Remove toner: Reuse paper

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“The making of a modern palimpsest”

This thesis contains fifty-one thousand words, thirty-seven figures and seventy tables. It is the result of my own work.

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Abstract

This thesis reports on experiments into whether abrasives, lasers or solvents can remove ordinary black toner print from ordinary white office paper in a way that leaves the paper reusable. If it could be 'un-printed' then the office-paper could be reused without the need for recycling.

This thesis starts by comparing six options for altering the life-cycle of office paper – incineration, localisation, annual fibre, fibre recycling, un-printing and electronic-paper – in terms of how they might cut climate change gas emissions. Un-printing might cut such emissions by up to 95%.

Does the technology to un-print exist? A review of existing techniques, organised according to whether they remove, obscure or de-colour the original print, suggests that the technology only partially exists. In particular, it is not clear whether toner print can be removed by abrasives, lasers, or solvents without damaging the paper so much that it become unusable. These three approaches are tested experimentally.

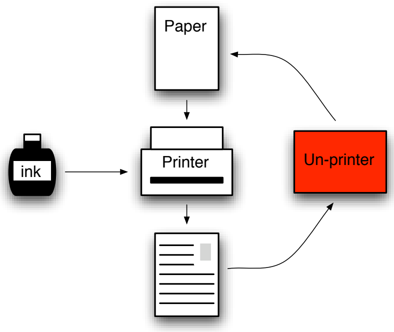
Abrasives can remove toner-print with limited damage to the underlying paper by operating in an adhesive wear regime. This involves making ten passes with a fine P800 abrasive rubbing at high speeds (6 m/s) and low loads (0.5 N). Longer wavelength lasers are able to entirely remove the toner-print and able to leave blank paper undamaged by operating at 1 W and 10 kHz in the 1064 nm wavelength and scanning across the surface eight times at 400 mm/s. Unfortunately the paper beneath the print is yellowed during removal. A 40:60 mixture chloroform and dimethylsulfoxide effectively dissolves toner without dissolving paper if agitated with ultrasound for four minutes.

None of the processes are ready to replace paper but there is potential in the solvent and abrasive approaches. The solvent approach requires research into benign solvents and solvent recycling. The abrasive research requires research into abrasive life.

Contents

1 Introduction

You've finished this thesis. What do you do with it next? Throw it in the bin? Gently place it in the recycling box? Or drop it into the un-printer so that the print can be removed and the paper immediately reused?



1.1 Statement of the problem

This thesis reports on experiments into whether abrasives, lasers or solvents can remove ordinary black toner print from ordinary white office paper in a way that leaves the paper re-usable.

1.2 Limitations

The research reported in this thesis has five major limitations:

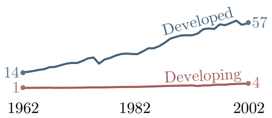
1. Only office paper is considered.
2. Only the removal of print is considered.
3. Only toner print is considered.
4. Only a single print-paper combination is tested.
5. The toner, paper and printing process are not varied.

The remainder of this introduction will explain the choices that lie behind each of these limitations. It will then outline the organisation of this thesis, cite where work in this thesis has been published and acknowledge the help that has been received.

1.2.1 *Only office paper is considered*

Paper can be classified according to its end use (e.g., packaging and board, sanitary, printing and writing), its production process (e.g., chemical, mechanical or recycled), whether it contains lignin (if it does not it is known as 'wood free'), whether the surface of the paper has been coated, whether the paper has been cut to a particular size and by its colour. This research only covers office paper, defined as cut size (e.g., A4, A3, letter), white, uncoated, wood-free printing and writing paper. It does not address newsprint, glossy magazine papers or the coated papers used in ink-jets and some colour photocopiers.

The Food and Agricultural Organisation division of the United Nations estimate[1] that approximately three hundred million tonnes of paper products are produced each year. Of this, half is used in packaging, just over a tenth is used by newspapers, just under a tenth in sanitary and household products and the remaining third is categorised as 'printing and writing'. The production of printing and writing paper has more than doubled since the 1980s[1], to reach just under 60 kg per capita in the developed world and just over 5 kg per capita in the developing world.



