“Paper Restoration using Laser Technology”
PARELA

CRAFT Project EVK4-CT 2000-30002

DETAILED TECHNOLOGICAL REPORT

(SECTION 6)

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Chapter 1: Introduction

1.1 Introduction

By John Havermans[1], Rianne Teule[2]
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Daily, numerous documents (made of e.g., paper, photographic material) are consulted, and especially because of the increased use of communication media like internet, more and more documents in archives, libraries and museums are accessed. They basically form the most important information storage media in use! If we limit ourselves to consider "modern" materials, in for example Italy alone, public libraries have about 25 million books in need of restoration (e.g., cleaning, preventive intervention, and deacidification). Such a figure is ever increasing, and an amount of material three times larger is conserved in Universities, private collections etc. regarding to archives, the space is occupied by paper materials which would stretch out to more than 1.2 million linear meters.

Based on the recently finished archive assessment in the Netherlands, figures showed that the number of objects to be involved in a certain cleaning are about nine million sheets (1.5 km of paper) for their 80 km counting collection, stored and assessed under controlled environment [1]. Extrapolating this ratio for a small country as the Netherlands only, shows that about 6.5 km or 39 million sheets are threatened by dirt and are should be cleaned. These figures give an idea of the importance and economical relevance of the problems that are still to be solved for the treatment of these materials. Deterioration of those documents is continuing, especially if the substrate is not stable to the sometimes poor-environmental storage conditions, while specific types of contaminants may accelerate this process. Even the improved accessibility will deteriorate the original documents faster than before and in this particular case preventive conservation is a must.

Manual cleaning methods (if they are suitable) can only deal with an average speed of about 450 objects per year per person. Furthermore, working with organic solvents during a cleaning application may cause serious health problems for the restorers. These items were the motivation to start the development of a new innovative conservation cleaning method based on laser technology.

1.2 Contract information

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The work, carried out from 2001 – 2003 was funded by the European Commission, Community Research, within the Fifth Framework Programme; CRAFT, Thematic programme Environment and sustainable Development, section Cultural Heritage and the City of Tomorrow. Contract number EVK4–CT–2000–30002 "Paper Restoration with Laser Technology – PARELA".

The overall co-ordination for this research was carried out by Art Innovation, Hengelo, The Netherlands. The technical co-ordination was in hands of TNO, Delft, The Netherlands.

1.3 Backgrounds

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The paper-based cultural heritage in our Archives, Libraries and Museums needs to be conserved to keep the collection in a well accessible state. The conservation of paper objects deals with severe damage with variable origin, e.g. binding and book-block damage, chemical damage and damage due to moist [2, 3]. Chemical damage is divided into sub-categories as *foxing* (coloured stains are formed on the paper), *use* (the tax form with coffee stains and written notes in textbooks) and *old repairs* (the use of self adhesive tapes).
At present the repair (*i.e.*, cleaning) of these types of damage, if feasible, is very time consuming. Current cleaning techniques are often based on the use of organic solvents, liquid nitrogen, water, or a scalpel-blade knife. As scientific research in the conservation field progresses, the drawbacks of these conventional methods become more and more obvious. The use of a scalpel-blade (mechanical cleaning) can cause fibre damage, while chemical cleaning produces emission of highly volatile organic compounds, which can be harmful to the restorers. The application of Laser technology in cleaning provides the restorer with a precise and controllable technique which, when used with care, is capable of removing layers whilst maintaining the underlying layer intact. Laser radiation can be accurately manipulated, enabling precise cleaning of a surface. Advantages of the use of lasers are:

- removal of extremely thin layers,
- no use of toxic solvents,
- no mechanical contact with the artwork,
- high reproducibility of cleaning effect, cleaning effect is less dependent of individual restorer using conventional cleaning methods,
- easily supplemented with on-line control.

The feasibility and advantages of laser cleaning techniques have been demonstrated by several research institutes for surfaces like paintings, stone and paper [4]. It is however a relatively new field of work, and this specific application of lasers is still under development [5-9].
Researchers at the Fo.R.T.H. Institute in Crete did extensive studies on the application of excimer lasers for the cleaning of painted surfaces. A review was published by Zafiropulos, demonstrating the removal of pollutants using pulsed UV lasers at several wavelengths [10]. The value of the laser as a restoration tool was demonstrated for the removal of surface material, but also as a non-contact diagnostic tool, providing important information regarding the chemical and physical structure of the artwork [7].

Paper conservation deals with totally different issues and materials. Paper is a fairly random network consisting mostly of cellulose fibres. Although the fibre source during the last 150 years has changed from cotton or linen rags to wood, its nature is still vegetal [11]. The great extent of cellulose gives papers not only its strength, but also its comfortable feeling. Other main paper components are, e.g.:

- Fillers like kaolin clay and calcium carbonate,
- Optical brighteners for whiteness improvement and
- Starch derivatives as sizing agents.

The strength of paper depends on the quality of the cellulose fibres. In general, any degradation of long cellulose chains to shorter chains leads to a reduction in strength [12-14]. The degradation of paper can either be induced internally, due to the presence of acidic compounds, or externally, e.g. by air pollutants and radiation [15].
During the laser ablation process, the fibres beneath the dirt can be affected as well. This may result in the oxidation of fibres, which usually occurs when light or heat is introduced [16]. Oxidation can cause yellowing as was illustrated by the work published in 1999 on the removal of ink by lasers. The researchers suggested that adjusting the laser pulse duration could reduce the cellulose oxidation caused by laser cleaning. Previous research of the authors showed comparable negative side effects, but the result by laser cleaning was better compared to manual cleaning [17, 18].

Furthermore, lasers were applied for the removal of fungal-induced stains from paper [19]. These coloured stains, named "foxing", are grouped together with other coloured stains in paper [20]. The researchers demonstrated that three of the four artificially induced types of fungi could be removed safely from the paper using a laser, and that the fungi were inactive after treatment. However, the paper substrate was only analysed using Scanning Microscopy. As no artificial ageing was applied, no long-term possible side effects were presented.
The potential of the use of lasers for paper restoration was demonstrated in the EUROCARE EU1681 project 'Laser cleaning of paper and parchment' (LaClePa). Ancient parchment manuscripts were cleaned using an UV pulse laser (308 nm), while different spectroscopic techniques were applied for monitoring of the cleaning process. Furthermore, the paper substrate stability was investigated by analysing the carbohydrate composition of the treated and untreated paper. It was concluded that no significant deterioration took place after the laser treatment [21]. However, the positive result is strongly dependent on the experimental parameters during the cleaning process.

1.4 Scientific and socio-economic objectives

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The main objective of this project is the establishment of a laser cleaning system suitable for accurate and safe restoration of paper objects. The focus lies on the incorporation of a reliable control system, consisting of one or more suitable detectors. In order to successfully develop such an innovative restoration tool, detailed research is carried out to gain sufficient knowledge of fundamental processes occurring when laser light interacts with paper and the material to be removed. We discriminate four types of objectives.

Scientific objectives:

- establish the optimal laser parameter setting by studying the effects of laser treatment on test-samples and original samples on the deterioration of the paper
- establish the long-term behaviour of laser treated samples
- establish the effects of the environmental working conditions

Industrial objectives:

- design and production of laser cleaning stations for paper that is attractive and accessible for small and medium conservation companies.
- production and incorporation of modular diagnostic system for (semi-)automated process control.
- production of high level control software incorporating the results of this project.

Economic objectives:

- the exploitation of specifically developed laser systems for restoration of paper objects. First focus lies on the application on conservation problems that can not be treated using conventional techniques, i.e. about 5 % of the paper conservation work. Secondly, the system will be (partly) automated in order to enable fast restoration, which will be beneficial since conventional restoration is time-consuming and therefore expensive.

Social objectives:

- improvement of the working conditions of restorers. Due to the limited number of conservation approaches (either mechanical or chemical) the restorer frequently has to choose a less than optimal conservation method. Being aware of the dangers this presents to the artwork, compensation is sought in increased care and concentration on the side of the restorer, often greatly lengthening the duration of the treatment. In many cases, the resulting strain leads to mental and physical fatigue and eventually RSI (Repetitive Strain Injury)
- the use of lasers will reduce the use of chemicals for paper restoration, which is beneficial to both the environment (waste disposal), and the health of the restorer.

1.5 Laser cleaning and paper – some theoretical considerations

Basics and Applicability of Lasers in Paper Restoration

By Wolfgang Kautek
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Soiled biogenetic fibrous substrates such as paper and parchment consist of a phase mixture of particulates, condensed foreign phases and cellulose or protein polymers, respectively as shown in Fig. 1.1 [e.g. 22]. The phase separation of these condensed films and particles from the matrix is the purpose of laser cleaning. It offers the advantage that leaching and dilution processes common in solid liquid extractions can be avoided. The fundamentals and phenomena of the laser separation procedure is reviewed and discussed by different researchers and can be found in several publications [e.g. 23, 24].

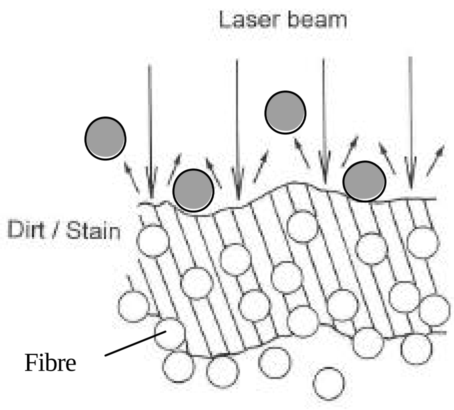

Fig. 1.1 A model of dirt on fibrous substrates, removed by laser

The laser-induced evaporation of the foreign phases is compared with real gas thermodynamics involving the principle of continuity of states and critical states. Though the laser process starts optically it ends mainly thermally. Specific phase heating can be attained by means of differential optical interaction with various phases in contrast to classical incongruent evaporation processing of chemical engineering.
In paper cleaning, real systems deviate from the high optical contrast case so that drastic heating of the fibrous matrix has to be taken into account. Thus, various diagnostic investigations on molecular degradation and secondary aging effects of the fibrous substrates come into play in laser cleaning applications [e.g. 25, 26]. A laser cleaning system for high-precision cleaning of flat large area substrates under Laser Class I conditions (with no safety goggle requirement) has been developed. A high pulse energy diode pumped Q-switched Nd:YAG laser operating at 1064 nm and 532 nm was integrated in a laser-processing compartment with various on-line diagnostics and an efficient exhaust system.

Elementals on paper and paper ageing [15]

By John Havermans
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The strength properties of paper depend on the quality of the cellulose fibres used. In general, any degradation of long cellulose chains to shorter chains will lead to a reduction in strength. This can be summarised as follows: Cellulose may be degraded by hydrolysis or oxidation. Traces of metal ions, such as iron and copper together with SO_2 or NO_x promote the hydrolysis of cellulose. Cellulose may also be hydrolysed in an alkaline environment. Short-wave UV-radiation may break chains by photodissociation. Crosslinking reactions may make the cellulose structure stiff and brittle, thus increasing the likelihood that the chain breaks. Under the influence of oxygen or light, lignin may degrade more rapidly than cellulose. Hemicellulose is hydrolysed more easily than cellulose and lignin. Since structurally weakened zones are more accessible in the water-swollen state, degradation occurs in the enzymatic and liquid-phase by hydrolysis of fibres. The degradation leads to a significant decrease in fibre strength and a decrease in the degree of polymerisation. In the vapour-phase hydrolysis of fibres and leads to only a moderate decrease in fibre strength.
The degradation of cellulose can be classified into two main routes:
- Reactions in which the end product is D-glucose (clean hydrolysis).
- Reactions in which a range of products of low molecular weight are formed. tural ageing involves

reactions such as oxidation, thermal oxidation, crosslinking and hydrolysis.

Table 1.1 Possible degradation reactions for cellulose

Reaction	**Involves**	**Products**
Hydrolysis (thermal)	cellulose + H_2O	D-glucose
Acid-catalysed hydrolysis	cellulose + H_3O^+ (diluted)	D-glucose
Alkali-catalysed hydrolysis	cellulose + base	low-molecular weight products
Oxidation	cellulose + “O” (T, hν)	partially oxidised and depolymerized

Oxidation and *thermal oxidation* of the primary alcohol group to an aldehyden and subsequently to a carboxylic acid on the C6 site may occur relatively rapidly. Oxidation of secondary alcohol groups at the C2 and C3 sites may also occur. Initially this leads to the formation of ketones. Further oxidation leads to breaks in the ring and the formation of carboxylic acids. After each cleavage of the glycosidic linkage an aldehydic end group is formed (Sjöström 1993). Thermal oxidation at room temperature and in the presence of light may break the glycosidic bond and cause depolymerisation. Oxidation will be promoted when oxidation agents and/or metal ions *e.g.* iron and/or manganese, are present. With some polymers *e.g.* carboxy-methyl-cellulose (CMC), oxidation with hydrogen peroxide or hypochlorite is applied to reduce the molecular weight somewhat, thus improving the biodegradability. Sometimes peroxides are formed, and they can be very strong oxidation agents resulting in radicals, especially in the presence of certain transition metal ions. The autoxidation of cellulose, proposed as a free radical mechanism, can be initiated using only one free radical. These radical reactions can easily introduce carbonyl groups along the cellulose chains at the C6, C3 and C2 positions. After the formation of these carbonyl groups, chain cleavage can take place according to the so-called β-elimination. This reaction can take place fairly easily at several pH levels, but is especially rapid at pH levels higher than 8. At higher pH levels, monosaccharides as well as the end groups in polysaccharides will be converted to various carboxylic acids. (1→4)-Linked polysaccharides, including cellulose and most hemicelluloses are then degraded by an endwise mechanism, also called a peeling reaction.
Finally, thermal treatment especially heating of cellulose using e.g. microwaves will cause the oxidation of glucans like starch and cellulose and this is in fact a preparative route for the synthesis of levoglucosan.

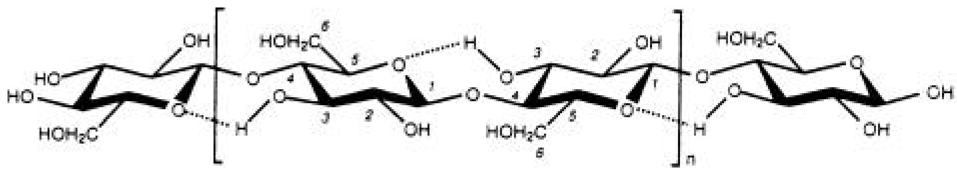

Fig 1.2 Cellulose, the building using of paper materials. Between the brackets its repeating part, the ß(1→4)-Linked cellobiose unit is shown.

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Chapter 2. Materials and Methods

2.1 General

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3) Quillet s.a.,France

During the set up of the project, it was unanimously decided to select new and old (original) materials. As within a previous EU project (EU STEP CT-90-100) reference materials were made, either by specially making them at a paper mill or by ordering at a commercial location, it was decided to apply these materials, that were stored under specific conditions that were kept as constant as possible (dark, 23°C and 50% relative humidity).
Naturally aged papers were obtained under licence from the National Archives of The Hague, the Netherlands Institute for Cultural Heritage, Art Conservation BV and Hai Yen Institute for Conservation of Works of Art.
This paragraph describes the reference paper samples and the dirt types applied as these materials are being used throughout the project. The original samples are described in the separate chapters due to the specific description of the samples and their application.

2.2 Reference papers

By John Havermans[1],
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To understand the behaviour of cellulose fibres, the main component of paper, it is necessary to know the exact paper composition. Also to reduce the large amount of reactions witch can take place, it was a need to include paper without sizing, fillers or other additives.

In table 2.1, the selected new papers are presented. Besides the paper-code, the nicknames of these papers, the place of the stock, description the fibre compositions are given[1].

Table 2.1 The selected new materials

PAPERCODE ***/ NICK-NAME***	**STOCK**	**DESCRIPTION**	**FIBRE COMPOSITION**
PAPER-1 *Sulphite*	TNO	Bleached sulphite softwood cellulose paper / no fillers / no sizing	100% softwood
PAPER-2 *Linters*	TNO	Cotton linters cellulose paper / no fillers / no sizing	95% cotton 5% softwood
PAPER-3 *Acid mechanical*	TNO	Ground wood containing paper / alum-rosin sized	75% ground wood 25% softwood

Sulphite (PAPER-1) Bleached sulphite softwood cellulose paper.
The bleaching sequence was DEHD where the first D was treatment with chlorine dioxide, ClO_2, at low (30 °C) temperature and pulp consistency (3%). E was alkaline extraction with sodium hydroxide, NaOH, H was hypochlorite treatment (NaOCl) and finally D was a chlorine dioxide treatment at elevated temperature (60 °C) and higher consistency (10%).

