Paper Re-Use: Toner-Print Removal by Laser Ablation

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Abstract

*This article explores the possibility of using a laser to remove toner-print from office paper. Removal of print would allow paper to be re-used instead of being recycled or disposed into a landfill. This might reduce climate change gas emissions per tonne of office paper by between 45% and 95%. Although there is little previous research on the area, a number of related articles on paper conservation methods using laser radiation can be found in literature. Different authors have studied the effects of laser energy on blank paper and its application for cleaning soiled paper. However, this study examines toner-print removal from paper by laser ablation. In this article a laser in the visible range is applied to a single toner-paper combination with a range of energy fluences. Results are evaluated by means of colour measurements under the L*a*b* colour space and SEM images. Analysis of the samples reveals that there are parameters under which it is possible to remove toner from paper without causing significant discolouration or damage to the substrate. This means that it is technically possible to remove toner-print for paper re-use.*

Introduction

The paper industry is ranked between the 3rd and 5th of the most significant industrial causes contributing to climate change according to the International Institute for Environment and Development [1], as paper production and consumption accounts for approximately 1-2% of man-made climate change gas emissions. There are four main approaches to reduce these numbers: decreasing consumption, changing to carbon-neutral fuels, improving the energy efficiency of each stage in the life cycle of paper and cutting out stages in this life cycle. The latter could be achieved by removing print from paper (un-printing), as this would allow paper to be re-used instead of being recycled or disposed into a landfill. Counsell and Allwood [2] estimate that un-printing could reduce climate change gas emissions per tonne of office paper by between 45% and 95%, demonstrating greater potential compared to other efforts to reduce paper and board consumption such as incineration, localisation, annual fibre, fibre recycling and electronic paper.

A survey of different processes that could erase toner-print was performed by Counsell and Allwood [3]. They classified them according to whether removal processes used adhesion, ablation, abrasion or solvents, finding that most of the evidence from previous research is in the form of patents which provide little or no data on whether and how the techniques work. The only indication of previous research on toner removal by laser ablation is an article by Ihori et al [4], published in Japanese, where three distinct types of print are exposed to laser radiation at 1064 and 532 nm. Although they report that both types of lasers detach toner-print, the damage and degree of re-usability of the paper is not clear from their results.

This paper addresses the problem of toner-removal by discussing the use of a 532 nm laser on a single toner-paper combination employing energy fluences under 1.6 $^{J}/_{cm^2}$. The objective of this research paper is to establish whether toner-print can be effectively removed from paper by means of laser ablation in the visible range of light and, if so, to evaluate whether this technique is capable of producing sheets of high enough quality to replace new paper.

This article begins by reviewing relevant previous work on the subject. The second and third sections present the experimental results obtained from distinct laser removal trials. The final sections evaluate and discuss these results to establish the technical feasibility of this solution.

Background: Lasers in Paper Conservation

Different authors have studied the application of lasers for cleaning soiled paper, i.e. removal of dust and carbonaceous particles from paper fibres. The idea behind this process is that if a laser fluence level can be chosen to stay below the ablation threshold of the paper at the same time that it exceeds that of a contaminant, paper could be cleaned without suffering any damage. The same principle could be applied for toner removal by laser ablation.

A study performed by Kaminska et al [5] compared the performance of lasers at 355, 532 and 1064 nm to remove a mixture of charcoal and dust contamination on hand made cellulose paper. Surface inspection by SEM as well as a colorimetric analysis was performed on the samples, concluding that all three lasers were able to clean the charcoal and dust mix from paper. The application of UV and IR lasers (355 and 1064 nm respectively) resulted in higher damage and yellowing to the paper substrate whilst the most effective cleaning occurred at 532 nm. Kaminska et al identified two types of cellulose degradation processes arising from laser ablation: photo-chemical reactions caused by UV radiation leading to photo-oxidation and thermo-chemical reactions due to IR radiation responsible for localised heating and thermal decomposition.

Additional research on the subject performed by Strlic et al [6] also explored the effect of removing charcoal powder from paper using an Nd:YAG laser at 532 and 1064 nm. They reported that laser energy at 1064 nm generates a higher discoloration or yellowing of the substrate. They state that the yellowing is produced by thermal degradation reactions which lead to the formation of yellow chromophores in cellulose. Paper yellowing was reduced by using energy at 532 nm and allowing the substrate to cool down between successive laser shots by decreasing the pulse-repetition rate.

A contrasting result has been reported by Kolar et al [7], who carried out specific tests to evaluate the applicability of an

Nd:YAG laser at 532 nm for cleaning paper using fluences below 2.5 $^{J}/_{cm}{}^{2}$. Paper samples soiled with carbon particles were used for the experiments. They found that although this type of laser radiation does not produce immediate damage on blank paper, irradiation of soiled samples resulted in yellowing and degradation of the substrate, contradicting the claims that this type of radiation does not damage or discolour paper. Kolar et al also suggest that photo-thermal deterioration of the cellulose is responsible for the yellowing.