Printing & writing paper kg/capita. Data:FAO [1]

The category of printing and writing paper includes book and magazine papers, as well as the coated papers used by ink-jet printers and some colour photocopiers. Data from the Confederation of European Paper Industries[2] suggests that 10% of paper produced in Europe is the uncoated wood-free paper typically used in offices, equivalent to about 10 million tonnes a year. This matches an estimate[3] of the market for cut-size paper in Europe as around 13 million tonnes and the estimate[4] that the average European office worker prints, copies or writes on between five and thirty sheets of paper a day.

Despite the concept of the 'paperless office', the use of printing and writing paper is increasing. Sellen & Harper [5] explain this with reference to the rapid increase in information available at our desktop, and to the rapid increase in cheap printers. They believe that the use of paper has shifted from communication and knowledge storage towards knowledge creation. This is corroborated by a Xerox survey, reported in the New York Times[6], that estimates that 45% of office paper is used for temporary purposes, and 21% of black-and-white printed copier paper is used for less than a day.

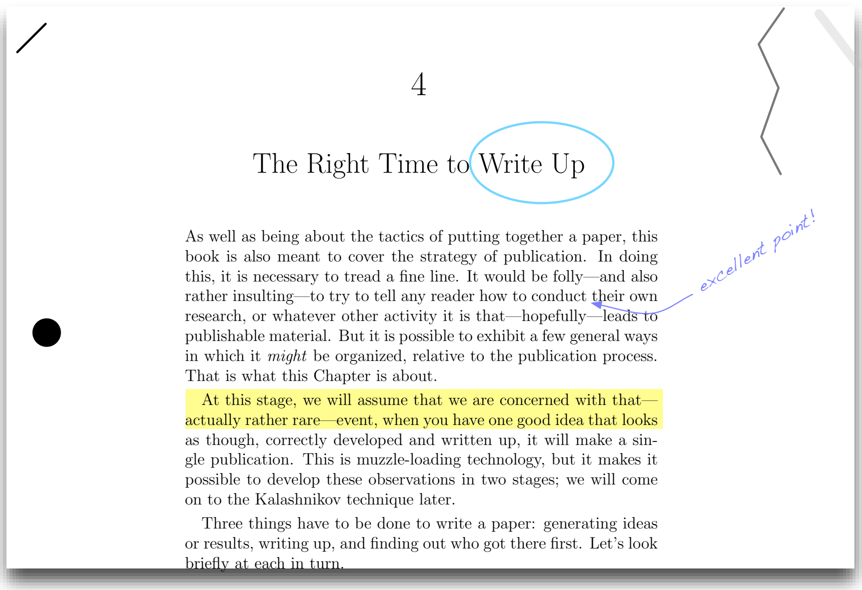
Once it has been used, paper is thrown away or recycled ready to be used again. 40% of the mass of paper produced in Europe is made from recovered paper fibre[7] but this statistic disguises large variation across paper types. Between 7%[3] and 8%[8] of office papers are made from recovered paper fibre, and perhaps only 12–15% is collected in recycling bins for further recycling. Rather than being turned back into office paper, most high grade paper that is recycled is put to other use – often as sanitary paper[8].

In summary, this research is focused on a small part of the overall paper consumed – the five to thirty sheets of virgin white A4 paper that each person uses in their office each day and that tends, on the whole, not to be made from recycled material or recycled.

1.2.2 *Only the removal of print is considered*

This research only tackles the removal of print. It does not address other aspects of office paper recycling such as the ironing out of folds or the repairing of holes and tears. Nor do the experiments in this research explore obscuring or de-colouring of print which might be considered as alternatives to removal.

A sheet of office paper could be reused if its holes, folds, creases and tears were repaired, and its redundant text and pictures were un-printed. Doing so would overcome four obstacles that may prevent waste office paper being reused for its original purpose:



4

The Right Time to Write Up

As well as being about the tactics of putting together a paper, this book is also meant to cover the strategy of publication. In doing this, it is necessary to tread a fine line. It would be folly—and also rather insulting—to try to tell any reader how to conduct their own research, or whatever other activity it is that—hopefully—leads to publishable material. But it is possible to exhibit a few general ways in which it *might* be organized, relative to the publication process. That is what this Chapter is about.

excellent point!

At this stage, we will assume that we are concerned with that—actually rather rare—event, when you have one good idea that looks as though, correctly developed and written up, it will make a single publication. This is muzzle-loading technology, but it makes it possible to develop these observations in two stages; we will come on to the Kalashnikov technique later.