Table 2.2 Material performance Sulphite

General Information		Chemical information			Mechanical information	
Raw material	softwood bleached sulphite cellulose	*Virgin fibres*	pH extract	6.0	Moisture content	7.6%
Sheet size	50 × 65 cm	*Sheets*	pH extract	6.3	Ash content	0.45%
Grammage	78 g/m^2	*Source water*	pH	8.4	Tear MD	370 mN
Fillers	none		Conductivity	108 mS	Tear CD	390 mN
Sizing	none		[Ca^{2+}]	16.8 mg/L	Fold number	500 (MD)
Quantity	2000 kg		[Mg^{2+}]	1.6 mg/L	Fold number	190 (CD)
Package	PE coated packs 500 sheets a pack	*White water*	pH	7.7	Beating	26°SR
			Conductivity	225 mS	Tensile MD	1.7 kN/m
Ordering date	21-08-1991		[Ca^{2+}]	10.9 mg/L	Tensile CD	0.9 kN/m
Date received	19-12-1991		[Mg^{2+}]	1.4 mg/L	Specific surface (BET)	1.21 m^2/g

Application period PaReLa : 2001-2002

Linters (PAPER-2) Cotton linters cellulose paper
The cotton linters paper was made of linters bleached with elemental chlorine and hypochlorite.

Table 2.3 Material performances Linters

General Information		Chemical information			Mechanical information	
Raw material	cotton linters cellulose	*Virgin fibres*	pH extract	7.0	Moisture content	6.8%
Sheet size	50 × 65 cm	*Sheets*	pH extract	7.3	Ash content	0.005%
Grammage	76 g/m^2	*Source water*	pH	8.6	Tear MD	520 mN
Fillers	none		Conductivity	222 mS	Tear CD	530 mN
Sizing	none	*White water*	pH	8.4	Fold number	630 (MD)
Quantity	2000 kg		Conductivity	280 mS	Fold number	200 (CD)
Package	PE coated packs 500 sheets a pack		[Ca^{2+}]	19.2 mg/L	Beating	29°SR
			[Mg^{2+}]	2.1 mg/L	Tensile MD	1.3 kN/m
Ordering date	21-08-1991				Tensile CD	0.7 kN/m
Date received	19-12-1991					

Application period PaReLa : 2001-2002

Acid mechanical (PAPER-3) Groundwood containing paper

Table 2.4 material performances Acid mechanical

General Information		**Chemical information**			Mechanical information	
Raw material	groundwood	*Sheets*	pH extract	5.9	Moisture content	7.2%
Sheet size	50 × 65 cm				Tear MD	250 mN
Grammage	80 g/m^2				Tear CD	320 mN
Fillers	kaolin approx. 20%				Fold number	400 (MD)
Sizing	alum-rosin/starch				Fold number	60 (CD)
Lignin	present				Tensile MD	
Casein	present				Tensile CD	
Quantity	2000 kg				Specific surface (BET)	1.49 m^2/g
Package	PE coated packs 500 sheets a pack					
Ordering date	05-11-1991					
Date received	14-11-1991					
Application period PaReLa : 2001-2002						

2.3 Definition of conservation problems

By Hadeel Abdul Aziz[1], John Havermans[1] and Rianne Teule[2]
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In order to define conservation problems, each participating conservator was asked to point out the three major cleaning problems present in the work shop. By this means, we were able to establish a priority summary of the cleaning problems.

	Nr. of votes
• Surface dust (including soot)	5
• Stains (pigment stains, foxing)	4
• Adhesives (sellotape) & glues	4
• Grease, oil	1
• ‘Sticky fingers’	3
• Inks and stamps (water-based, organic based)	3
• Tidemarks	1
• Fungi	

Based on the fact that the project time is limited was clear that not all conservation cleaning problems could be solved and therefore a selection was made. This selection was based on the pre existing knowledge on laser cleaning present at BAM and Art Innovation. From a practical point of view and feasibility, two conservation problems were selected for the PaReLa project: adhesive tape removal and the removal of inks and stamps.

2.4 Conventional cleaning methods – A short review

By Veronique Rouchon-Quillet
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When comparing laser treatment with conventional cleaning, it is necessary have a survey of all cleaning methods used by each partner. Atelier Quillet s.a. collected and summarized the results of a questionnaire of conventional cleaning methods that was distributed amongst the SME partners. Hereby the method and/or cleaning effort were taken into account for each conservation problem. This resulted in the next survey consisting of a cleaning proposal, agreed by all partners, for each conservation problem:

- *Surface dust & soot*
  Methods: Rubber (many different kinds), cleaning by mechanical action.
  Result: Partial removal of the dust and sooth.
  Proposal: Combine dust and soot as one case and rubber as a conventional cleaning technique.
- *Foxing:*
  Methods: Solvent immersion/vacuum table
  Proposal: Use most efficient and less destructive chemical reagents, e.g.: most oxidative. Fix acceptable concentration, temperature, and time of immersion
- *Adhesives:*
  Methods: Industrial tapes (vs. traditional glues), vacuum table (partial removal & risk of tide marks), combination of immersion and scalpel.
  Proposal: Too many possibilities and a great variety of tapes.
- *Glues: cellulosic and proteinic*
  Methods: Immersion: dissolution and enzymatic action (used to separate).
  Proposal: It is proposed to focus on proteinic glues, because the problem of yellowing is mainly on proteinic glues. Cellulosic is only problematic if it is very dirty. Method: Immersion in water possible in combination with mechanic action. Define temperature and time.
- *Grease/oil:*
  Methods: Vacuum table for local treatment
  Proposal: For laboratory models, use immersion. This is more efficient.
- *Sticky fingers:*
  Methods: Eraser, immersion
  Proposal: Eraser, immersion/use of cotton, same solution of soap and water (45 ºC.)
- *Inks/Stamps:*
  Methods: Vacuum table (local) to avoid diffusion into paper, immersion, stamps on the surface: easy to remove with scalpel.
  Proposal: Test all methods, depending on ink/stamp. Separate different cases.
- *Tidemarks:*
  Methods: Cleaning by immersion and or by using a vacuum table.
  Proposal: Immersion of the object.

2.5 Preparing test samples

By Hadeel Abdul Aziz[1], John Havermans[1], Piet van Dalen[2], Jan Stokmans[2], Marieke Kraan[3], Bernadette van Beek[3], Frank J. Ligterink[4], José L. Pedersoli Jr.[4], Pascale Rudolph[5], Wolfgang Kautek[5], Rianne Teule[6], Veronique Rouchon-Quillet[7] Susan Corr[8], Hai-Yen Hua-Ströfer[9], Anna Beny[10], Tomas Petéus[11], Doris Müller-Hess[12] and van Zuilen[13]

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10) Barbachano &Beny S.A., Spain
11) Conservator J.T.F. Petéus, Sweden
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13) Restauratie-atelier de Tiendschuur, the Netherlands

To have reproducible results, and especially results that do not depend on the way samples were treated test patterns were developed. For the determination of the sensitivity of selected analyses reference samples were made. These (clean) samples were subjected to laser treatments, where after spectroscopic, color, mechanical and chemical analyses were performed on treated samples
Besides, models were made in order to represent different conservation problems. These models are paper samples containing unwanted material (dirt). The dirt has been put on the test systems in a reproducible way, so each paper sample sheet contains more less the same properties. Another advantage for using test systems, except homogeneity of the samples compared to real objects, is the fact that test systems can be produced in larger amounts. So significant statements regarding the paper property measurements can be made. Two models, representing daily conservation problems were created, containing artificial adhesive contamination and ink stains. The procedure for creating the models has been documented digitally, see figure 2.1 as an example.

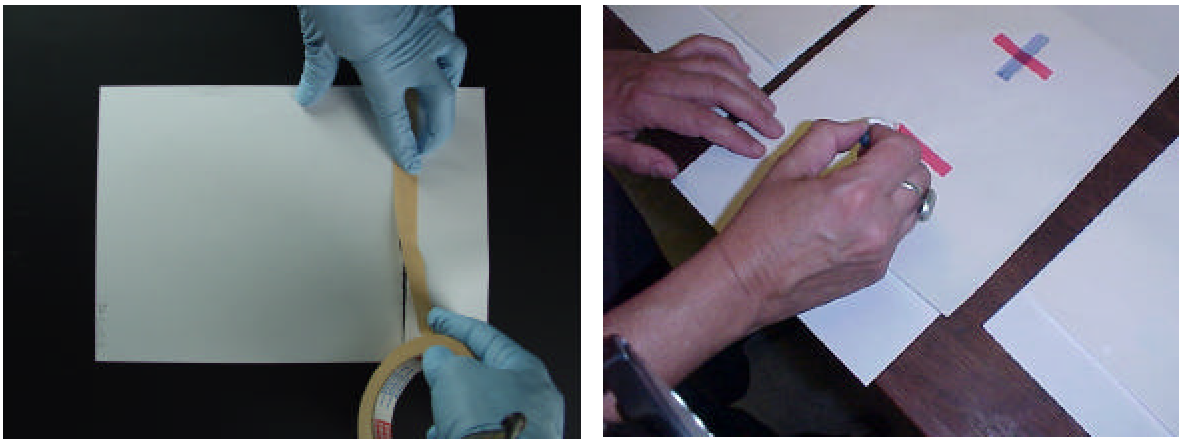

Fig. 2.1 Procedure preparation adhesive model test system (left) and ink model test system (right)

Two ink patterns were designed to represent two different types of cleaning problems characterised by the presence of a stain in the vicinity of a fugitive ink: a droplet pattern and a cross bar pattern. Basis of both patterns is a rectangle of fugitive ink on paper. The droplet pattern representing a typical situation of water damage is created by application of a drop of water on a part of the rectangle. The crossbar pattern is created by application of a second vertical rectangle of blue ballpoint ink on top of the horizontal rectangle. Anticipating different cleaning results for different ink colours and different paper types, three colours (red, green and blue) of water soluble ink and the three paper types, as previously described in this chapter, have been used in all possible combinations to prepare the ink models.
Furthermore ink models were prepared in order to determine the behaviour of mechanical properties of inked papers after being laser treated. Therefore two different types of inks were used a blue ballpoint

ink (BIC) and a blue water based ink (Ecoline). These were applied on a the three paper substrates in all possible combinations. For the ballpoint ink the next procedure was followed. The ink line was put on the papers in machine direction of the paper samples by using a ruler. The length of the ink line is 30 cm with a line thickness of 0.5 mm. Hereby the line was drawn manually on the paper samples, by the same person, in order to diminish differences in samples preparation. During preparation the same ball point pen was used. For the water-based inks, the line was created by using a matrix printer. Hereafter the sheets with the inked line was cut into thin, approximately 1 cm, slices where after the test specimens were subjected to tensile strength measurements.

All tape models were prepared through application of self adhesive tapes on paper. Three types of self adhesive tape commonly found on paper objects, have been used: 3M Scotch Tape #840 S (acrylic adhesive); Sellotape L (rubber based adhesive); and Tesa Crêpe tape (rubber based adhesive). All possible combinations of these tapes with the three paper types were prepared.

As a rule the cleaning of aged substances on aged papers is in general more difficult. To simulate this effect all ink and tape models were artificially aged ('pre-aged') before cleaning treatments. To simulate if any undesired side effects might occur as a result of a cleaning treatment all models were also artificially aged after cleaning ('post-aged').
Within the Parela project several other models have been prepared and aged. For clarity these samples are not included in the description here.

As many participants are involved in sample preparation, artificially ageing, laser treatments, analyses and aesthetical evaluation, organisation, distribution and logistics of sample flow including time schemes are important aspects.
The complexity of the flow scheme for the samples is illustrated in the next Figure concerning the ink model test system.

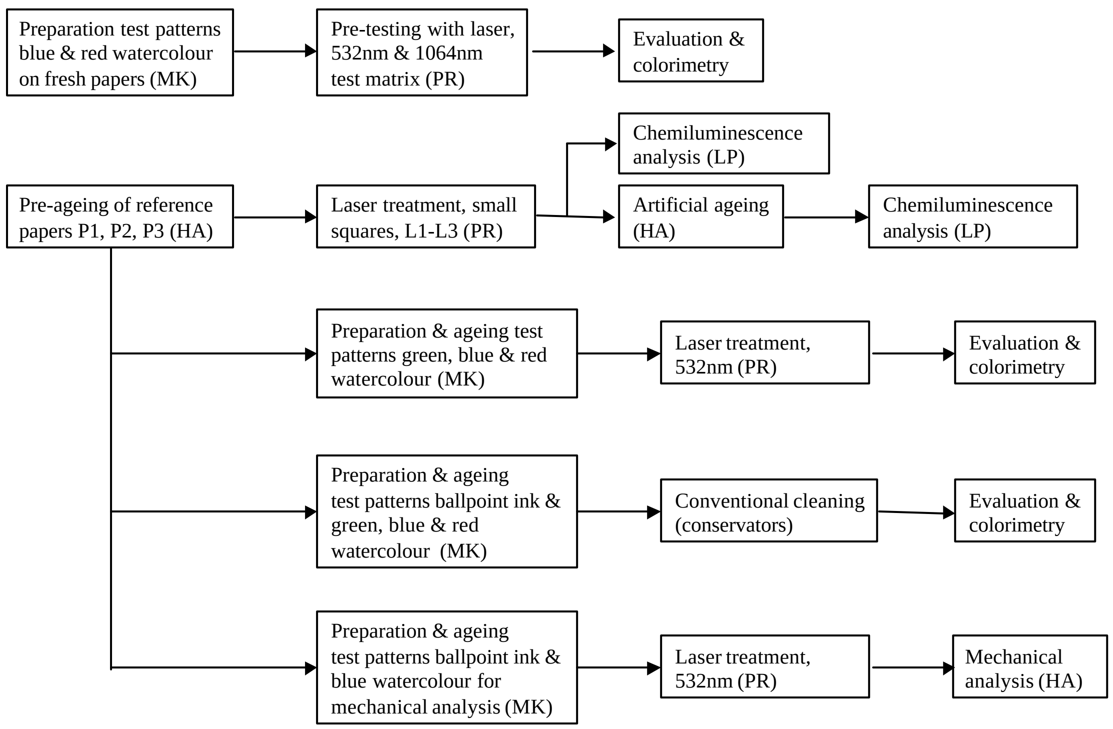

Fig. 2.2 Flow scheme ink model test system

Each group of test systems or reference samples was divided in sample series number. Every sheet was coded with a unique number in order to prevent confusion. For the adhesive test system Art Conservation prepared 126 A-4 sheets. The ink model test system consists of 96 sheets. Besides, preliminary test systems were created and laser treated. After preparation and ageing the samples were treated, using both conventional cleaning methods and laser treatments.

2.6 References

1. Havermans, J.B.G.A., J.P.v. Deventer, R. van Dongen, F. Flieder, F. Daniel, P. Kolseth, T. Iversen, H. Lennholm, O. Lindqvist, and A.S. Johansson, *The Effects of Air Pollutants on the Accelerated Ageing of Cellulose Containing Materials - Paper. EC/DGXII/STEP Project CT 90-0100*. 1994, TNO, Delft, The Netherlands.

Chapter 3. The behaviour of laser treated samples

3.1 Introduction

By Pascale Rudolph[1], Frank J. Ligterink[2], John Havermans[3], José L. Pedersoli Jr. [2], Hadeel Abdul Aziz [3]

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Laser treatment of organic materials for conservation purposes such as paper objects of cultural and historic value has been studied with increasing interest from the conservation community [e.g. 1]. It has to take into account the typically high susceptibility of those materials to thermal and photochemical degradation. Therefore, characterization of paper alterations caused by laser irradiation is relevant, to evaluate laser cleaning as a safe alternative in paper conservation practice. Whereas some of those alterations are clearly perceptible, e.g. discolouration, surface roughening or disruption, invisible chemical changes may as well take place, which might cause the paper to degrade faster.

In our studies, optical and chemical alterations of different fresh, pre-aged, and post-aged paper types caused by laser treatment using different parameters (wavelength, energy density, and overlap) were characterized by several analytical methods.

Discolouration of the paper substrate as a result of laser treatment is considered undesirable especially during long-term storage, as is the aim for having the papers cleaned. The average molecular mass or, inter-convertibly, the average degree of polymerisation (DP) of cellulose, the major structural component of paper, is an important analytical criterion to quantitatively monitor the degradation of paper [e.g. 2]. Cellulose is a linear, syndiotactic homo-polysaccharide consisting of D-anhydro-glucopyranose units connected by β-1,4-glycosidic bonds. The depolymerisation of cellulose will negatively affect the mechanical properties of paper, leading to a loss of strength and flexibility, and to an increased brittleness [e.g. 3]. On the other hand, the apparent increase in cellulose DP due to the cross-linking of cellulose molecules, which occur as a result of e.g. thermal degradation, may affect the hydrophilic and mechanical properties of paper. Size exclusion chromatography (SEC) is the preferred method to characterize the molecular mass distribution (MMD) of polymers, including cellulose [e.g. 4].