A number of other studies with similar conclusions can be found in the literature and will not be discussed here in detail (Krüger et al [8], Kolar et al [9], Jalbert et al [10] and Ochocinska et al [11]). In summary, it is evident that valuable research has been done to study the effects of laser ablation on blank and soiled paper. Best cleaning results seem to be obtained with a wavelength of 532 nm as no evident mechanical and chemical damages appear to be produced on blank paper. It seems that there are specific combinations of operational parameters which could reduce yellowing or even avoid it, suggesting that, under the right conditions, it might be possible to ablate toner-print without deteriorating paper.

Experimental

Previous experiments performed by Counsell [12] at the University of Cambridge evaluated the use of UV and IR radiation (193, 355, 1064 and 10600 nm) to ablate toner. It was found that although all wavelengths removed toner-print, longer wavelengths did so with less damage to the paper. Best results were obtained with radiation at 1064 nm. Unfortunately the paper beneath the print was yellowed as the print was removed. This agrees with the results reported by the different paper conservation researchers mentioned before. This section describes a series of experiments that have been designed to overcome this problem by employing laser radiation at 532 nm to remove toner-print from paper.

Test samples were 1.3 x 1.9 cm black rectangles printed in a Hewllet-Packard 4200dtn black and white laser printer on white, un-coated, wood-free, 80 $^{g}/_{m}{}^{2}$ Canon copy paper. According to data from HP [13], this toner is composed of 40-50 wt% polyester resin, 40-50 wt% iron oxide and 1-2 wt% amorphous silica. Laser tests were performed with a QuikLaze 50ST2 laser manufactured by New Wave Research. Three different fluence levels were tested while keeping the rest of the parameters constant. A summary of test values can be seen in table 1.

The level of damage of the paper was assessed by taking Scanning Electron Microscope (SEM) images of the results using a Carl Zeiss 1540 XB Cross Beam FIB/SEM system. Colour measurements were performed by scanning the samples with a CanoScan Lide 25 scanner from Canon and converting the resulting images to the LAB colour space by using ImageJ software. The same software was used to measure the L*, a*, and b* values from the LAB colour model, where L* defines the lightness of the colour (brightness perception, where L*=0 for black and L*=100 for white), a* measures green and magenta tones (negative values indicate green while positive values indicate magenta) and b* quantifies the yellow and cyan colours in a sample (b* negative indicates cyan while positive indicates yellow). Both *a** and *b** should be near zero for objects with neutral colours such as black and white.

The samples were positioned on the laser table in the focal plane of the laser before each test was started. The microscope was then adjusted to focus the image after the samples were correctly positioned. Test preparation was completed by configuring the laser parameters in the control screen (wavelength, energy level, scan speed, frequency, etc.) according to the values previously shown in table 1. All tests consisted of scanning a 1 mm^2 area in a raster pattern, as shown in *Figure 1*. Only one laser pass was applied to each sample.

Table 1: Test Parameters

	Test 1	Test 2	Test 3
Fluence	0.5 $^{J}/_{cm}{}^{2}$	1 $^{J}/_{cm}{}^{2}$	1.6 $^{J}/_{cm}{}^{2}$
Pulse Frequency	15 Hz		
Scan Speed	150 $^{\mu m}/_{sec}$		
Spot Size	150 µm x 150 µm (rectangular)		
Number of Passes	1		
Line Spacing	50 µm		

Results

The results from colorimetric and SEM analyses are presented. Further discussion is offered in the following sections.

Colour Measurements

A visual inspection of the results suggests that different removal levels are achieved depending on the energy density applied per pulse. In general, higher fluences seem to produce higher toner removal. *Figure 2* presents the L*a*b* colour measurements at the different energy densities tested. Reference colour measurements from black toner and white paper are provided for comparison.

Colour measurements of ablated areas indicate that the values from the three variables (L*a*b*) become similar to those of white un-lased paper as the energy fluence is increased towards 1.6 $^{J}/_{cm}{}^{2}$, indicating that paper maintains its whiteness after treatment.

SEM Analysis

Microscopic images of the lased samples are shown in *Figure 3*. An image of blank un-lased paper is included for comparison (image *a*). Evaluation of the results obtained at different energy densities indicate that minor traces of toner can be seen on the fibres after treatment with the lowest fluence level (image *b*). These traces disappear as the energy density is increased (images *c* and *d*). No damage can be appreciated on the cellulose fibres at any energy level when compared to blank un-lased paper, suggesting that toner was safely and efficiently removed from paper.