Three things have to be done to write a paper: generating ideas or results, writing up, and finding out who got there first. Let's look briefly at each in turn.

The first obstacle is that holed, creased or torn papers tend to jam printers and photocopiers. If paper cannot be fed through a printer or photocopier, then it has much more limited opportunities for reuse: for pen or pencil print, or for non-writing uses such as stabilising wobbly tables. The second obstacle is that tears and weakened corners may prevent paper from being reliably fastened with staples, clips or in ring binders. The third obstacle is that most printing processes rely on the light even colour of paper to contrast with the dark colour of their print. Therefore the redundant text on waste paper may make it difficult or confusing to read over-printed text. The fourth obstacle is that waste paper may bear private or sensitive text.

Appendix §A contains a very brief review of techniques that could repair paper by removing holes, creases and tears. It concludes that paper conservators are able to carry out these repairs, but that they are potentially difficult to automate. Repair without un-printing is likely to be less useful than the other way around. Therefore this research has focused on the problem of un-printing.

Furthermore, the experimental chapters of this thesis only consider removal of print and do not investigate approaches that decolour or obscure print. This focus has been chosen because obscuring and de-colouring have been better researched, and because removal offers some advantages. The advantages arise because obscuring print results in layers of print and obscuring material building up on the surface of paper. De-colouring print also leaves layers of colourless print building up on the surface of the paper. In both cases subsequent prints would need to be made on a substantially different surface to the virgin paper of original prints. Eventually, in both cases, the build of layers may restrict further printing. Neither situations arise if print is removed.

1.2.3 Only toner print is considered

This research only tackles the removal of toner print used by laser printers and photocopiers. It does not tackle the removal of pen inks, of pencil, highlighter, ink-jet print or of the print produced by commercial printers.

There are three common types of office print: toner prints; pigment based inks; dye based inks*. Toner print is laid down by laser printers, photocopiers and some fax machines. Pigment and dye based prints are laid down by ink-jet printers and pens.

* Less common types of print that are occasionally found, but not considered here, include thermal printers (principally in older fax machines) and pencil.

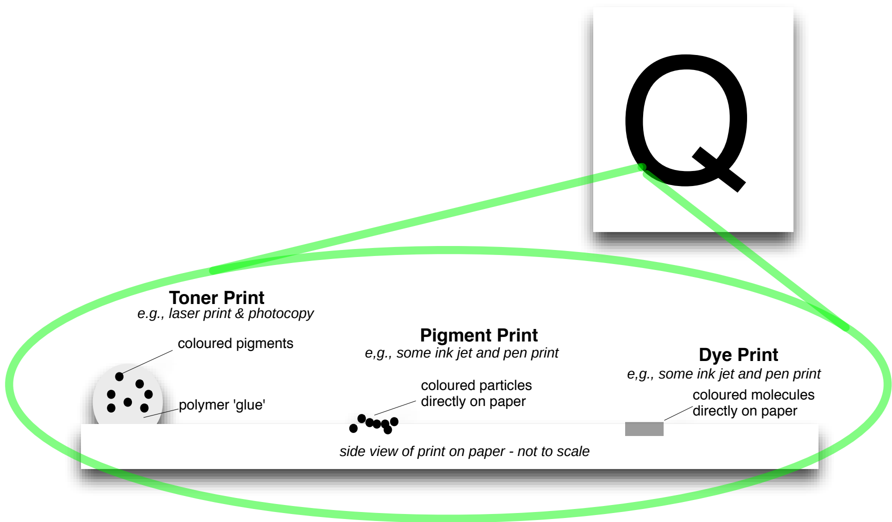


Figure 1.1 Three common types of office print

These three types of print differ in the size of their particles and the method by which the colour is attached to the paper.

Toner print has the largest particles of the three print types. It consists of $5 - 25\,\mu\text{m}$ diameter irregular particles of a thermoplastic resin containing a black pigment. After printing, the resin acts as a 'glue', holding the pigment onto the paper surface, although this mechanism of this has not been well studied (more on this below). During printing, the resin is given an electrostatic charge to allow it to be positioned in the correct place on the paper surface. Once positioned, the toner is fixed in place by a combination of heat and pressure which cause the thermoplastic to soften, sinter and wet against the surface paper fibres. A typical printed sheet bears about $50 - 100\,\text{mg}$ of toner, made up of perhaps $10 - 1000\,\text{million}$ individual particles[9]. The exact composition of a toner varies by manufacturer and is usually a trade secret. They are usually classified according to the type of polymer (an acrylic or a polyester) and whether they include a magnetic component (typically iron ferrite).