Chemiluminescence is the phenomenon of ultra weak light emission arising from the relaxation of excited states populated in chemical reactions [5]. The self-recombination of secondary peroxy radicals, i.e. the Russel mechanism [6], yielding excited triplet state ketones and singlet oxygen is generally accepted as the most probable reaction mechanism causing chemiluminescence:

R-CXH-OO· + ROO· ? R-C(X)=O* + ROH + O_2*

The chemiluminescence of cellulose has been recently studied in the course of thermal and thermal oxidative degradation [7]. Three independent light emitting processes have been identified in dynamic CL experiments under inert atmosphere: (1) decomposition of emitting species (presumably oxygen-cellulose charge transfer complexes) formed by sample pre-irradiation with visible light, at 85 ºC; (2) decomposition of macromolecular peroxides, at 135 ºC; and (3) chain-scissions, at T > 160ºC, which are accompanied by a decrease in degree of polymerisation. The two first CL processes are of interest to investigate the effects of laser interaction with paper. Whereas direct photolysis of cellulose is not observed at wavelengths greater than 310 nm, photosensitised degradation generating macromolecular radicals is expected to take place to some extent in the paper systems treated with UV lasers. For the lasers of longer wavelengths, such a photochemical effect is far less expected. Detection of peroxides or other emitting species eventually formed by laser treatment would offer insight into the early stages of alteration caused by the different lasers on the investigated paper samples.

Due to a treatment the surface structure and or the cellulose ultra structure might change and therefore it might change the sensibility for the uptake of certain air-pollutants. The energy produced by the laser can promote radicals and these radicals may subsequently deteriorate the cellulose chains. This will result in more reactive cellulose end-groups. Also if paper contains lignin (a polymeric aromatic wood component) this effect can be more severe. Based on previous studies on the effects of paper degradation by air pollutants, we considered investigating papers used in the EU-CRAFT Parela projects more seriously on their uptake of sulphur dioxide. It is suggested that SO_2 absorbed in papers

is held in two ways, either reversible or irreversible. The reversible one is the adsorption of the SO_2 to the paper surface. The physically adsorbed the SO_2(g) can be dissolved in the moisture present in the paper and can be converted to sulphite according to:
$SO_2 + H_2O$? SO_3^{2-}(ads) + $2H^+$(ads).
The sulphite can react easily to sulphate as it is thermodynamically unstable, and therefore the overall reaction can be considered as an irreversible one. Damage to the paper can accordingly be related to the adsorption of SO_2(g). Also based on results from the European Research project on paper ageing (ref) it was concluded that the method used for studying the deposition of air pollutants on metals is extremely suitable of investigating paper samples and that a good correlation exist in the long term behaviour and the adsorption behaviour of SO_2.

3.2 Materials

The reference papers applied described in Chapter 2. The inked samples were created by applying an ink line on the papers. The ink line was put on the papers in cross direction of the paper samples by using a ruler. The length of the ink line is 30 cm with a line thickness of 0.5 mm. Hereby the line was drawn manually on the paper samples, by the same person, in order to diminish differences in samples preparation. During preparation the same ball point pen was used. The samples exposed to air pollutants were prepared from sampled sheets of similar paper grade, however these papers were stored for eight years at two different storage conditions – a purified archival storage condition and an non purified archival storage condition. The size of the specimens per sample was 3x8 cm, within a specimen an area was treated by laser having a surface of approx. 2.5x6 cm.

3.3 Experimental

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Laser treatment

For he basic studies on the material behaviour after laser treatment different laser wavelengths were used: in the ultraviolet range (355 nm), in the visible field (532 nm), and in the infrared region (1064 nm). In all cases a Nd:YAG-laser delivered the laser beam. The system (Spectron Laser Systems, SL 852) used with the third harmonic wavelength at ? = 355 nm had a maximum output energy of 16 mJ with a pulse duration of 13 ns and a repetition rate of 1.25 Hz. The beam was focused by a quartz cylinder lens (310 mm focal length) to a spot dimension of (200 x 2000) μm^2 (area 0.04 cm^2). In this set-up the samples were mounted and scanned on a controlled x-y-z stage. Another laser, a computerized prototype laser cleaning system, based on a high pulse energy diode pumped Q-switched Nd:YAG laser operating with a pulse duration of approximately 10 ns at 1064 nm and 532 nm is specified with output energies of 5 mJ for ? = 1064 nm and of 2.5 mJ for ? = 532 nm. The set-up consisted of a scanning optical system (254 mm focal length) which delivered a spot size of approximately 100 µm and energy densities (fluences) in the range of up to $F_{max}(1064) = 21$ J/cm^2 and $F_{max}(532) = 10$ J/cm^2. A repetition rate of less than 1 kHz could be controlled freely. The fluences and number of pulses were varied. Lower and upper limits of the fluence ranges to be studied for each wavelength were chosen around prior determined ablation threshold fluences. The criterion for the ablation threshold used in this study is the fluence level for which a visible destruction of the paper matrix with $N = 35$ pulses per area was observable and additionally a treatment on another area with $N = 10$ pulses yielded not in a damage.
For colour and M_w measurements matrix patterned samples were prepared on fresh and pre-aged, PAPER-1 and PAPER-2 papers. A matrix of (6x4) or (5x4) squares (approx. 8x8 mm^2) for each wavelength/substrate combination was laser treated with varying fluences and pulse numbers. For the

ultraviolet laser at ? = 355 nm, the fluences were varied between $F = 0.25\text{-}1.75$ J/cm^2, for the green laser at ? = 532 nm between $F = 0.08\text{-}2.35$ J/cm^2, and for the infrared laser at ? = 1064 nm between $F = 1.2\text{-}6.7$ J/cm^2. Additionally the pulse numbers ranged from $N = 1$, 2, 5, and 9. For CL measurements fresh papers Paper-1 and Paper-2 were laser treated at $\lambda = 355$ nm with fluence $F = 1.35$ J/cm^2, and Paper-3 with $F = 0.19$ J/cm^2, respectively. The laser treatment at $\lambda = 532$ nm used a fluence of $F = 0.83$ J/cm^2 for Paper-1 and Paper-2, and $F = 0.08$ J/cm^2 for Paper-3. The pulse number was always set as $N = 3$.

For the removal of the ink lines and to study the mechanical properties the laser treatment at $\lambda = 532$ nm used a fluence of 0.64, 0.87, 0.08 J/cm^2 for Paper-1, -2 and -3 respectively (with N=3).
Finally for the applied studies on the uptake of air pollutants the fixed laser treatment at λ =532 nm (N=3) used a fluence of 0.6 J/cm^2 for Paper-1 and paper-2, and 0.06 J/cm^2 for paper-3.

Artificial ageing

In order modelling the age of the materials pre and post ageing experiments were carried out on the fresh and treated papers. The artificial ageing was performed by exposure the materials to air at 90 °C and 50% relative humidity, in the dark, for 12 days [8].
In order to assess the long-term effects of laser treatment subsets of laser treated papers (papers Paper-1, Paper-2, and Paper-3 and inked papers) were artificially aged.
Post-ageing for the UV laser ($\lambda = 355$ nm) and for the green ($\lambda = 532$ nm) was done, respectively, by exposure to air at 80 °C and 65% relative humidity, and 90 °C and 50% relative humidity, both in the dark for 12 days.

Before putting the ink lines on the samples the samples were pre-aged. After the ink was put on the samples the samples were post-aged, this to let the ink attach to the paper, as ink on real objects would occur. Hereafter the samples were laser treated. And finally, a last post-ageing step was performed in order to determine the long-term effects of laser treatment on the inked samples.

The same ageing steps were performed on the reference samples, thus making comparison of the inked samples with non-inked samples possible
In Fig. 3.1 a schematic overview is given for the different treatments of the ink models.

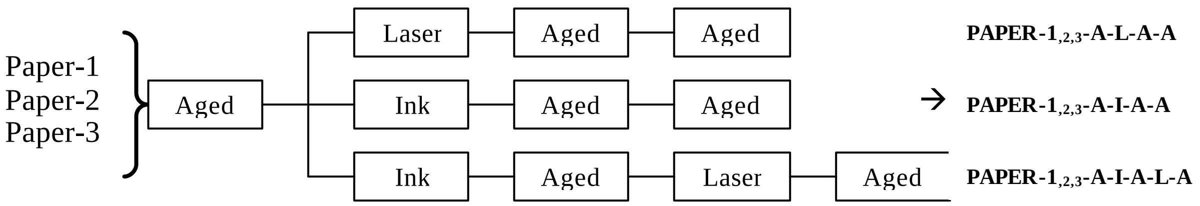

Fig. 3.1: Schematic overview treatments ink models (A = ageing; L = laser treatment; I = inked).

Artificial pollution

All the paper specimen were pre-conditioned for a minimum three days in order to reach a moisture content similar to the final testing conditions. For this purpose, the specimen were put in a desiccator containing a saturated salt solution (KCl) producing a relative humidity of about 85% at room temperature.

The experiments were carried out using time-resolved analyses of the deposition of SO_2 [3, 9]. The equipment used created by allowing purified and dried air to enter through two different channels. One part was saturated with water vapour at the exposure temperature (22 °C) and the other part was used as a barrier for the pollutants SO_2 or SO_2 and NO_2. These were added from permeation tubes with contained the pollutant in a liquid form. The concentration of the pollutants was controlled within 2 ppb. The experimental pollution conditions were 22 °C and 85% RH. Two separate experiments were carried out using 120 ppb SO_2 and subsequently using 120 ppb SO_2 and 350 ppb NO_x. The exposure time per experiment was 24 hours.

Analyses

Colour measurements

Colour measurements on laser treated areas and untreated background were carried out using a Minolta CM-2002 spectrophotometer equipped with a 5 mm aperture sample holder CM-A49. The spectrophotometer is connected to an integrating sphere, illuminated with a UV-filtered pulsed xenon arc lamp. The illumination/viewing condition is (D/0). Monitoring of changes in gloss was considered important. For this reason spectral reflectance was measured with the specular component included (SCI). Data acquisition and colour analysis was performed with Minolta Chromacontrol (S) V 1.17 software. CIE-L*a*b* colour coordinates were calculated for the 10° standard observer and illuminant D65. Background measurements performed on the untreated areas were always repeated three times at different locations to determine the variability within each single paper sample. Measurements on the laser treated areas were done only once.

Size exclusion chromatography

Size exclusion chromatography (SEC) was used to characterize the molecular mass distribution of cellulose in laser treated areas and untreated background. The macromolecules are separated according to their hydrodynamic volume in solution by driving the solution through a porous, three-dimensional network in a chromatography column. From the chromatogram average molecular masses, and the corresponding average DP values, can be determined with good precision. In our studies weight-average molecular masses (M_w) are reported.

Cellulose is not soluble in organic solvents typically used as mobile phases in SEC. In this study, cellulose was chemically modified prior to analysis by reaction with phenyl isocyanate (PIC). The resulting soluble cellulose tricarbanilate (CTC) derivative shows enhanced UV detection properties. Advantages of this procedure are that full trisubstitution is achieved in one reaction step, the MMD of the parent polysaccharide remains unaffected, and the long-term stability of the CTC. The derivatisation procedure was adapted to accommodate the use of small samples of (1x1 mm^2). The use of alternative solvent systems was not considered due to the absence of UV active groups on native cellulose. Due to the screening action of lignin in the derivatisation procedure, the use of the method to determine the M_w of cellulose was limited to the lignin free papers PAPER-1 and PAPER-2.

For size exclusion chromatography, equipment from Waters Chromatography B.V. (Etten-Leur, NL) was used. The mobile phase tetrahydrofuran (THF HPLC grade) was delivered by an isocratic 515 pump with a flow rate of 0.3 ml/min. Sample injection, usually 10 µl, was performed by a 717 autosampler. The separation of the macromolecules was done with three, coupled PLgel Mixed B columns from Polymer Laboratories Ltd. (Shropshire, UK) thermostated at 30 °C. The SEC system was calibrated with PIC-derivatised pullulan standards and with narrow molecular mass polystyrene standards to cover the whole needed mass range. Both standards showed good correlation. Final MMD's were calculated on the basis of cellulose. Detection was performed by a 996 photodiode array detector at a wavelength of 254 nm for the polystyrene standards and at 235 nm for the PIC-derivatised pullulan standards and the CTC samples. The SEC system was controlled by Waters Millennium[32] software, which was also used to perform data acquisition. The data files were exported as ASCII files to a computer using in-house software for subsequent MMD calculation.

Chemiluminescence
Chemiluminescence experiments (CL) were carried out on a Lumipol-2 photon counting instrument manufactured by the Polymer Institute of the Slovak Academy of Sciences (Bratislava). The CL of the paper samples was recorded during dynamic experiments performed in nitrogen by maintaining a gas flow of 3 l/h. Paper discs (Φ = 5 mm) were placed onto an aluminium pan, conditioned for 10 minutes at 40 ºC, and then heated up to 200 ºC at a heating rate of 2.5 ºC/min. The CL response of laser treated areas of the test papers has been compared to that of untreated areas. The measurements have been carried out a few days after the irradiation of the papers, as well as after artificial ageing of the irradiated samples. This allowed the study of both immediate and long-term effects of laser treatment on the CL of the samples. All measurements of laser-treated areas of the paper were carried out in duplicate, and those of untreated areas in triplicate.

Tensile strength
The tensile strength of the paper samples was measured, by cutting the samples in thin slices. Hereby a Lorentzen & Wettre apparatus, using a 500 N load cell, measured the tensile strength. Besides tensile strength measurements, every sample was studied by eye and a judgement was made whether the sample broke on the laser treated line or not. For each set of samples this resulted in an average tensile strength (quantitative identification) and an average break percentage (qualitative identification).

Morphological investigations
The morphology of a selection of the samples was investigated using

a) Visual and stereomicroscopic investigation. Samples were subjected to normal daylight and judged by a magnification of 1 and 50.
b) Scanning Electron Microscopy in combination with X-ray microanalysis (SEM/XRMA), was applied to analyse the fibre structure using secondary electron imaging and to analyse present local elemental analysis, using backscattered primary electron imaging.

3.4 Results and discussion

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Determination of ablation threshold

The ablation threshold fluences F_{th} as defined previously, for all fresh and pre-aged papers with all laser wavelengths were determined. With a focal spot size of approximately 100 µm, the ablation thresholds for the test papers were determined.

The pre-aged papers seem to be more sensitive against laser radiation and therefore, their ablation threshold fluences are lower. Especially for the infrared laser, all papers show in the aged stadium a decrease of resistance against laser radiation. The difference is of the order of ~30%.

The colorimetric measurements were performed at Paper-1 and Paper-2. In Fig. 3.2, a comparison of colour measurements on fresh Paper-1 to pre-aged Paper-1 for all three laser wavelengths is shown. The laser fluences and pulse numbers were varied. A laser treated matrix pattern of (6x4) or (5x4) resulted, respectively.

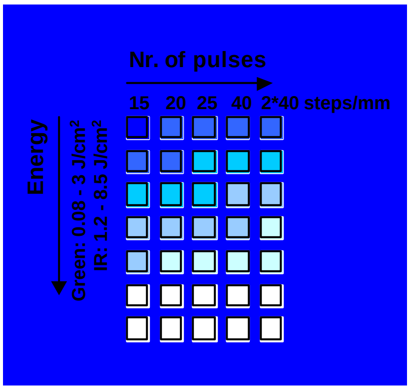

Fig. 3.2: Example of threshold establishment

Differences of ?E* > 1 are visible by naked eye. Maximal differences of ?E* < 3 were observed (with an error of approximately ± 0.2); especially after infrared laser interaction the values are different. Treatments with the green and ultraviolet laser resulted in similar colorimetric changes. These were after laser irradiation more pronounced for pre-aged than for fresh samples (especially Paper-2). This observation corresponds with the threshold fluence behaviour where normally the threshold of fresh paper F_{th}(fresh) is slightly higher than for the pre-aged samples F_{th}(aged).

On the colorimetric samples also the M_w of cellulose was determined. Paper-3 was excluded because of its lignin content. The laser parameters were varied as mentioned previously. Typical values for M_w are in the order of up to 7 x 10^5 Da. M_w results for fresh Paper-1 and pre-aged Paper-1 treated with all three laser wavelengths are presented in figure 2. The pre-ageing procedure yielded in a decrease of approximately 2 x 10^5 Da. A comparison between the background and the laser treated matrix areas showed that the ultraviolet laser radiation resulted in a significant decrease in the M_w value for higher fluences and higher number of pulses. Whereas the green and the infrared laser light interaction caused no M_w effect related to laser parameters or only a slight decrease towards rougher conditions, respectively. The results for Paper-2 showed similar behaviour.

The chemiluminescence measurements were performed at all three fresh and post-aged paper types. A comparison of fresh Paper-1 and Paper-2 to post-aged samples for the laser treatment with the green wavelength is shown in figure 3. No significant differences between the CL responses of treated and untreated areas for the two papers, both fresh and artificially aged, are observed. The bleached sulphite softwood cellulose paper Paper-1 show the typical CL peroxide decomposition peak centred at 125 ºC. Its position and intensity is not altered by laser treatment and/or artificial ageing. For paper Paper-2 a shoulder centred at 150 ºC can be seen, which is not affected by laser treatment but whose intensity is reduced by artificial ageing.

Contrary to the results obtained with the green laser, significant differences between the CL responses of all three papers are observed. Laser treatment causes the CL intensity of the fresh papers Paper-1 and Paper-2 to increase in the temperature interval of 40–125 ºC. A second difference in the CL trace of Paper-2 is the disappearance of the CL shoulder centred at 150 ºC in the laser-treated sample. The

fresh paper Paper-3 (a rosin-sized mechanical pulp paper, not exhibited here) shows a higher CL emission for the entire temperature interval of the measurement as a result of laser treatment. Artificial ageing reduces considerably the differences between the CL response of laser treated and non-laser treated areas of all three papers, especially Paper-2 and Paper-3.
These results suggest the generation of emitting species as a result of UV laser treatment, which react further into non-emitting products in the course of artificial ageing. The depletion of the emitting species decomposing between 130 ºC and 170 ºC in paper Paper-2 by laser treatment seems to be reversed to some extent by artificial ageing.