Discussion

It is evident from colorimetric and SEM analyses that laser radiation at 532 nm is capable of removing toner-print from paper without discolouring and damaging paper considerably. The amount of toner removed depends strongly on the energy fluence level whilst cellulose fibres appear to remain in a good shape when compared to blank paper.

Colour analysis of the ablated areas resulted in L* (lightness) values of 83.8, 91.7, and 95.2, a* (green and magenta) values of 3.6, 3.1, and 1.1, and b* (yellow and cyan) values of -0.7, -1.5, and 0.9 for fluences of 0.5, 1, and 1.6 $^{J}/_{cm}{}^{2}$ respectively. Values from reference white un-lased paper samples have been measured at L*= 99.9, a*= 0, b*= 0. This means that for the highest fluence level tested, the difference in L* between lased and un-lased paper is of less than 5%, while the differences in a* and b* are around 1%. This indicates that lightness remains at an acceptable level while practically no yellowing can be observed.

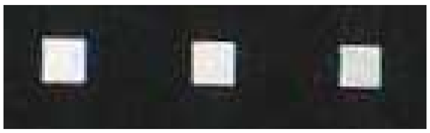

Figure 1. *Test samples (Toner removed from white areas).*

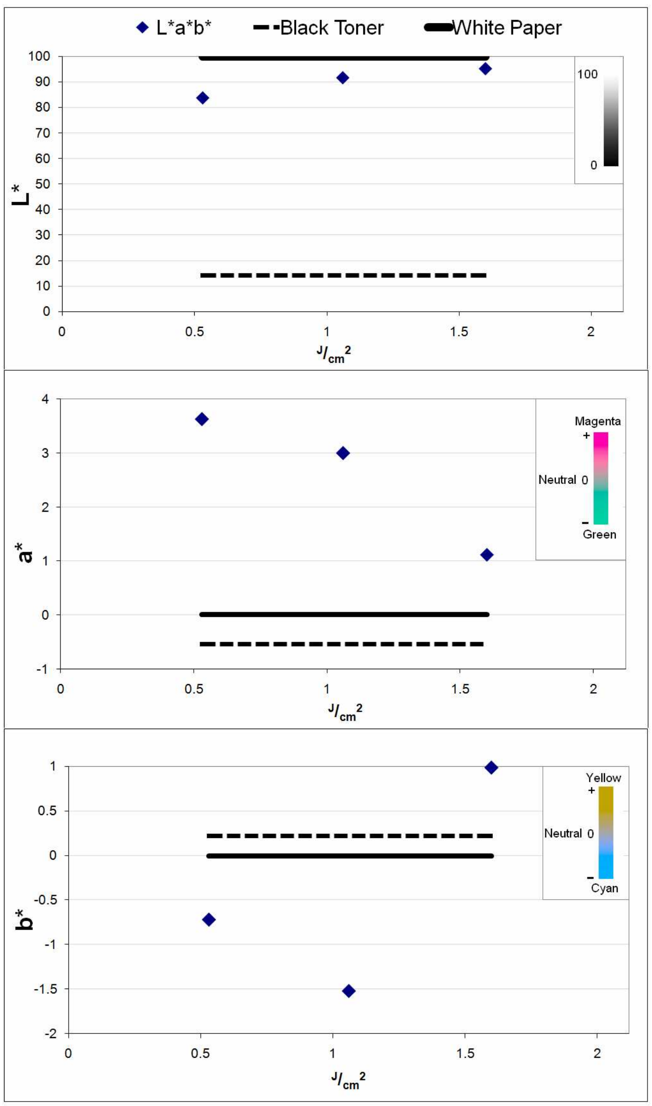

Figure 2. *L*a*b* colour measurements versus energy fluence.*

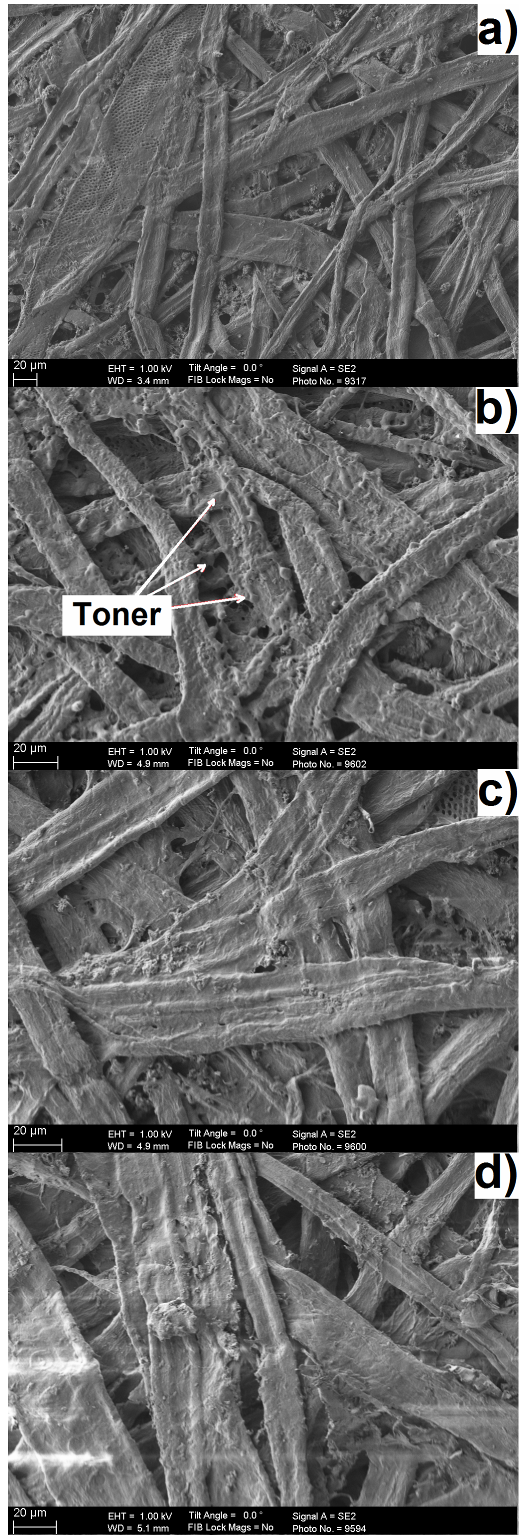

Figure 3. *SEM images of test samples. [a) white paper, b) 0.5 $^{J}/_{cm}{}^{2}$, c) 1 $^{J}/_{cm}{}^{2}$, and d) 1.6 $^{J}/_{cm}{}^{2}$]. Toner residues can be seen at the lowest energy level in b). Lased samples in c) and d) show no significant damage when compared to white paper shown in a).*

Black toner-print absorbs more than 95% of radiant energy at a wavelength of 532 nm while the absorptance of paper remains lower than 85%, as reported by Williams [14]. Considering the toner composition reported by HP (40-50 wt% polyester resin, 40-50 wt% iron oxide), it is believed that the high energy absorption of the toner results in a temperature increase that leads to the thermal degradation of its polymer