Figure 1.2 is a scanning electron microscope image of toner-print on office paper. Seventy to ninety percent of a sheet of office paper is typically fibrous bundles of cellulose, a type of glucose polymer, similar to the one running across the centre of the image. These bundles are usually flattened cylinders, $10 - 50\,\mu\text{m}$ in width and $1 - 5\,\text{mm}$ in length, stacked randomly in up to ten layers

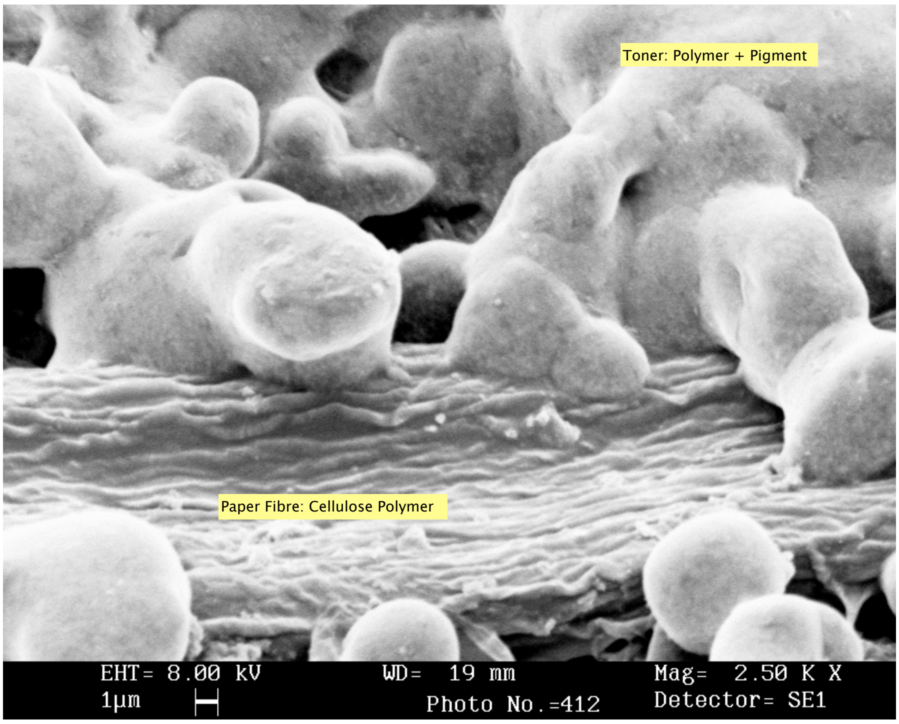


Figure 1.2 Scanning Electron Microscope close up of toner on paper.

across the thickness of the paper. The remainder of a sheet of office paper is usually a combination of fillers (often clays), whiteners (often titanium dioxide), traces of lignin and additives that adjust the strength and water absorption properties of the paper. In the image, the toner particles are the grey blobs surrounding the fibre. They appear black to the visible eye, but are represented as grey in the scanning electron microscope image (figure 1.2).

Only a small body of research has been published on how the toner print is attached to the paper. In most cases the focus has been on how the properties of the paper, printer or print can be adjusted to maximise the strength of the attachment. Prime [10] developed models for the relationship between the quality of the bond between toner and paper and the properties of the toner and the heating and pressing process. He expanded on the work of Lee [11] to include pressure as a variable to represent heat-pressure fixing systems as well as heat only systems. Like Lee, he suggests that there is a strong correspondence between the temperature related viscous flow of the toner and the quality of the final bond. He also suggests that the process of sintering and wetting onto the paper is rarely completed during fixing. Sanders *et al.*[12] examined how the type of paper influenced the fixing process. He suggested that the strength of the toner fix increases with the surface energy of the paper surface – implying that the way that the toner polymer wets to the paper is important.

Pigments are a constituent of toner print and are small (perhaps below 50 μm) solid particles of a coloured material. In ink or ink-jet printing, they are normally deposited on the paper surface in a drop of liquid. The liquid evaporates, leaving the pigment attached to the paper fibres by inter-molecular forces. Pigment based prints often include other chemicals to increase the strength of the bond between the pigment and paper fibres.