Cleaning of model samples

Although it is accepted that models and real objects never behave the same, they give the possibility to test standardized working procedures such as a microtest. Therefore, the laser treatment started with a test matrix, in which the number of pulses and the energy was varied in two dimensions (see figure, squares approximately 5 x 5 mm^2). After inspection of the test matrix by eye - looking at the roughness, visible damage, and cleaning effect - the operator chose two parameter sets to apply on the test systems. An additional quantification tool can be the spectral analysis of the laser treated areas in comparison to a field with the desired colour.
Different kinds of model test systems were designed. Therefore, the project partners formed an ink- and an adhesive-subgroup.
The *ink-group* concentrated their interest regarding stamps. Looking at inks, in view of the large range of materials the group proposed to study the two extreme cases first: Ink that stays on top of the paper surface and ink that penetrates the paper completely. Most important conservation problems are stains from water-soluble inks and 'graffiti' from felt-tip pen or ballpoints. Also, with solvent-based ink in felt-tip pens migration through the paper occurs, causing halos around drawing lines. This problem is difficult to imitate and needs a lot of pre-testing. For ink patterns, green, red and blue watercolour ink (Talens, 'ecoline'), and ballpoint ink (Parker, 'BIC') were used. The pre-test systems were prepared and laser treated at BAM with λ = 532 nm and λ = 1064 nm. The laser treatment followed the above mentioned microtest pattern on a larger ink area. The two "best looking" parameter sets were applied at a 'graffiti' problem and a bleeding situation.
Generally, the results on the ballpoint ink were good, especially with λ = 532 nm. Also the removal of ballpoint ink from the green watercolour was satisfactory, leaving the watercolour intact. Removal of the green watercolour is difficult, due to low absorptivity.
First trials with conventional methods on the green watercolour were also not satisfactory, but the use of a vacuum table might be more successful.
From the conservators point of view a complete non-destructive cleaning is not always the aim. More conservative parameters (less laser pulses, moderate energy) leaving some of the ink behind is more in the view of the conservator's aesthetic.
The current tests were repeated after artificial ageing, since it is known that the water solubility of ink (especially containing gum arabic) decreases with time.
The project partners who are interested in adhesives form the *adhesive-subgroup*. They selected three different kinds of tape: Scotch 840, Sello tape, Crepe tape TESA. They used with λ = 532 nm green laser light. The laser treatment follows again the micro-test pattern. The tests were repeated after artificial ageing. Further results related to the removal of adhesive tapes will be discussed elsewhere in this report.

Determination of ablation threshold fluences

The ablation threshold fluences F_{th} as defined above, for all fresh and pre-aged papers with all laser wavelengths were determined. With a focal spot size of approximately 100 µm, the ablation thresholds for the test papers were determined.
It was found that the pre-aged papers were somewhat more sensitive against laser radiation and therefore, their ablation threshold fluences are lower. Especially for the infrared laser, all papers show

in the aged stadium a decrease of resistance against laser radiation. The difference is of the order of ~30%.

Colorimetry

The colorimetric measurements were performed at Paper-1 and Paper-2 for all three laser wavelengths with increasing fluences and pulse numbers.
Differences of ?E* > 1 were visible by naked eye. Maximal differences of ?E* < 3 were observed (with an error of approximately ± 0.2); especially after infrared laser interaction the values are different. Treatments with the green and ultraviolet laser resulted in similar colorimetric changes. These were after laser irradiation more pronounced for pre-aged than for fresh samples (especially Paper-2). This observation corresponds with the threshold fluence behaviour where normally the threshold of fresh paper F_{th}(fresh) is slightly higher than for the pre-aged samples F_{th}(aged).

Size exclusion chromatography

On the colorimetric samples also the M_w of cellulose was determined. Paper-3 was excluded because of its lignin content. The laser parameters were varied as mentioned previously. Typical values for M_w are in the order of up to 7 x 10^5 Da. Based on the results, we found that pre-aged papers had in a decrease of approximately 2 x 10^5 Da. A comparison between the background and the lasered matrix areas showed that the ultraviolet laser radiation resulted in a significant decrease in the M_w value for higher fluences and higher number of pulses, whereas the green and the infrared laser light interaction caused no M_w effect related to laser parameters or only a slight decrease towards rougher conditions, respectively. The results for Paper-2 showed similar behaviour.

Chemiluminescence analysis

The chemiluminescence measurements were performed at all three fresh and post-aged paper types. No significant differences between the CL responses of treated and untreated areas for the two papers, both fresh and artificially aged, were observed. The bleached sulphite softwood cellulose paper Paper-1 showed the typical CL peroxide decomposition peak centred at 125 ºC. Laser treatment and/or artificial ageing did not alter its position and intensity. For paper Paper-2 a shoulder centred at 150 ºC was observed, which is not affected by laser treatment but whose intensity is reduced by artificial ageing.
The chemiluminescence of the paper samples Paper-1 and Paper-2 treated with the UV laser showed in contrary to the results obtained with the green laser, significant differences between the CL responses for all the three used paper grades. Laser treatment causes the CL intensity of the fresh papers Paper-1 and Paper-2 to increase in the temperature interval of 40–125 ºC. A second difference in the CL trace of Paper-2 is the disappearance of the CL shoulder centred at 150 ºC in the laser-treated sample. The fresh paper Paper-3 (a rosin-sized mechanical pulp paper) showed a higher CL emission for the entire temperature interval of the measurement as a result of laser treatment. Artificial ageing reduces considerably the differences between the CL response of laser treated and non-laser treated areas of all three papers, especially for Paper-2 and Paper-3. These results suggest the generation of emitting species as a result of UV laser treatment, which react further into non-emitting products in the course of artificial ageing. The depletion of the emitting species decomposing between 130 ºC and 170 ºC in paper Paper-2 by laser treatment seems to be reversed to some extent by artificial ageing.

The uptake of sulphur dioxide

Comparison of Paper-1 and Paper-3.

Based on the obtained results (see Fig 3.3), it was found that paper-3, a mechanical pulp paper, adsorbs more SO_2 than paper-1, the pure softwood pulp paper (See Fig 1). These results are in agreement with previous studies by Havermans and Johansson [3, 9]. The higher SO_2 absorption can be attributed to the presence of lignin in paper-3. If we include the presence of NO_2, a synergistic effect for the absorption of SO2 was found. The increase of the SO_2 absorption can be explained due to the increase of oxidation and adsorbed sulphur. However, according to Johansson, the overall mechanisms of oxidation of SO_2 involving NO_2 still remain unclear. It has been suggested that there might be a catalytic act of NO_2 on the SO_2 oxidation.

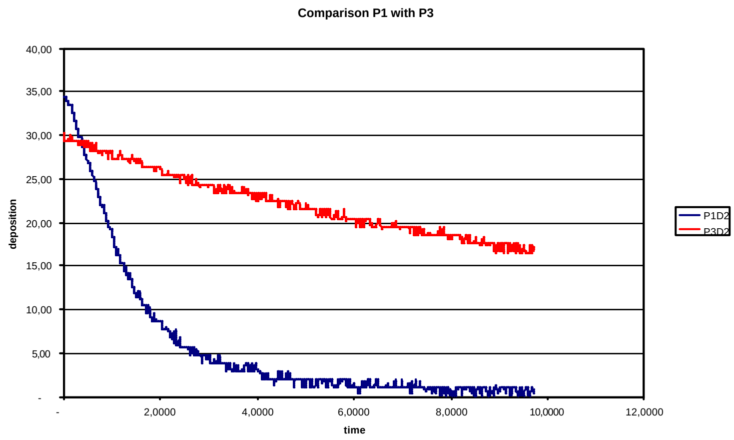

Fig. 3.3: An example of the deposition of SO_2 on two different paper substrates. The upper (red) line represents the acid mechanical pulp paper (Paper-3), the lower line (blue) represents the bleached sulphite softwood paper (paper-1). On the x-axes the deposition in ppb is given, while on the y axis the time (hours) is given.

Comparison of storage conditions

Based on previous research it is suggested that deterioration of paper results in an increase of uptake of air pollutants due to the formation of reactive sites of the cellulose and changes in the ultra structure of the cellulose fibres. The storage of the papers for 9 years and using different storage conditions, do indeed show a small change in the SO_2 uptake when NO_2 is present.

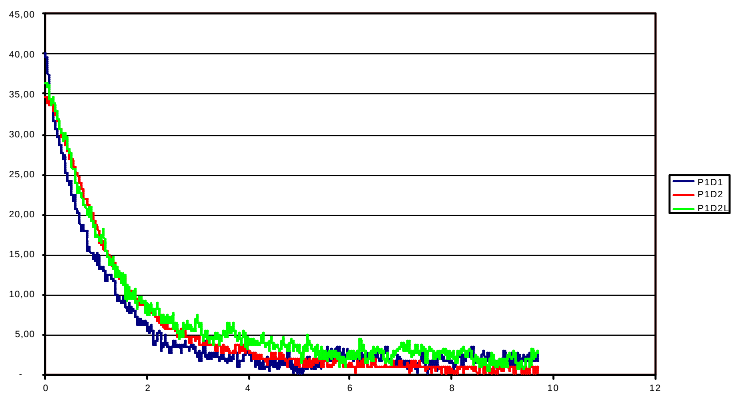

Fig 3.4: Three materials compared on their deposition of SO_2. The red line represents Paper-1 stored under air-purified conditions, the green line represents the same paper, but then laser treated. The bleu line presents Paper-1 stored under non-air purified conditions. The storage time was eight years. On the x-axes the deposition in ppb is given, while on the y axis the time (hours) is given.

No significant changes were found in absorption for the presence of only SO_2 between the different types of storages (see Fig. 3.4).
Especially for the paper-3, the mechanical pulp one significant change was found of about 4 ppb. This firstly indicates the synergistic role of NO_2 for paper deterioration at an ambient environment. Based on the results, we conclude that storage of paper under ambient atmosphere indeed deteriorates the paper faster than stored in a purified atmosphere.

Comparison of cleaning methods

Looking firstly on the pure cellulose paper, it was found that the behaviour of the deposition of SO_2 was independent on the storage condition and cleaning. This is shown
in Fig X. The initial uptake was between the 35 and 40 ppb, while the curve for all the samples are comparable. The uptake of SO_2 for the long term is for the paper stored under a purified atmosphere somewhat lower then for non-purified storage atmosphere, thus due to natural ageing under non-purified storage the long-term uptake is somewhat enhanced, but is found similar to that of the paper cleaned by laser.

Considering to the effects of the uptake of SO_2 for the reference and laser cleaned paper the results per experiment were compared. This is presented in the figure below, where the reference sample is plotted on the x-axis and the laser treated sample on the y-axis. If the line should be having an angle of 45 (Tan(?) = 1) then no difference in SO_2 uptake would be present between the non and laser treated samples.

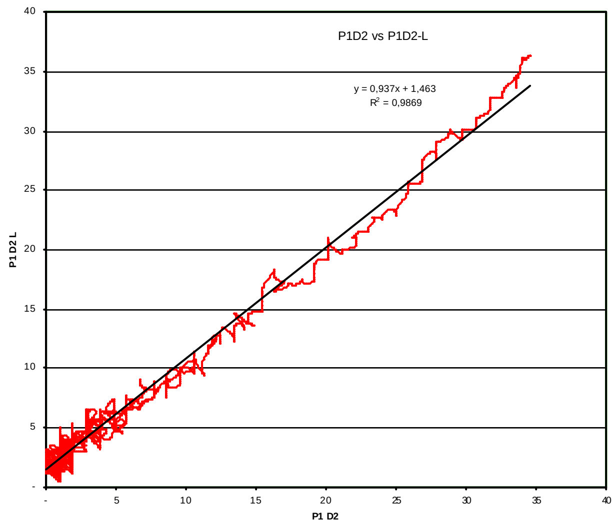

Fig 3.5: An example of the correlation between two experiments. Here the deposition of SO_2 on Paper-1 after eight year storage at an air purified room is plotted (x-axis) against the same paper but then after leaser treatment (y-axis)

Using statistical calculations between the measured values (t-test and F-test) we must conclude that the uptake of SO_2 for the laser treated samples do differ significantly from the non-laser treated samples. Based on the given example, we found that Tan(?) = 0.937 and the intercept with the y-axis was 1.463. This indicates that there is a somewhat reduced initial SO_2 uptake after laser treatment, while for the long term the uptake shall be somewhat enhanced.

A similar procedure was followed for the other combinations. Thus for the SO_2 uptake of the lignin containing paper (Paper no. 3) and for the uptake of SO_2 when NO_2 is present. The results are summarized in the table below. For all cases the reference paper was plotted against the laser cle aned paper.

Table 3.1 The parameters of the papers after laser treatment. The calculations were done using the untreated paper as a reference.

Comparison	**Tan(?)**	**Intercept**	**Correlation coeficient R^2**
With only SO_2			
Paper-1	0.937	1.463	0.987
Paper-3	0.999	0.940	0.933
With SO_2 and NO_2			
Paper-1	0.907	1.748	0.987
Paper-3	1.905	-1.461	0.989

Thus looking at the Tan(?) value, representing the ratio of the initial SO_2 uptake between the laser treated and non- laser treated paper, we suggest that only for Paper-3, the lignin containing paper, the uptake was seriously enhanced after laser treatment and at the presence of NO_2. As we know that NO_2 does enhance the uptake of SO_2, we can conclude that treatment by laser also gives a synergistic effect on the uptake of SO_2 for lignin containing papers. The intercept in can be seen as a ratio for the long-term uptake of SO_2 between the treated and non-treated paper samples. Due to the fact that we calculate a negative intercept it might indicate that for the long term the SO_2 uptake shall be less then for the non-cleaned samples.

For the other cases laser treatment is somewhat decreasing the initial SO_2 uptake, which sounds positive, however due to the fact that the intercept is higher than 0, we suggest that for the long term papers cleaned by laser shall have a somewhat enhanced uptake of SO_2.

The effects of ink

The chronological sequence of these three cases studies in our work are:

- a pre-aged, laser treated, double post-aged set of samples (PAPER-$1_{,2,3}$-A-L-A-A),
- a pre-aged, inked, post-aged, laser treated, post aged set of samples (PAPER-$1_{,2,3}$-A-I-A-L-A),
- a pre-aged, inked, double post-aged set of samples (PAPER-$1_{,2,3}$-A-I-A-A).

An illustration of the qualitative identification of the inked lines is given in the Fig 3.6a Fig 3.6b. In these the figures the breaking percentage of the inked laser treated samples (left, Fig 3.6a) and the inked non-laser treated samples (right Fig 3.6b) of paper-1 are compared. From these figures it becomes clear that the laser treatment of the ink line makes this part of the paper substrate most sensitive for tensile strength, as most of the samples broke exactly on the laser treated inked line. This means that the inked line has become the weakest part of the slice of paper after laser treatment. Tensile strength on solely inked papers showed that hardly any samples broke on the inked line.

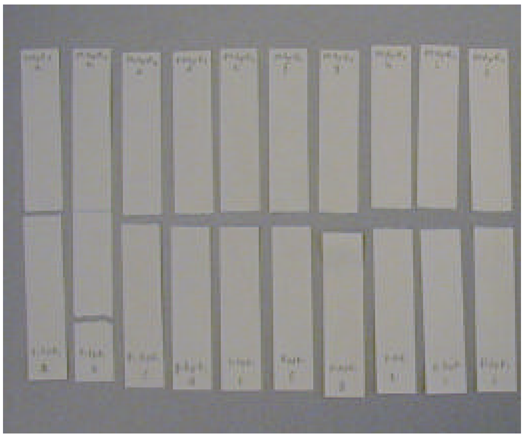

Fig 3.6a: PAPER-1-A-I-A-L-A
Laser treated samples
Breaking on the ink lines after ageing

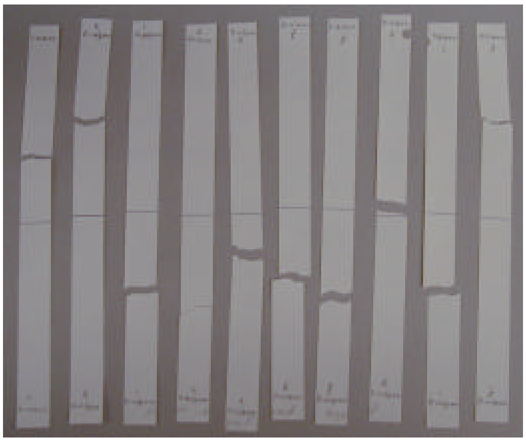

Fig 3.6b : PAPER-1-A-I-A-A
Non laser treated samples
Breaking random of the paper samples

Table 3.2 presents the results of the quantitative and qualitative identification for each paper type.

Table 3.2 Results of the tensile strength samples. Here the average strength in kN is given for the breakage of the samples. Also the percentage of samples that broke on the ink-line is presented.

