in particular "yellowing", under several circumstances. It was shown that this phenomenon is also an issue in other disciplines of laser cleaning (such as that of stone). However, the mechanisms involved are different. They are under thorough investigation. Poster contributions documented that paper is also a recent matter of interest with other European groups in Gdansk, Poland (G. Sliwinski et al., "Experimental investigations of stained paper documents cleaned by Nd:YAG laser pulses") and in Simancas, Spain (C. Perez et al., "Positive findings for the use of laser in the cleaning of cellulose based supports"). In all these reports, microscopy and colour metrics turned out to be most valuable. Chemical essays such as FTIR spectroscopy have been repeatedly proposed, but need proper evaluation in order to give any meaningful information on the shallow zones of chemical modifications. On the other hand, X-ray techniques (XRD) of the crystalline components of cellulose seem to be too insensitive for possible changes (comp. the poster by C. Perez et al.). Laser-induced plasma spectroscopy (LIPS) has been reported in analogy to

work with e.g. stone (C. Perez et al., and G. Sliwinski et al.). This technique definitely is an irreversible destructive method that should actually not be applied any more on any bioorganic fibre artefacts such as paper, parchment, and textiles. A preview poster on "Paper restoration using laser technology: a new European shared-cost project" by the collaborating groups in Berlin, Germany (W. Kautek et al.), at Heraklion, Greece (C. Balas et al.), at Hengelo, The Netherlands (R. Teule et al.), in Delft, The Netherlands (J.B.G.A. Havermans et al.), and other research partners in the Netherlands gave a concise review on the achieved findings of the EUREKA project "LACLEPA-laser cleaning of paper and parchment". A cornerstone in the practical work of paper and parchment restoration will be the further optimization of a novel laser cleaning system specifically tailored for this purpose by the Berlin group (W. Kautek et al.) recently. It has been set up recently there, and allows precise, fast, electronically automatized restoration work without the common need of obnoxious safety equipment such as eye goggles. The European project will focus on the perfection of this system by the implementation of recent high-tech diagnostic tools such as multi-spectral analysis.

Another cellulose artefact was wood in the form of Red-Indian totem poles originating from British Columbia. The restoration laboratory in Liverpool, United Kingdom (M. Cooper et al., "The application of laser technology to the conservation of a Haida totem pole") identified efficient fluence ranges with an Nd:YAG laser run at 1064 nm. However, also surface regions were observed where the destruction threshold was below the ablation threshold of contaminants, so that total removal of entire substrate regions had to be tolerated. Textiles in the form of an ancient gonfalon were presented by a group in Warzaw, Poland (A. Koss et al., "Laser cleaning of a flax XVII century gonfalon"). The often-observed complication consisted of the presence of metallic interwoven threads such as gold and silver. Simple dry laser cleaning turned out not sufficient because of redeposition of contaminant debris. Therefore, a combination of repeated intermittent solvent

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removal was suggested, which provided acceptable cleaning results.

Recent systematic studies on parchment, making use of diagnostic tools highly dedicated to the chemical identification of proteins, were presented by the Berlin group (W. Kautek et al.) co-authored by experts of collagen chemistry in Vienna, Austria (L. Puchinger et al., "Diagnostics of parchment laser cleaning in the UV, VIS and IR-wavelength range: a systematic SEM, TEM, IR, and GC study"). There are strong indications that the ageing of the artefact is all-important in the establishment of feasible laser parameters because collagen disintegration leads to considerable phase changes, and therefore, alterations of the thermodynamic and optical properties of the artefacts.

The *key issues* of the *state of the art* and future *developments* of laser cleaning of organic materials are summarized in the following.

1. Paradigm change of conservation

The conservator traditionally was concerned with room temperature techniques involving both mechanical and chemical methods. Laser cleaning however contrasts sharply because these approaches are replaced by the application of highly localized deposition of heat by the absorption of a laser beam. When materials are vaporized far away from thermodynamical equilibrium conditions, extremely high temperatures (~1000 °C) may occur. It is the art and science of successful and safe laser cleaning to control this phenomenon without causing harm to the artefacts.

2. Advanced chemical analysis and diagnostics

The most important inspection method will be the conservator's eye, as in the past with conventional techniques. Modern technology however will be able to assist. This is particularly necessary in such cases where material changes are invisible to the naked eye, such as micromorphological and spectroscopic alterations. Whenever laser cleaning on the basis of large optical contrast between contamination and substrate has to be realized without damage to the substrate, advanced chemical analyses in order to establish degradation fluence thresholds and possible ageing effects are mandatory. The groups in Gdansk, Simanca, Ljubljana and Berlin therefore have demonstrated a close collaboration between restorers and chemists. They showed that UV-VIS colour metrics, optical and electronic microscopy are standard. Laser-induced spectroscopy, highly dedicated depolymerization measurements, and other techniques may be needed. Laser-induced plasma spectroscopy relies on irreversible substrate destruction and therefore should be avoided in this context.

3. Inhomogeneity and precision

Artefacts generally exhibit a high structural and chemical inhomogeneity in order to be an object of art. This can be

both two-dimensional but also three-dimensional when e.g. various pigment layers are stacked above each other. This means that e.g. pencil or ink lines have to be avoided by the laser treatment. This can only be achieved when the high collinearity of the laser beam is exploited and controlled by a respective precise beam delivery system as e.g. demonstrated by the group in Berlin (W. Kautek et al.).

4. "Surgery"

There may be some cases in restoration where a scalpel may be acceptable in removing degraded material of the artefact. This role can also be played by a UV- or even far-UV laser. In this case, any material irradiated will be vaporized.

5. "Integration"

Laser cleaning may not be successful without any complementary application of conventional restoration process steps. An interesting example has been presented in the form of an ancient gonfalon where the contamination debris could be removed by repeated solvent treatment between the laser irradiation in the Warzaw laboratory (Koss et al.).

6. Ergonometry—no eye protection

The use of eye protection equipment such as inconvenient eye goggles is always mandatory in laser cleaning because high power lasers are used in all cases. Such goggles sometimes have to be coloured in order to shield from coloured beams. This feature can be an extreme drawback for restoration where even slight colour nuances have to be registered. Therefore, it would be a breakthrough in laser cleaning technology when this could be avoided. Actually this could be realized recently for paper and parchment cleaning by the Berlin group (W. Kautek et al.). A fully encapsulated system (i.e. "Laser Class 1") engineered for complete remote control allows safe ergonomic cleaning.

7. "Electronic mask"

The above remote control high-tech approach also provides the ideal means to put an "electronic mask" on the artefact so that fully automatized cleaning with precise avoiding of critical areas such as pencil pigment lines can be exempted while the rest of the contaminated area is cleaned with high speed. The Berlin group (W. Kautek et al.) was able to achieve this by computer control and a laser pulse repetition rate of 1000 Hz.

To conclude, one has to remark that laser cleaning of organic materials such as parchment and paper is still in an early stage. This area lets one expect a number of interesting results and detailed chemical knowledge about possible irreversible changes, which will determine the working window of fluences for the laser process.