fraction, detaching toner from paper. Thermogravimetric analysis (*Figure 4*) provides supporting evidence for this theory, as it can be seen that toner suffers a 50% weight loss at a temperature of 411°C. After this point its weight remains fairly constant, suggesting that the polymer is degraded while the iron oxide remains intact.

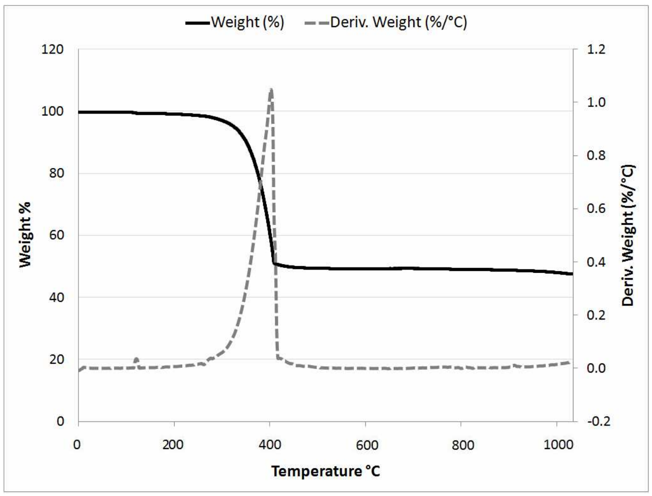

Figure 4. *Thermogravimetric Analysis (TGA) of toner.*

An analytical model is currently being developed to explain the laser ablation of toner in order to increase the understanding of the physical phenomena involved in this process. Current work in the area also includes testing the applicability of this technique in more than one toner-paper combination as well as performing an energy and CO_2 footprint analysis to determine the feasibility of using this method in a higher scale.

Conclusions

Removal of toner-print by means of laser ablation at 532 nm has been explored in this research. There is a clear relation between the energy fluence applied and the amount of toner that is removed, as higher energy densities yield better removal. Regarding the paper substrate, no apparent damage was found after exposure to laser radiation when inspected in a SEM. Colour measurements indicate that no significant discolouring of paper occurred after treatment.

The main conclusion from this study is that there are a set of laser parameters that entirely remove toner-printed characters and do not damage blank paper. This means that it is technically possible to remove toner-print for paper re-use. The economical feasibility of this technique and its environmental impact are currently being evaluated and compared to alternative means of reducing the climate change impact of office paper, as part of a major research programme. The long-term mechanical and chemical stability of paper after treatment will be evaluated in future work.

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