Sample	Strength [kN] average	Strength [kN] error	* Break %
P1-A-A-L-A	1,42	0,03	0
P1-A-Ip-A-A	1,48	0,04	10
P1-A-Ip-A-L-A	1,29	0,06	89
P2-A-A-L-A	1,32	0,02	0
P2-A-Ip-A-A	1,40	0,03	10
P2-A-Ip-A-L-A	1,33	0,03	26
P3-A-A-L-A	1,11	0,06	0
P3-A-Ip-A-A	1,12	0,06	0
P3-A-Ip-A-L-A	1,03	0,07	42

*Percentage of samples that broke on laser treated ink line.

Table 3.2 shows a clear effect of mechanical weakness for all three paper-grades, when being treated by a laser. When we compare the laser treated inked samples PAPER-$1_{,2,3}$-A-I-A-L-A with the inked non laser treated samples (PAPER-$1_{,2,3}$-A-I-A-A) it is clear that the tensile strength has decreased not only quantitatively. The tensile strength for the laser treated inked samples is significantly lower, for each paper type respectively 1,29 kN towards 1,48 kN, 1,33 kN towards 1,40 kN and 1,03 kN towards 1,12 kN.

Besides a significant trend is seen when looking at the breaking percentages of the laser treated inked samples PAPER-$1_{,2,3}$-A-I-A-L-A and the non laser treated samples (PAPER-$1_{,2,3}$-A-I-A-A). The breaking percentage for the laser treated inked samples is significantly higher; for each paper type respectively 89% towards 10%, 26 % towards 10% and 42% towards 0%.

Laser treatment on the non inked samples (PAPER-$1_{,2,3}$-A-L-A-A) do not seem to affect the tensile strength, neither quantitatively nor qualitatively.

Thus, the results obtained with the laser treated inked paper after artificial ageing only show a somewhat different result compared to those of papers without the laser treatment. Based on the theories of laser technology application we suggest that this phenomenon is based on the extremely secure local heat dose. Paper consists of cellulosic fibres and the fibre-fibre bond is causing the strength of the paper. Due to dark ink the laser treatment the temperature at the surface interface between the ink and the fibres increases drastically for a very short period of time. Considering now the reduction of its strength, we suggest that hornification occurs. This can be attributed to a structural change in the cell wall due to irreversible bonding of cellulose surfaces causing also losses in the strength. The fibrils aggregated into larger units on drying, which reduced the area accessible to water. As oxygen reacts preferentially in the amorphous region of cellulose, or preferable with the hemicellulose this effect will therefore occur heavier with wood containing paper, as they will contain more amorphous material. This is in accordance with what we found, the strength reduces more severe for Paper-3 (mechanical pulp paper) than for Paper-1 (bleached sulphite softwood paper). Paper-1 (cotton linters pulp paper) showed the least change in strength properties.

3.5 Conclusions

Colour changes after laser irradiation were more pronounced for pre-aged samples than for fresh ones (especially PAPER-2). This observation corresponds with the threshold fluence behaviour where normally the threshold of fresh paper F_{th}(fresh) is slightly higher than for the pre-aged samples F_{th}(aged).
The weight-average molecular mass of cellulose significantly decreases towards stronger laser interaction using an ultraviolet wavelength at ? = 355 nm. The effect is in the same order of magnitude as that of the artificial pre-ageing. Contrary, the results of the treatment with the green at ? = 532 nm and the infrared laser light at ? = 1064 nm is negligible, and only a slightly decrease of M_w towards higher fluences and pulse numbers is detectable, respectively.
The CL results are consistent with the results of M_w and colour measurements, i.e. no significant immediate or long-term alterations of the paper samples was promoted by laser treatment at ? = 532 nm below the ablation threshold fluence. On the other hand, immediate chemical alterations of the paper samples occur as a result of UV laser treatment. Cellulose is depolymerised, and new emitting species are formed, probably as a result of photosensitised (radical) degradation reactions induced by the UV radiation. Further reactions of these initial degradation products into coloured compounds may possibly yield significant discoloration of the test papers after artificial post-ageing.
The laser treatment with the second harmonic green light at ? = 532 nm below the ablation threshold fluence gave the most promising results on pure papers, with no discolouration and no other visible alteration, nor detectable chemical changes.

Based on the experiments carried out on paper samples treated by a 532 nm laser and by comparison these results with these of the reference papers, we conclude that there is a slight significant enhancement of the SO_2 uptake due to the laser treatment. This enhancement is the most severe for lignin containing papers. The fact that lignin-containing papers do have a higher uptake of SO_2 than bleached papers was in accordance with results from previous research. As the enhancement in SO_2 uptake lies in the range of less then 2 ppb, we suggest that this will not affect the quality of the papers under long-term storage. This suggestion is based on results obtained from a long term study of the quality of similar papers stored for over eight years in the purified storage room of the national Archive in The Hague, the Netherlands, where the SO_2 concentrations was approx between the 1 – 4 ppb.

When finally dark inks (in our case BIC Ballpoint inks) are removed from the papers by the 532 nm laser, it is concluded that both the tensile strength decreases and the break percentage of each set of samples dramatically was increased. Causes should be found in a structural change in the cell wall due to irreversible bonding of cellulose surfaces causing also losses in the strength. The fibrils aggregated into larger units on drying, which reduced the area accessible to water. This phenomenon is called hornification of the fibres and fibrils. Therefore we also suggest that there is a need for further research and tuning the laser parameters related to dark ink types.

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Chapter 4. Aesthetical evaluation and environmental impact of treated samples

4.1 Introduction

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Cleaning of valuable documents, drawings and objects of graphical art often is technically difficult, time consuming, and introduces a risk of causing undesired immediate or long term side effects. Especially difficult cleaning problems can arise in the context of local cleaning in the vicinity of sensitive media. Nevertheless paper conservators often do decide to carry out specific cleaning treatments on paper-based objects. The decision to carry out a specific cleaning treatment is based on several considerations.

Not all stains, dirt and other types of 'foreign materials' (from here on described as stains) actually do require removal. In many situations stains represent important information on the object's cultural or historical context. In these cases stains are considered to be an integral part of the object and actually add to the object's value. In other cases however the visual disturbance associated with the presence of a stain can prevail over historic considerations. Stains can be very distractive and ultimately prevent the viewer from 'reading' the object. In addition to this fact some types of stains are known to be unstable and are expected to develop into states of increasing levels of visual disturbance. In such cases a cleaning treatment of the object might be considered.

The decision to carry out a specific cleaning treatment should always be the result of balancing the anticipated improved aesthetics against possible risks associated with the cleaning action. A specific cleaning procedure is considered suitable for a specific application only when sufficient removal is expected with the restriction that no significant risk of immediate or long term undesired side effects is introduced as a result of the treatment.
Laser cleaning would be considered superior with respect to a conventional cleaning technique (solvents/mechanical) either by yielding a better immediate and long term aesthetical result or, in the case of comparable aesthetical results, by some other indirect (i.e. non aesthetic) improved performance. Examples of indirect improved performance might be a reduction of treatment time or better long-term mechanical behaviour of the paper substrate. Another important aspect nowadays when introducing a new technique is the safety and health for the end-user. Conservators and restorers often use (organic based) solvents as suitable conventional cleaning method. We all know that these solvents possibly emit harmful components, which may be inhaled by conservators and restorers. An inventory to the use of volatile organic compounds used during cleaning of objects at conservation workshops, that took place within the research of the PaReLa, showed that serious sources are present. For example a conservation workshop in The Netherlands restored approximately 5000 posters during the last four years [1]. Four employees worked at this project, whereby contaminated posters by adhesives (thin strip around the edges) were removed using organic based solvents. During this period an amount of € 50000 was pent on solvents representing several thousands of litres liquid organic solvents. A serious part of this amount was evaporated on a natural base. A Spanish conservation workshop treated 100 books from 13th century containing 500 pages each [2]. Previously (1960) the pages were laminated with adhesive sheets on both sides. Due to the fact tat these pages showed discoloration and that the polymer became sticky, the polymeric laminate was removed using about 3 litres of organic solvent per sheet. In total approximately 150000 litres of solvents were used corresponding with M€ 3 or € 20 per sheet. These Figures show that manual cleaning methods using organic solvents may cause serious health risks to employees, even if a fan hood is being applied. One of the main objectives of the, PaReLa project is the development of a laser cleaning system suitable for accurate and safe restoration of paper objects, thus also safe for the employees.

To establish specific applications for which laser cleaning would be suitable and superior over existing conventional cleaning methods, and to aid the design of the PaReLa laser station, the aesthetic aspects of several conventional and laser cleaning results were evaluated and compared to the results of conventional cleaning methods. To determine health aspect of laser treatments, exposure levels of Volatile Organic Compounds (VOC's) on conservators were studied and compared with exposure levels using conventional cleaning methods. The methodology and results of the aesthetical evaluation and environmental impact of laser treatments of these cleaning trials will be presented as well in this chapter.

4.2 Procedures and methods

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Two series of cleaning trials were done. A preliminary screening of laser cleaning possibilities and difficulties was performed on a variety of original objects with different types of paper/dirt combinations.
After this a second series of cleaning trials were carried out on specially prepared test samples representing a final selection of two types of cleaning problems: removal of inks and self adhesive tapes. For this second series both conventional and laser cleaning treatments were carried out and results of both types of cleaning results have been compared.
For determining the environmental impact of laser treatments investigations were carried out using original objects.

Original objects and specially prepared test samples

By Piet van Dalen[1], Jan Stokmans[1], Marieke Kraan[2], Bernadette van Beek[2], Veronique Rouchon-Quillet[3], Susan Corr[4], Hai-Yen Hua-Ströfer[5], Frank Ligterink[6], T. Petéus[7] and van Zijlen[8]
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The selection of cleaning problems that are cumbersome or impossible to treat using conventional methods made by the paper conservators participating in the project included the following types of foreign matter commonly found on paper objects: surface dust; adhesives (natural and synthetic); pressure-sensitive tapes; inks and stamps; 'sticky fingers' (skin surface lipid, possibly combined with dust); stains from foxing, fungi and oil. See also chapter 2 of this report.

A group of original objects (of low cultural value) representing the selected cleaning problems was collected. Those dirt/objects combinations include:

1) Adhesive layer (probably animal glue) covering a printed text on a rag paper;
2) Adhesive from a pressure-sensitive tape on a mechanical pulp paper;
3) Fungi stains covering a writing ink text on a blue-dyed 20th century paper;
4) Felt tip pen on a modern alkaline office paper;
5) Water-based stamp (methyl violet) on a mechanical pulp paper;
6) Oil-based stamp (probably carbon black) on a late 19th century paper;
7) Surface dust on a rag paper. Besides the variations in the compositions of both foreign matter and substrates, the distribution of the former on and in the paper varies significantly from object to object, and in most cases the foreign matter is non-uniformly distributed.

Chemical characterisation of the foreign matter on these objects was done at ICN using infrared spectroscopy. Cross-sections and surface distributions where characterised using visual microscopy and scanning electron microscopy at ICN. Target areas were marked and photographically documented under standard illumination conditions on slide-positive film, before laser treatment and after.

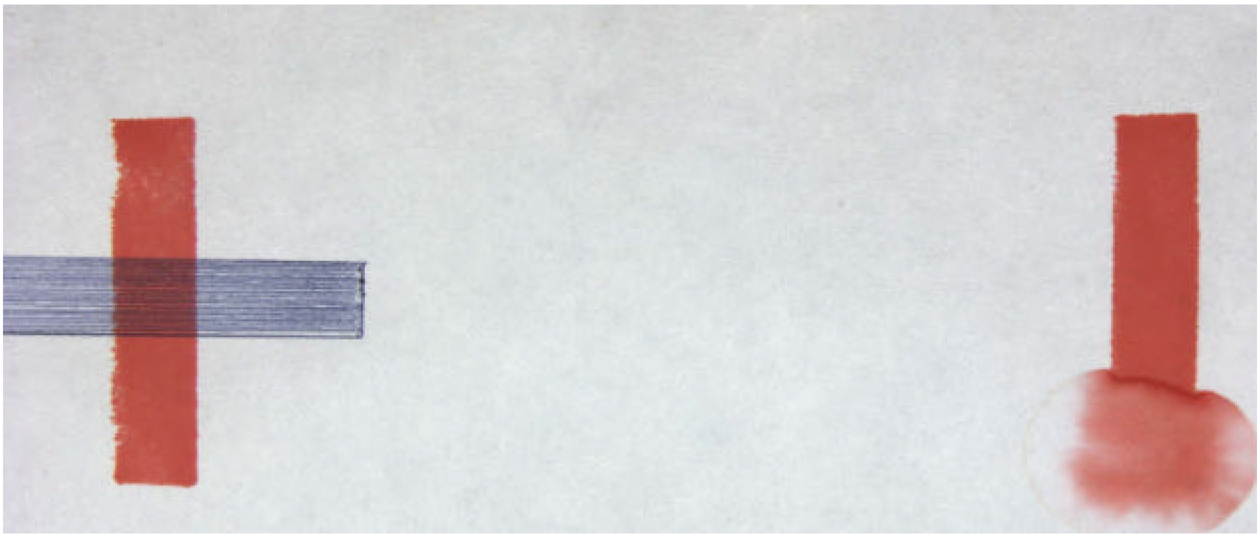

Fig. 4.1: Example of specially prepared ink model test system

Laser cleaning

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Laser cleaning of originals was carried out using two lasers at BAM operated at 355nm, 532 nm and 1064 nm and the ArtIn excimer laser station at 248 nm, for details see chapter 3. Laser cleaning of ink and tape models was performed at 532 nm only. Selection of laser treatment parameters was based on past experience with comparable materials and pre-testing on the objects and models to be treated. The progress of treatment was assessed visually by examining the object after each sequence of pulses. The treatment was interrupted whenever an undesired alteration of the paper (discoloration, change in surface texture) or the media present (ablation) was observed. Visual appearance before and after laser treatment was documented photographically.

Conventional cleaning of ink and tape models

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For the purpose of comparison with laser cleaning results, different paper conservators within the project were asked to perform optimal cleaning of ink and tape models using conventional paper conservation tools and methods as locally available to them. In case of the ink models a crucial aspect of the cleaning task was the presence of a fungitive ink that should experience no further bleeding. As

a consequence only local cleaning methods were feasible. For the tape removal as well only local cleaning methods were assessed.
Three main types of cleaning agents can be distinguished: removal of a substance with use of a solvent or liquid; removal of a substance by mechanical means, typically a scalpel; and reduction of a stain using chemical bleaching. Numerous variations on cleaning strategies exist and seldom-different methods and agents are combined within a single cleaning task. The fact that cleaning has
In some cases the mechanical removal of adhesives can be aided through the application of heat. Many different solvents or bleaching agents can be chosen to dissolve or bleach a specific substance. Another important aspect of a cleaning strategy is the way in which solvents are applied. Control over solvent migration within the paper substrate is a critical factor in many cleaning tasks. Absorbent materials such as blotting paper or talc are used to either absorb or release controlled amounts of solvents. Alternatively a vacuum table can be used to restrict the lateral action of a solvent.

Evaluation protocol aesthetical evaluation

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Crucial aspect of the aesthetical evaluation of cleaning results was the prior establishment of an evaluation protocol. Preliminary evaluation trials by conservators within the project showed that two aspects within a cleaning result evaluation had to be assessed separately.

First aspect of a cleaning result is the removal efficiency. Removal efficiency is correlated with the reduction of contrast between the stain and it's surroundings. It was found that the aesthetical evaluation of a certain contrast reduction however, would depend also on the impression of the total image. Especially in the case of cleaning of models this context needs to be specified clearly prior to the evaluation of cleaning results.

Second aspect of a cleaning result evaluation is the occurrence of side effects. A cleaning action should not introduce significant new visible features that can be associated directly with the cleaning action and somehow foreign to the object. Examples of undesired side effects are the introduction of a tideline associated with the local application of a solvent, the occurrence of yellowing or a change of surface structure. Another type of undesired side effect is the introduction of irregularities within the stain as a result of a partially effective removal of the stain.

If both aspects of a cleaning result are evaluated positive the overall evaluation of a cleaning result is described to be 'acceptable'. In all other cases the cleaning result is said to be 'not acceptable'.

Procedure determining exposure levels

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The investigations were carried out using original objects. These objects, posters, contain adhesives (Tesa-crepe) and were obtained from Art Conservation, Vlaardingen (the Netherlands). The posters originated for the Dutch “Film museum”. Fig. one shows such a poster. For the manual cleaning organic based solvents were used, i.e., ethanol and iso-amyl acetate of a common technical quality degree.

Before applying the leaser cleaning system, the carrier of the adhesive tape was removed manually from the poster by rubbing it gently of the adhesive layer. Subsequently the poster was positioned in a vertical table of the laser station.
For the manual removal of the adhesive take, the carrier of the adhesive was firstly treated with hot air, where after the carrier was removed by means of a blade. After completing the removal of the carrier the poster was transferred to fan hood and the object was treated with respectively ethanol and iso-amyl acetate [3]. Subsequently, by means of a rubber-eraser, the layer was removed.

During working activities an employee was equipped with a belt containing TENAX adsorption tubes. These tubes were positioned at left- and right breathing zone of employee. Besides the direct exposure to employee, background level concentrations in both working places were determined. This procedure was carried out for both working locations. After completing sample procedures the adsorption tubes were analyzed.
For measuring the background concentrations we expected to measure higher VOC levels in the conservation workshop than in the laser-lab. Therefore it was decided to use passive sampling techniques, based on the principle of diffusion, for the conservation workshop location. As lower levels were expected for the laser-lab, active sampling techniques, whereby in contrary to diffusion air is pumped through the adsorption tubes, were used for the laser-lab.
The adsorption tubes were thermically desorbed using a Perkin Elmer ATD 400. The desorbed components were analyzed with a HP 6890 gas chromatograph equipped with a non-polar column coupled to a HP 5793 mass-spectrometer The components where identified by comparison with mass-spectra in the NIST mass-spectral library and their retention times. The concentrations were calculated using an external standard [4].
At the laser lab the laser station and a remote controlled computer system were present. At the time of air sampling, persons were working at the location on electronics. A screen of glass separates the laser station and the computer system due to safety legislations for the use of laser equipment. A local exhaust hood removes any emissions from laser treated objects. The dimensions of the laser lab are about 10x10 m^2. The conditions during sampling were 26-29 °C and 49-50 % relative humidity.
At the conservation work shop shelves were present, several acid cases and cupboards are used for the storage of chemicals. Large tables were present in the room for restoration activities. In direct contact with the workshop, a part of it is in use as canteen and another part as an administrative office. The dimensions of the workshop are approximately 25x10 m^2. The conditions during sampling were 27-28 °C and 35-47 % relative humidity.

4.3 Results

Aesthetic evaluation and discussion

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Results of laser cleaning

Out of twenty-eight laser-cleaning trials on the selection of seven different original object/dirt combinations, a total of seven cleaning results were judged to show sufficient removal efficiency without significant undesired side effects.
These successful cleaning results were obtained in case of removal of a deposit of brown discoloured rubber-based adhesive from a pressure-sensitive tape on a mechanical wood pulp

paper at 532 nm, the removal of a black oil-based printing ink on a rag paper at 532 nm, the removal of a methyl violet stamping ink at 532 nm, and the removal of evenly distributed surface dust on a rag paper at all three wavelengths.
In all twenty-one other cleaning trials on original objects results were unsatisfactory. In many cases the cleaning effect on several types of stains was limited

Undesired side effects typically associated with lasers operated 248 nm and 355 nm were yellowing and changes in paper fluorescence indicating an increased risk of long term discoloration effects. At higher fluence levels all lasers are able to dislocate or remove fibres from the paper surface. However disruption of the paper substrate at deeper levels inside or even through the paper matrix was most prominent for 1054 nm laser light.

All three laser stations available in the pre-design stage of the project, to various extents showed difficulties with positioning of the beam resulting in undesired side effects. These problems were related either to the fact that some stations were not designed to operate on small surface areas, or to occasional problems with laser beam alignment or control of laser beam quality. As a result undesired damage of the paper substrate in areas directly adjacent to the stain area occurred due to over-exposure to laser light. Lack of control over the laser beam homogeneity in some occasions lead to uneven cleaning action.

Laser cleaning of the ink models was evaluated to be unsatisfactory for all 9-droplet patterns tested. Due to the action of the water that was used to create the droplet patterns, all inks had penetrated deep into the paper substrates. Results of the laser cleaning trials clearly show that removal efficiency of these deeply penetrated inks is insufficient. Major undesired side effects appearing at higher fluence levels were brown discolorations of ink areas and the disruption of the paper surfaces.

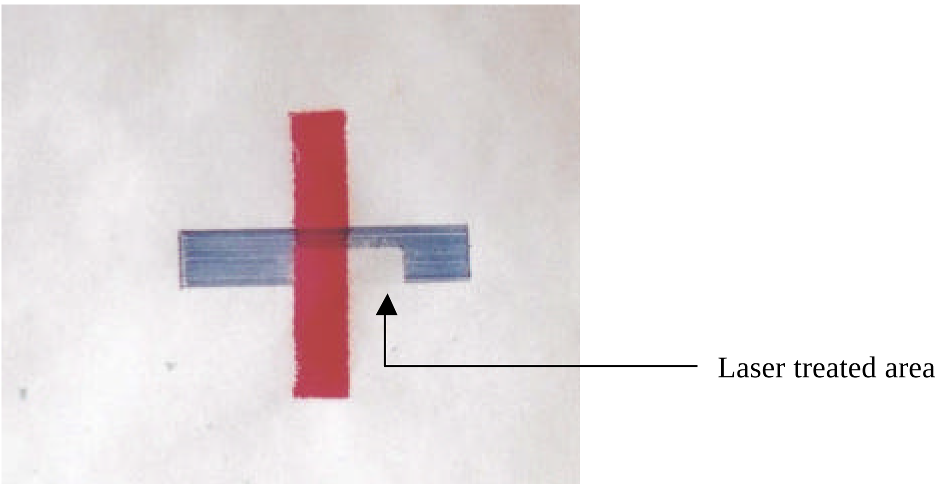

Fig. 4.2: example laser treated area of specially prepared ink models

Laser cleaning of the crossbar patterns was evaluated to be satisfactory in five out of nine samples. The superficial distribution of ballpoint ink on top of fugitive ink in case of these five samples was removed successfully without the occurrence of significant undesired side effects. The ballpoint ink could not be removed successfully form paper type Paper-1 samples due to the occurrence of yellowing of the paper substrate after post-ageing. Furthermore fading of the red ink in the paper type Paper-3 sample resulted in rejecting this cleaning result.

Laser cleaning results of all nine tape-samples tested were evaluated to be unsatisfactory. Manual removal of the tape carriers prior to laser cleaning proved to be necessary. In case of the acrylic type adhesive carrier removal was only achieved at the cost of introducing solvents.

In case of rubber type adhesives carrier removal is easily achieved using mechanical action plus heating.
Pre-ageing treatment of the tape models had resulted in brown discoloration of all rubber based adhesives but also caused deep penetration of adhesive components into the paper substrate in case of the rubber based adhesives. Removal efficiency for these deeply penetrated adhesives was evaluated to be insufficient in all cases. The acrylic type self adhesive tape did not show any significant discoloration. Laser cleaning in this case did not introduce any additional removal of acrylic adhesive residues from the paper substrate.

Results of conventional cleaning of ink and tape models

Three different paper conservators using different variations of cleaning methods and performed conventional cleaning of the ink models. None of the results of conventional cleaning of the ink samples was evaluated to be satisfactory. Typically the local application of water or solvents resulted in the formation of tide-lines caused by transport of either ink components or paper degradation products. Post-treatment ageing in most cases lead to an increased visibility of these tide-lines. Although several solvent application methods were used limit lateral transport in the paper, sufficient control of solvent transport in the lateral direction proves to be quite difficult. Although performed with great care, mechanical removal of ballpoint ink also did not provide satisfactory results due to uneven and insufficient removal.

Conventional cleaning of tape models was evaluated satisfactory in six cases out of twenty-one. Non-satisfactory results were due to insufficient removal efficiency of adhesive residues or the occurrence of tide-line formation. In case of acryl type tapes some difficulties in removal of the tape carrier were encountered resulting in skinning effects. Selection of specific solvents appears to be critical to successful cleaning. However no systematic approach was followed other than choosing a solvent based on prior experience.

Results environmental impact laser treatments versus conventional cleaning

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Table 4.1 and table 4.2 are showing the results, obtained from the analyses of the TENAX tubes, located at the left and right breathing zone of the employee. Table 4.1 shows the measured concentrations at the conservation workshop, while table 4.2 presents the observed concentrations at the laser lab.

Table 4.1 Measured VOC concentrations at the conservation workshop.

Exposure concentrations employee [microgram/m3]		
Components	Breathing zone	Background level
benzene	24,5	1,3
n-heptane	11,6	4,1
methylcyclohexane	1,4	1,4
toluene	22,5	10
n-octane	2,6	1,4
ethylbenzene	3,6	3,4
p,m-xylene	11,0	8,5
styrene	6,5	6,5
o-xylene	3,3	3,4
n-nonane	5,3	1,8
C3-benzenes	17,0	13
t-VOC	**109,2**	**54,8**

Table 4.2 Measured VOC concentration at laser lab.

Exposure concentrations employee [microgram/m3]		
Components	Breathing zone	Background level
benzene	2,1	2,1
n-heptane	3,4	2,4
methylcyclohexane	1,5	1,3
toluene	20,7	13
n-octane	0,6	0,8
ethylbenzene	3,6	2,2
p,m-xylene	10,7	6,7
styrene	1,4	1,0
o-xylene	3,3	2,0
n-nonane	1,3	1,5
C3-benzenes	29,8	17
t-VOC	**78,3**	**50,3**

It was shown that the background concentrations of some compounds at the conservation workshop were somewhat higher than found at the laser-lab. However, the t-VOC for both rooms was somewhat comparable (50-55 $\mu g.m^{-3}$). This minor effect might be due to several reasons. First of all, the workshop is located in an urban area, while the laser-lab was located at the outside of an urban area. Secondly, at the conservation workshop, many materials were stored. All these materials might have their own type of emission of VOC.

Furthermore, we found, that for several of compounds, higher levels of VOC were found at the conservation workshop than for the laser-lab. Looking at the total VOC, we found at the conservation workshop a t-VOC of 109 $\mu g.m^{-3}$, while for laser lab a t-VOC of 78 $\mu g.m^{-3}$ was found. This compared to the background of 50-55 $\mu g.m^{-3}$, we suggest that laser cleaning contributes to a more healthy building than manual cleaning.

If we compared the results, to the average and acceptable office indoor concentrations of selected components (1 to 5 $\mu g/m^3$) in offices, we must conclude that, based on the presence of 11 identified compounds, for both labs the value of 5 was exceeded for 6 compounds at the conservation work shop, and for 3 components at the laser lab [5, 6]. This indicates that both labs, and especially at the conservation workshop, the indoor air is less clean than a
normal office. If we compared the values with the official maximum tolerated values (MAC) as established by the Dutch Ministry for Social Affairs, we conclude that the found values for the separate compounds at both working locations are at least 100 – 100000 times lower than the official MAC value (see table 3) [7].

Table 4.3 MAC values at a Time Weighted Average of 8 hours. Source [7].

Components	MAC values TWA 8 hours microgram/m3
benzene	3250
n-heptane	1200000
methylcyclohexane	-
toluene	150000
n-octane	1450000
ethylbenzene	215000
p,m-xylene	210000
styrene	107000
o-xylene	210000
n-nonane	-
C3-benzenes	100000

4.4 Conclusions

Local cleaning in the vicinity of sensitive inks or other media proves to be a difficult task in paper conservation, which requires extreme control over the cleaning agent chosen. Aesthetic evaluation of the results of conventional cleaning and laser cleaning trials shows that both types of methods do not always result in sufficient removal efficiency.

The removal efficiency of solvents based methods will depend on the choice of an optimal solvent. Some substances exhibit only limited solubility. Sufficient removal efficiency for laser cleaning was found to be limited to fairly superficial types of stains. Penetrated inks or adhesives could not be removed with laser light.

Furthermore it was shown that both conventional and laser cleaning do involve associated risks. Conventional treatments based on the local application of solvents often cause undesired transport of ink, adhesive or paper degradation components. Accumulation of these components in so-called tide-lines will often become visible over time. If only local cleaning is possible the occurrence of these tide-lines is very difficult to avoid. On the other hand yellowing and discoloration effects of paper substrate and media have been observed in some cases after artificial ageing as a result of laser cleaning. It remains difficult to predict these effects for specific cases.

From the test results evaluated here major application of laser cleaning appears to be the removal of superficial types of stains that can not be removed easily due to limited solubility of the stain material or due to the presence of sensitive media in the vicinity of the stain.

Based on the investigations performed at the conservation workshop and at the laser-lab, we conclude that laser cleaning of posters contaminated with adhesives (Tesa-crepe) results in a significant lower exposure for employees towards volatile organic compounds. This decrease is approximately 40%, compared to conventional cleaning of similar posters.

For both working places, the maximum tolerated values per individual component are not reached. For some components (e.g. n-heptane) the found concentration in the indoor air remains 100,000 times lower than the maximum value (MAC). However, compared to office working locations, the indoor air for both investigated working places can be considered as less clean.

4.5 References

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Chapter 5. Development of a monitoring system for laser cleaning of paper

5.1 Introduction

A number of laser cleaning effects on paper have been observed during the preliminary evaluation of project results. Apart from the sought after laser cleaning effect where the unwanted material is removed and the remaining paper material is left intact, various side effects induced by laser cleaning have been observed.

These unwanted side effects will be listed here without an in-depth explanation into the nature of their causes as this is already described in other sections of the mid-term report. The most commonly observed side effects of laser cleaning on paper are:

- "***Fluffing***" of the paper surface induced by the forceful expulsion of particles located between the fibrous structure of the paper, causing the fibres to stand up. This effect can be seen clearly under raking light conditions.
- "***Thinning***" of the paper thickness by excessive removal of material (ablation). This effect can be observed with transmitted visible light, reflected infrared or ultraviolet reflectance.
- "***Charring***" or "***Carbonization***" of the paper or pigments often caused by high levels of laser radiation. This effect can be seen in reflected infrared.
- "***Yellowing***" or discoloration of the paper surface or pigments. Obviously this effect is measurable with colorimetry. Ultraviolet reflectance and fluorescence can reveal discolorations at an early stage.

Preliminary results of the laser cleaning process on paper clearly show that laser treatments using a wavelength of $\lambda = 532$ nm has no or a very limited effect on the mechanical properties of paper, which is a relief to curators and conservators. However laser treatments seem to have a more profound effect on colorimetric properties.
The measurement of colorimetric changes during and after laser treatment therefore seems to be a more sensitive tool to monitor the laser cleaning process than mechanical analyses.

Furthermore, colorimetry can potentially be performed on very small areas which will aid conservators who are currently experiencing difficulty in comparing the colour of small laser treated areas with the desired cleaning effect.

The incorporation of decision algorithm(s) to discriminate between dirt and paper and between dirt and media, as well as to control the number of pulses per spot size, using criteria such as contrast/colour differences as monitored in the different regions of the electromagnetic spectrum (UV, VIS, IR), is a significant step forward in the application of laser cleaning of paper.

5.2 Feasibility study for monitoring and diagnostics

Based on the first project results, multi-spectral imaging and colorimetry promise to be the most sensitive methods to monitor, diagnose and control the laser cleaning process.
Within task 5.1 "Multi-spectral image analysis during laser treatment" a number of laser treated objects were analysed using colorimetry and multi-spectral imaging techniques to observe the value and sensitivity of these proposed monitoring methods. Imaging analysis was performed on various laser treated inks, laser removal of surface dirt and laser removal of adhesives. Furthermore, the colorimetric performance of a monochrome CCD camera was assessed.

Multispectral Imaging analysis on laser cleaning of inks.

Imaging results on the matrix test samples where a gradual increase in laser energy ($\lambda = 532$ nm) and number of pulses is applied in a matrix wise fashion clearly shows an increase in effectiveness of laser treatment up to a point where unwanted side effects become more and more obvious.

Whereas the charred area in color imaging is only observed clearly in the most down-right square, a more gradual increase in absorption of infrared radiation (and hence progressive charring) can be noticed in infrared reflection imaging.

Likewise, in ultraviolet reflection, the surface reflectance first increases as the squares become progressively cleaner (seen as brighter patches) up to the point where the paper fibres absorb more ultraviolet light due to chemical changes and the patches become darker.
The optimal cleaning result with the least side-effects is marked with a circle in the above images. The treated paper is of type P3: acid mechanical pulp paper, alum-rosin sized, kaolin coated.

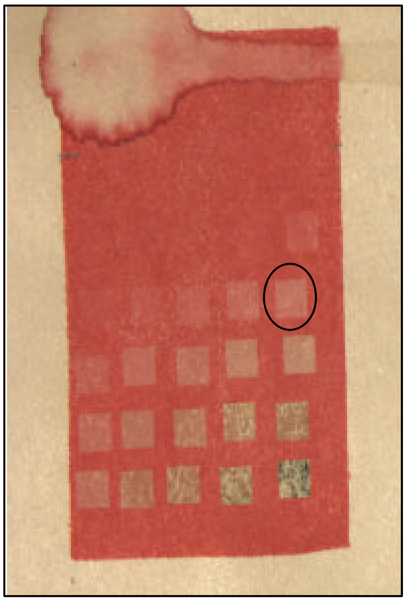


Image 1: P3.T2.N5 Colour image

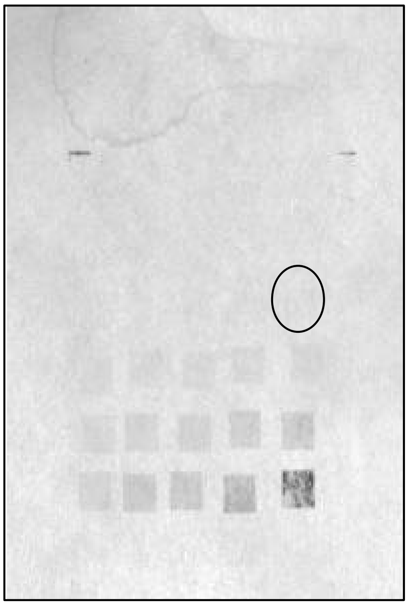


Image 2: P3.T2.N5 infrared 1 image

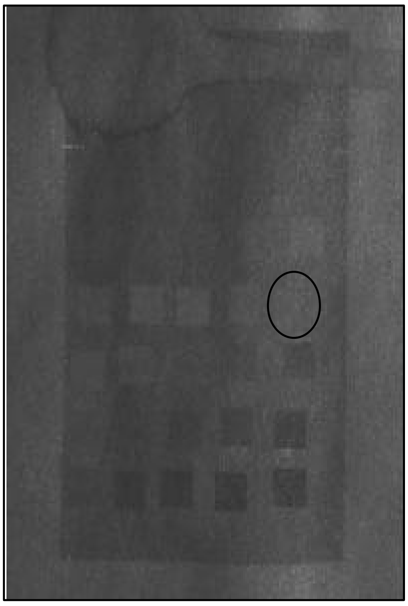


Image 3: P3.T2.N5 ultraviolet reflectance

In the following example, the infrared reflection image shows a gradual lightening of the laser-cleaned patches before a clear charring effect occurs. Thinning of the paper might cause this increased transmittance of infrared light. Also note the carbonization in the last two most down-right patches. Furthermore, this example in which the same ink and laser parameters were used as in the previous

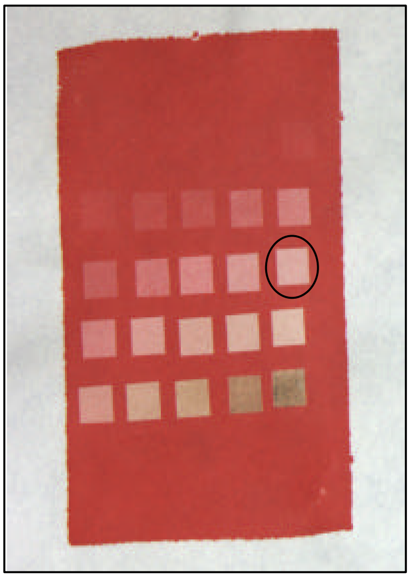


Image 4: P1.T2.N5 Colour image

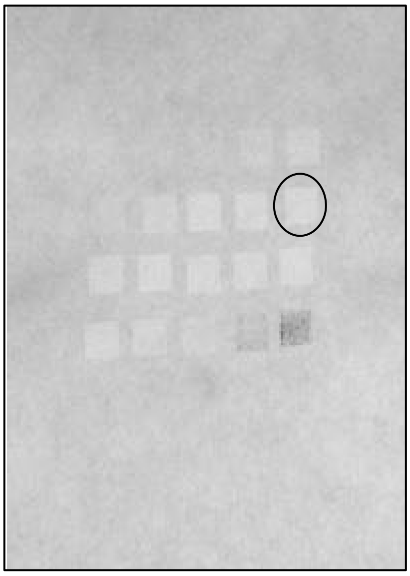


Image 5: P1.T2.N5 infrared 1 image

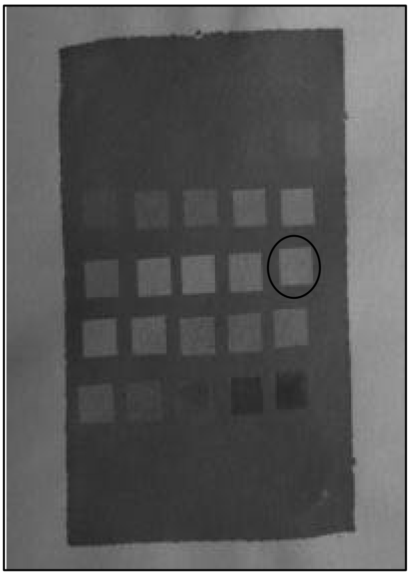


Image 6: P1.T2.N5 ultraviolet reflectance

example, clearly illustrates the strong influence, which the paper itself has on the cleaning process. The treated paper is of type P1: bleached softwood pulp paper, no fillers, no sizing. The optimal cleaning result with the least side-effects is again marked with a circle in the images below.

An additional number of samples were analysed to study the value of multispectral imaging as a monitoring tool. The first sample (No.0) was constructed in the lab for calibration purposes by filling half of the sample with adjacent blue ink lines. The other three were original old papers of different material and surface dirt. Cleaning was performed on at least two different locations on all papers.

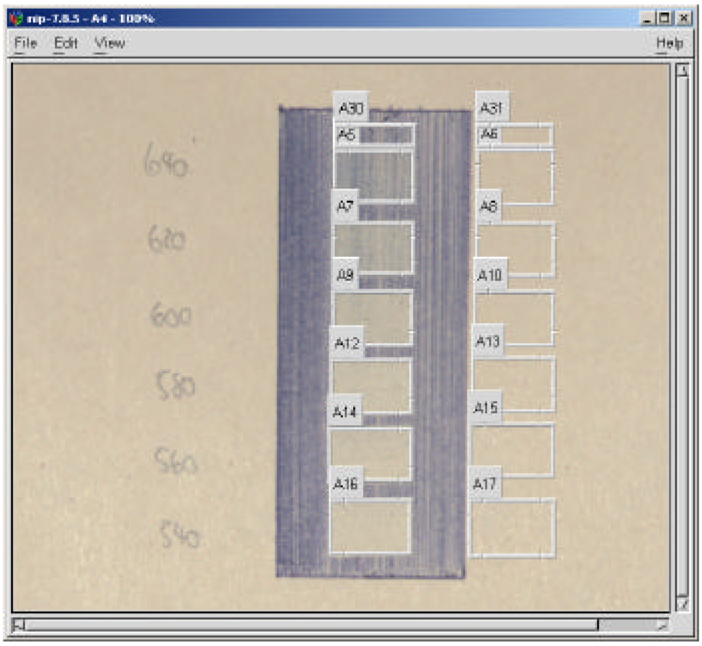
The imaging results are displayed in the next table. The X marks the wavelengths at which the laser cleaned pattern is not visible and Y were the pattern is visible. The shaded Y's mark the spectral regions were maximum contrast was achieved.

	UVR	FLU	VISIBLE	COLOR	IR1	IR2
No. 0	X	Y	Y	Y	X	X
No. 1	X	X	Y	Y	Y	X
No. 2	X	X	Y	Y	Y	Y
No. 3	Y	X	Y	Y	X	X

From the above results it seems that the color image was the most important successful in the monitoring of laser cleaning, however, it must be noted that the number of samples imaged was very limited. Since the color spectrum covers a wide spectral region, a new test was performed to characterize which part of the color region is most efficient as a monitoring tool. The separate color components of the color images were compared using the software of the ARTIST system. The red channel of the images was found to be of little importance since the contrast was very poor. The green channel had a better contrast. However, the blue channel consistently exhibited the highest contrast for each of the samples.

Colorimetric performance of a monochrome CCD camera

Since colorimetry has been designated in this project to be of great importance to monitor laser treatment, the feasibility study was concluded by investigating the practical use of a CCD camera to measure colours. Previous research at Art Innovation has shown that accurate colour imaging is no simple or trivial task; reproducibly measuring colours under varying circumstances and on different materials is a surprisingly complex issue. Regular colour CCD cameras with video signal transfer have not proven to be accurate enough mainly owing to the type of colour filters used (the so called Bayer pattern filter) and the sacrifice of colormetric information to obtain high frame rates.



By choosing a monochrome CCD camera, using specially manufactured color filters and retrieving the raw digital image data from the sensor chip many colourmetric flaws and pitfalls of conventional cameras can be circumnavigated.

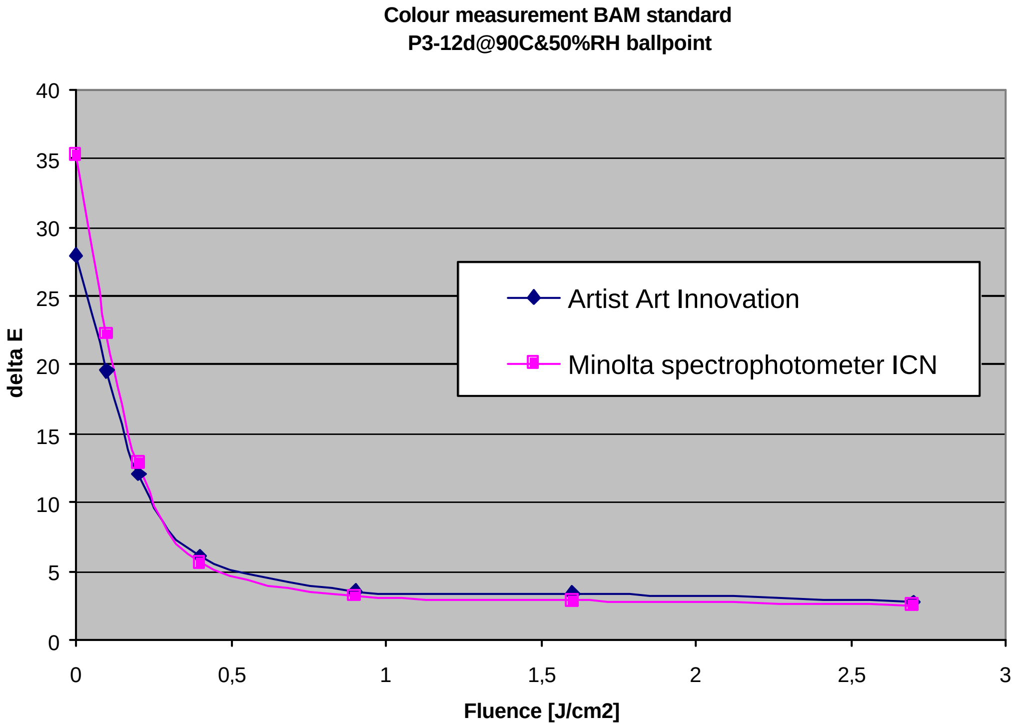
A basic setup as described above with a simple monochrome sensor and filter arrangement and the means to retrieve the digital sensor data was used to perform preliminary color tests in order to evaluate if the colour quality was promising enough to pursue this design strategy.

The goal was to record colour data with the basic setup in a reproducible way with an average accuracy. Later fine-tuning of the design would then produce the necessary colormetric accuracy for the project.

For this test a paper sample (see image 7) with ballpoint ink was laser cleaned at the BAM institute. The sample was imaged at Art Innovation and subsequently sent to the ICN institute for exact color measurements using their Minolta photo spectrometer.

The color measurement performed at both institutes attempted to mimic the colour measurement method, which will probably be used during actual monitoring of the laser cleaning process. The color difference ΔE between a laser treated area and the immediate clean area (without ink) is calculated. At a certain moment an optimum in “cleansing” will be obtained where the cleaned surface is “colormetrically” as close as possible to the original area.

The results obtained with the imaging setup and the dedicated spectrophotometer are plotted in graph 1 on the following page. The close resemblance between the two plotted lines shows that an imaging setup can practically obtain the same accuracy as a dedicated spectrophotometer when monitoring color differences between certain areas.



Graph 1: Colour difference measurment of laser cleaned ballpoint ink.

The biggest deviation is observed at the first (leftmost) point in the graph, representing the color difference between the ballpoint (rectangular area 30) and the untreated area (rectangular area 31). This difference can be explained easily since the Minolta spectrophotometer will measure the color co-ordinates of a single small point which might be locate just on or next to a ballpoint line, causing a large spread in possible results. In effect a camera setup will not experience this problem as the average color co-ordinates are calculated of the whole rectangular area.

The colorimetric results indicate that a properly selected camera with specially manufactured color filters and digital output can be used to obtain fairly accurate colour measurements suitable for monitoring the laser cleaning process.

5.3 Design and development

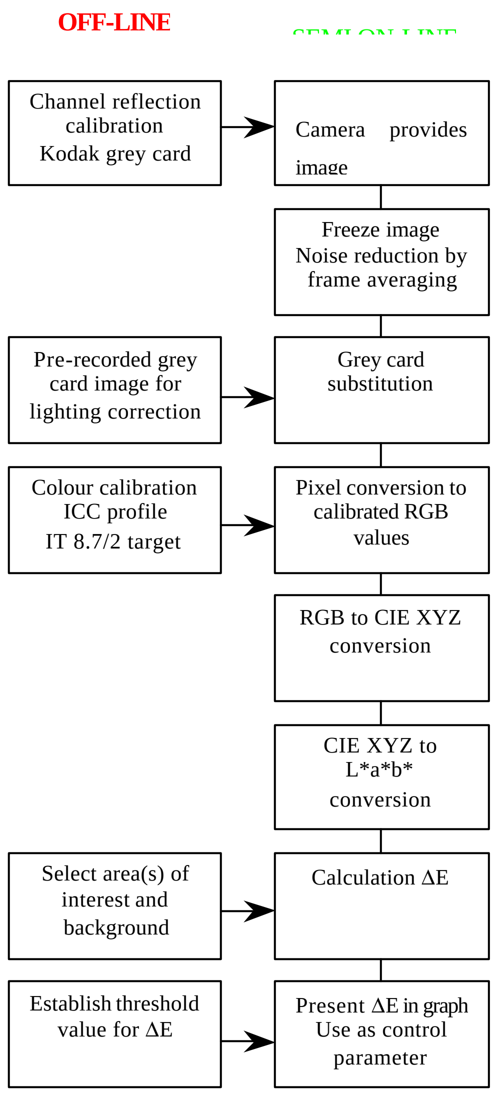
The lasers, which are most suitable for cleaning paper and parchment are operated at pulse frequencies of 1000 Hz and more. The time lapse between 2 pulses is therefore in the order of milliseconds, which is far too short to record high resolution images in one or more wavelengths, process their colorimetric information and calculate possible process control adjustments.

A feasible and practical scenario for monitoring, is if the laser operates uninterrupted for a certain period of time after which the effect of the treatment is evaluated. However, monitoring and control subsequently takes up a considerable part of the total treatment time.

The requirements for this project furthermore demand that considerable colorimetric accuracy be obtained. In the following paragraphs, the workflow and design improvements on the basic imaging system are described, which will guarantee the colour accuracy as stated in the specifications for the monitoring system.

Workflow for colorimetric monitoring

The workflow for this semi on-line monitoring method is given in the figure below.



Calibration and recording of accurate colours

Naturally a good starting point for recording accurate colours is to use a very high quality sensor. However, since the price of the monitoring system is to be proportionate to the price of the overall laser workstation, a reasonably cheap sensor of acceptable quality is chosen.

Much of the effort involved in obtaining accurate colours is now spent on optimizing the sensory data and accurately processing the colour information within. The applied techniques to perform this optimization are described in the following paragraphs.

Improvement of the signal to noise ratio

The technique of frame averaging instead of sensor cooling with Peltier elements is used to obtain good signal to noise ratios in order to achieve an optimal colour gamut and ensure the necessary bit depth.

Frame averaging is performed by rapidly recording multiple images in succession. Per pixel position the value of all successive images is added and subsequently divided by the number of images resulting in an average pixel value. Frame averaging filters out electronic noise, enabling cheap and "noisy" cameras to produce high quality image results. The advantage of frame averaging is that it is a cost-effective measure to improve camera performance and is easily implemented in the software. Nevertheless, the drawback is that it requires off-line processing time.

Sensor calibration procedure

For good imaging results, gain and exposure of the sensor must be adjusted for each imaging mode (separate filter). A normal colour image for example is constructed from images taken through a Red, Green and Blue filter consecutively. The procedure for obtaining correct sensor settings is described below:

- the aperture of the camera-lens is set to the required F-stop level
- a grey card with subsequently 18% and 90% reflection on each side is placed in front of the camera so that it completely fills the viewing window
- a "live" (continually updated) histogram function is activated to calculate the reflectance of the grey card image
- gain and exposure of the sensor are adjusted in order that the recorded reflection matches the reflection values of both sides of the grey-card
- the process is repeated for all imaging modes.

Correcting inhomogenous illumination

Spatial differences in lighting illumination can result in significantly different colour measurements from spot to spot. Obtaining complete homogenous illumination of the sample under investigation would require a sophisticated and expensive illumination configuration.

Inhomogenous illumination can be corrected by placing a grey card in front of the camera so that it completely fills the viewing window and an image of this grey card is recorded. The average grey level of the imaged grey card is calculated.

Correction of following images takes place by subtracting the pixel values from the grey card image from the current image and subsequently adding the calculated average grey level.

Colour calibration according to ICC standards

A final method to improve colour accuracy is to calibrate the camera system by imaging a target that has a complete range of colours of which the colour co-ordinates are exactly known. By comparing the values of the recorded colours with the values as they should be, the differences between both can be established and subsequently corrected.

A method to define the exact color space of a digital camera is to record a so-called IT8.7/2 colour input target. With this image and the reference data of the card, the colour space of the camera and the optimal transformation of the camera colour co-ordinates (RGB) into a device independent colour co-ordinate system (L*a*b*) can be calculated. These results are recorded in a so-called colour or ICC profile.

A colour profile that accurately characterizes a device gives the best results in a color-managed workflow. ICC profiles can be embedded into any of the following RGB, CMYK, or grayscale files:

.psd, .eps, .tif, .jpg, .pct, or .pdf. An embedded profile remains with the file, so the device's color space information can then be read by any ICC-aware application.

5.4 Specifications diagnostic equipment

The results of the feasibility study and proposed workflow as described earlier can be used to draw up the specifications for the monitoring system.

- Economically feasible: < 15k euro
- User friendly, simple operation
- (Semi) On-line analysis
- Small dimensions for easy integration into laser work station
- High resolution to accurately measure small areas of laser treatment
- Color measurements with an accuracy of at least $\Delta E < 2$
- Multiple imaging modes:
    - ultraviolet reflection
    - infrared 700-950 nm
    - accurate color imaging quantifiable with L*a*b* colour co-ordinates

- Single imaging mode:
    - blue filter

5.5 Conclusions

The research into the applicability of multi-spectral imaging as a monitoring tool yields promising results with respect to the near infrared (700 to 950 nm) and ultraviolet reflection (< 400 nm) mode and accurate color imaging.

Little added value has been found in including the additional infrared range from 1000 to 1200 nm. Dramatic laser induced changes have been observed in fluorescence imaging, however, the strong time dependency of these effects requires the necessary caution in interpretation.

In cases were the price of the monitoring system is very limited and multispectral imaging is not longer economically feasible an effective monitoring system can still be built using only a monochrome CCD camera and a blue filter.

Chapter 6. Development of laser cleaning station for paper

6.1 Introduction

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A prototype laser station was developed for cleaning paper surfaces selectively. The term selectively in this case refers to the fact that it is possible to accurately clean certain areas and skip those areas that should not be irradiated by the laser. In this way it is for instance possible to clean around written text, or using different laser settings on different (selected) areas. In this chapter the technical details of the cleaning station and the working procedure are discussed. An emphasis is put on the development of a cleaning station that allows for selective cleaning, rather than identifying safe laser settings, which was already investigated in chapter 3.

6.2 Pre existing knowledge

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The Federal Institute for Materials Research and Testing (BAM) has designed and set up a prototype of a laser cleaning system suitable for high-precision cleaning of flat large area substrates (e.g. paper and parchment objects) under Laser Class I conditions (the operator does not require safety goggles). It allows fast scanning of the objects through a remote computer control system. The operator can follow the process on the computer screen through a camera system. The scanning can be controlled manually or programmed in the computer, defining the pulse energy, number of pulses, laser spot overlap and shape of the area to be treated. As an alternative, an optical fibre with an ergonomic hand piece can be used for manual cleaning of objects under Laser Class IV conditions (requiring eye protection). The workstation features on-line visible, ultraviolet and fluorescence imaging for the identification and documentation of visible and chemical changes of the illuminated substrate areas.
The BAM Prototype Laser Cleaning Workstation features:

- Pulse laser (e.g. a high pulse energy diode pumped Q-switched Nd:YAG laser) in a laser processing compartment (Laser Class I), operating at 1064 nm and 532 nm, with the constructive option for 355 and 266 nm. Pulse duration < 10 ns, repetition rate < 1 kHz. Pulse energy range sufficient to allow > 10 J/cm² for all wavelength options. Pulse energy monitor.
- Remote-control laser scanner for medium size scanning fields (e.g. 14 x 14 cm²) with virtual mask-on-screen function for automatic high-rate laser treatment.
- Distance to object variable; Spot size variable (> 30 µm).
- MS-Windows-based remote control through keyboard, mouse and/or foot pedal. Variable pulse number, repetition rate and spot overlap.
- On-line visible imaging using a camera-monitoring system (direct or through scanner optics) with on-line image processing connected to laser control.
- Integrated exhaust system at the object surface.
- Optical fibre system for cleaning with a hand piece.

6.3 The laser

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A Nd:YAG laser with second harmonic (?=532 nm) was used in the prototype set-up (see also paragraph 6.2). The green laser light proved to be very suitable for the cleaning of paper, as was demonstrated in chapter 3. The laser was of the type GreTag. It was operated in Q-switch mode with a repetition rate of 1000 Hz. The exact pulse duration was not measured in this study. Also the beam power was not measured and could only be set in a relative number, *p*, which indicates a percentage of the maximum power (pumping power). So no accurate laser power control was possible and no

comparison could be made with earlier tests. Therefore cleaning tests at different lamp percentages, were carried out.
The beam was manipulated on the surface with a Haas1102 scanning mirror head. The manipulation was operated from a software program called LasVar. With this software a ‘marking’ program could be sent to the laser-computer to control the mirror scanning motion. The position accuracy of the manipulation was in the order of 5 µm. The system was previously used for laser marking of barcodes on metal and plastic materials.

6.4 Procedure for selective cleaning

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The general procedure of the selective cleaning technique involves three steps. First an image is recorded with a (multi-spectral) camera. Subsequently the image is processed in such a way that the areas to be cleaned are digitally isolated from the rest. Then finally the resulting black and white image is converted to a marking program to clean the indicated (black) areas.

Image recording

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With a multi spectral digital camera (the Artist) the image of an object was obtained. The advantage of a multi spectral camera is that it is possible to select a spectral range that yields the highest contrast between the areas to be cleaned and the areas that do not need to be cleaned. This improves and simplifies the digital isolation of the areas in the next step in the procedure. However, also a simple and cheap CCD camera could be used. This would reduce the cost considerably but the functionality would remain the same.
The camera was mounted next to the scanning head, see Fig. 6.1. After the image of an object was recorded the object was shifted underneath the scanning head. An optical rail and fixed positioning blocks on both ends of the rail made the shift very reproducible. The camera was mounted in such a way that the pixels on the camera chip were in line the xy-scan direction of the scanning head.

To match the origin of the scanning head with that of the camera, a software calibration was applied. A part of the recorded image was cropped out of the full size image in such a way that the center of this cropped image matched the origin of the scanning head. With this method, of shifting of the object, a positional accuracy from image position to scanning position of approximately 15 µm was achieved.

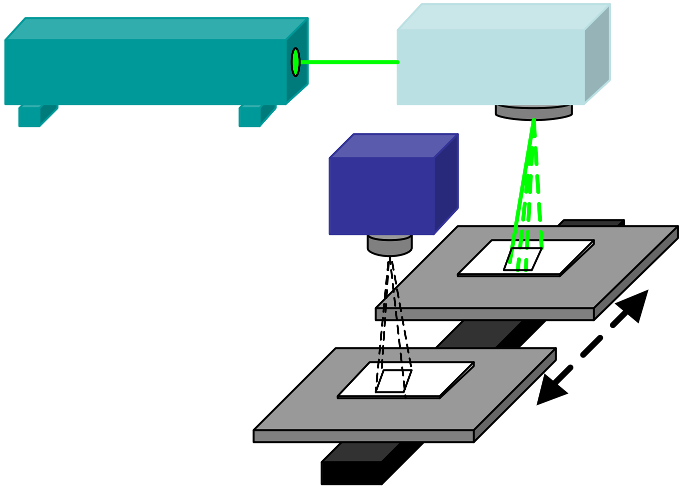

Fig. 6.1: Diagram of laser cleaning station set-up, consisting of the Nd:YAG laser, the scanning head and the digital camera.

Digital isolation

A recorded image was subsequently digital processed using an image-editing program. Depending on the recording different standard image processing methods were applied to digitally isolate those parts that need to be cleaned. Most used methods are summarized:

- Grey level adjustment. Depending on the type of object and the quality of the recording, a first isolation can be made by adjusting the gray level of the pixels in such a way that the contrast between the to be cleaned and the not to be cleaned areas is enhanced.
- Blur. By blurring those areas that should not be cleaned, they become slightly larger and safe borders can be established. The Gausian blurring technique was used.
- User selection. Of course the user can also isolate areas manually, by painting parts either black or white.
- Convert to black and white image. Finally the image is converted to a 1 bit black and white image, where black indicates the areas that need to be cleaned and white the areas that are not to be irradiated by the laser.

The different methods were mostly applied more than one time for each image, until finally the desired black and white image was obtained. The software used in the digital isolation was commercial imaging software, such as PictureWindowPro, Photoshop and Corol-PhotoPaint. No new software was developed for this purpose.

Convert image to laser program

Special software (prx2prg) was written at Art Innovation that converts the black and white image to a marking program for the laser. This program operates the scanning mirrors and sets the laser cleaning settings. The mirrors scan the object line by line.

The laser settings that can be selected are the percentage of total laser power, *p*, and the overlap, *o*, of the laser spot. The overlap is given as a percentage of the laser beam diameter (70 µm). So a 10 % overlap means the center of the individual spots are 63 µm apart, in both directions. To achieve the most homogenous beam intensity over the complete surface a closed packed scheme was applied for the overlap of the individual pulses, see Fig. 6.2.

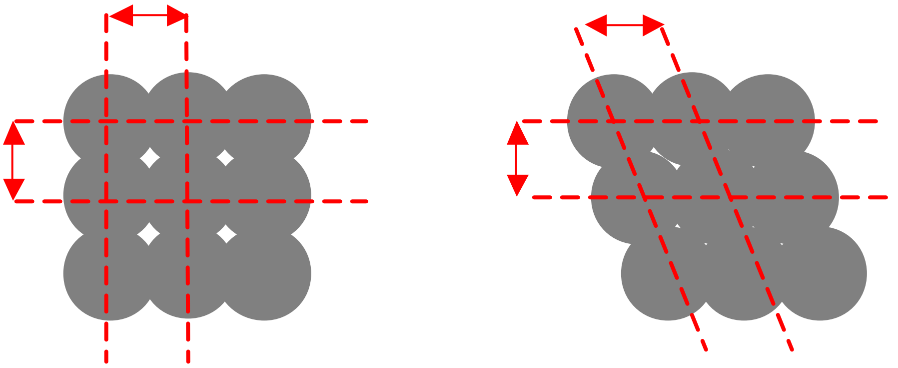

Fig. 6.2: Cubic packing on the left and closed packing on the right for 10 % overlap.

Laser settings for cleaning of paper

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A matrix with on one axis the percentage of the lamp power, *p*, and on the other axis the amount of overlap, *o*, was produced to identify proper cleaning settings, for this laser station. This was applied for the removal of ballpoint from regular paper. In Fig. 6.3 the matrix is shown.

Safe cleaning settings for the removal of ballpoint for paper are a laser power between $70\ \% < p > 72\ \%$ and an overlap of 50 %. These settings are specifically for this laser station. Corresponding laser power measurements have not yet been carried out, so comparison with the laser fluences obtained in chapter 3 can not (yet) be made.

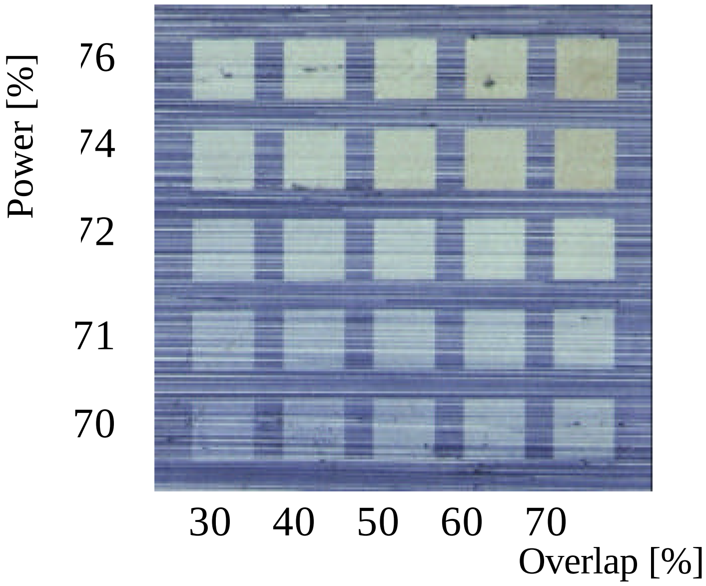

Fig. 6.3: Cleaning of ballpoint ink. The horizontal areas show the overlap % and the vertical areas the power of the laser in %

6.5 Cleaning demonstration

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As a demonstration several cleaning cases were dealt with, both on real documents as well as artificially produced objects. Three cases are shortly discussed in the coming paragraphs.

Cleaning of ballpoint ink

In Fig. 6.4 the three steps for the selective laser cleaning are shown for the cleaning of ballpoint for the backside of a poster. The number 06303 is digitally isolated and subsequently only the black area where the inks was present on the paper was cleaned.

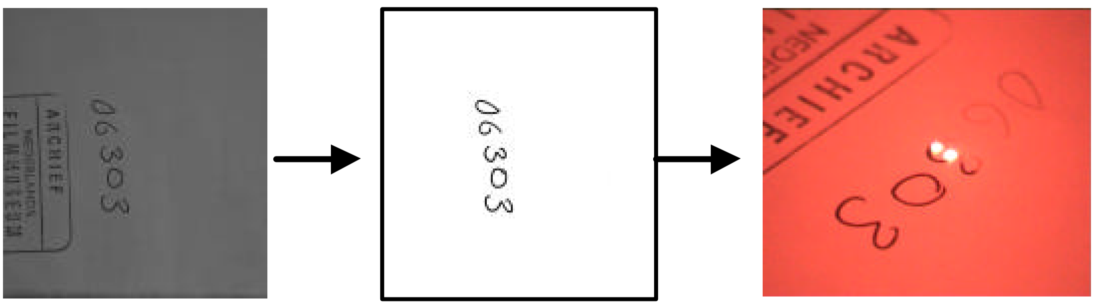

Fig. 6.4: Selective cleaning procedure involving three steps: (1) digital image taken from object, (2) isolate area to be cleaned (black), (3) selective laser treatment.

Selective removal of chalk

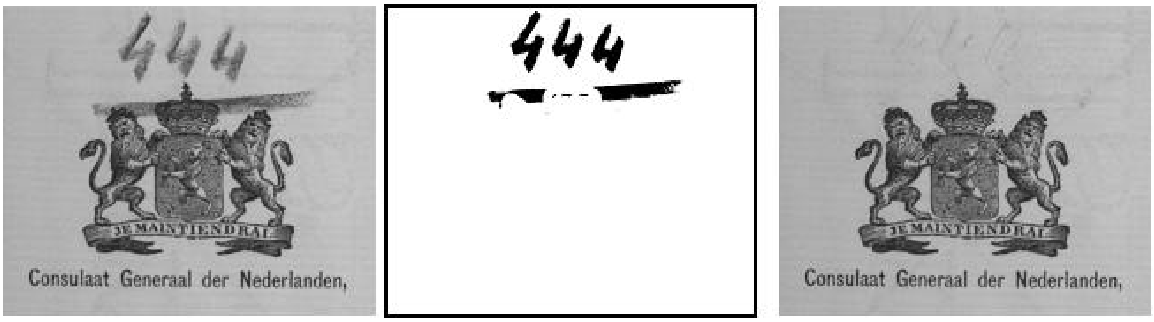

Fig.6.5: Selective removal of chalk from paper, (i) before cleaning the object, (ii) digital isolated black and white image and (iii) the after cleaning object.

Fig. 6.6: Detail view of the before and after image, showing the removal of chalk inside the crown, demonstrating the accuracy of the cleaning.

The selective removal of chalk inside the crown on the paper documents is a good example of the accurate cleaning possible with the prototype laser cleaning station.

Removal of rust residue for paper clip

The removal of rust residue from a paper document was an application that was not considered before but proved to be a real possible application. The rust stain could successfully be removed using the laser technology.

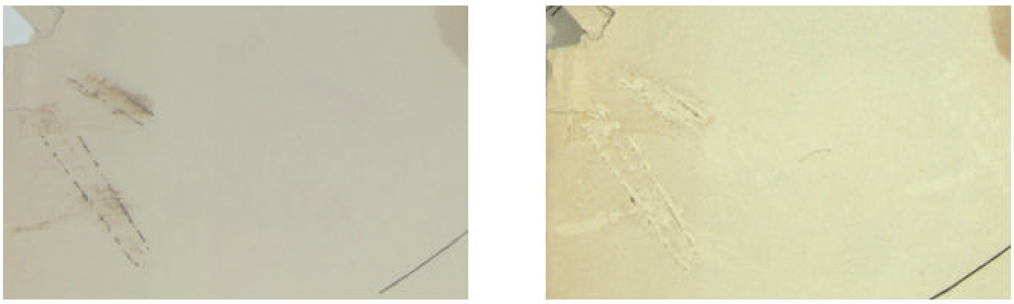

Fig. 6.7: Removal of rust residue from a paper clip.

6.6 Conclusion

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A prototype laser cleaning station for paper was developed. It was proved that by combining digital imaging with an accurate laser scanning system, it is possible to selectively clean specific areas on a document.

The digital isolation method allows for different laser settings to be applied at different areas. This was not carried out in these first experiments but could be useful. For instance if the document contains different kind of foreign material, which both are treatable but with different laser settings. In such a case it is possible to isolate the different areas and treat the different foreign material on them with different laser settings.

In this prototype the document needs to be shifted from the camera position to the laser scanning head position instead of co-axial camera viewing. This configuration makes it possible to reduce the design and production costs of future laser stations.