Dyes consist of individual coloured molecules, rather than solid particles. Like pigments, they are deposited on the paper surface in a drop of liquid that then evaporates. Unlike pigments, because they are individual (often liquid) coloured molecules, they may penetrate deep into the paper surface. Managing this penetration depth is one of the reasons that coated papers are used for ink-jet printers.

During a single use, paper might be marked with all three types of print: it may be photocopied, then annotated with a dye based pen, then be partially highlighted with a fluorescent pigment based marker. This implies that research on un-printing all three print types would be valuable. If only one type of print can be removed, however, it might be best to remove the one that is responsible for the largest area of print.

Data from Cresswell[3] implies that perhaps 85% of paper is printed with toner (by photocopiers or laser printers), 10% with ink-jet printers and 5% by fax machines (which may be toner, or may be thermal printers). The data probably under-estimates ink-jet printing, because it is based on the types of paper sold and therefore misses the proportion of ink-jet paper that is not done on coated paper – but it seems to agree with the everyday experience that laser printers and photocopiers are the dominant users of paper in many offices. The research in this thesis has therefore focused on toner-print.

1.2.4 Only a single print-paper combination is tested

There is significant variation in both the formulation of toners and in the structure of and additives in office paper. The tests reported in this thesis were carried out on a single toner-paper combination. The results may not hold for other toners or papers. Both the print and the paper that were tested are typical of an office environment. The paper was white, un-coated, wood-free, 80 g/m^2 Canon copy paper. The printer was a HP 4200dtn black and white laser printer. The exact toner formulation is proprietary to HP and has been reported as 40–50% polyester-resin, 40–50% ferrous iron-oxide, 1% amorphous silica[13].

The tests reported in this research were limited to a single combination of print and paper for economy – it was hoped that reporting on a broad range of approaches on a narrower set of samples would be more useful than the reverse. Further research will be required on any approaches that are of interest to ensure the results are valid for a wider range of toners and prints.

1.2.5 *The toner, paper and printing process are not varied*

The research has not attempted to vary the toner, paper or printing process in order to make the removal task easier.

The problem at the heart of this thesis is how to remove toner print from paper to allow the sheet of paper to be reused. In theory, this could involve developing a mixture of technologies including an un-printer, a special new toner-print, a new type of paper, or a new printing process:

This research has focused on the technology required for an un-printer and not pursued changes to print, paper or printer. There are two reasons for the focus. The first is that technologies that use altered print and paper already exist (these are discussed in the review chapter §3). The second is that a system that did not require a change to existing print, paper or printer technology would be preferable to one that did.

1.3 Organisation

The next chapter (§2) of this thesis places the work in context through an analysis of the environmental potential of removing print in comparison to other technical fixes to the climate change gas emissions created by office paper. The following chapter (§3) reviews the existing literature on un-printing, which mainly exists in the form of patent filings. Three chapters then report on experiments to remove toner print using abrasives (§4), lasers (§5) and solvents (§6). The seventh chapter compares the feasibility of the three approaches. The final chapter concludes with the implications of the research reported in this thesis.

1.4 Previous publication

Some of the material reported in this thesis has been published in Journals and presented at conferences. In all cases my supervisor, Julian Allwood, was co-author:

1.4.1 Journal papers

1. Reducing climate change gas emissions by cutting out stages in the life-cycle of office paper. *Journal of Resources, Conservation and Recycling*, 49(4):340–352, 2007.
   `doi:10.1016/j.resconrec.2006.03.018`

2. Desktop paper recycling: A survey of novel technologies that might recycle office paper within the office. *Journal of Materials Processing Technology*, 173(1):111–123, 2006.
   `doi:10.1016/j.jmatprotec.2005.11.017`

3. Removing toner-print using solvents so that office paper may be reused. *International Journal of Product Design and Manufacture for Sustainability*, in preparation, 2007.

4. Removing toner-print using a laser so that office paper may be reused. *International Journal of Something*, in preparation, 2007.

5. Removing toner-print using abrasives so that office paper may be reused. *International Journal of Something*, in preparation, 2007.

1.4.2 Conference papers

1. Rethinking office paper recycling. In *4th Int. conf. on design and manufacture for sustainable development, Newcastle, 12-13 July 2005.*

2. The feasibility and environmental consequences of scale change in office paper production. In *ISIE 2005, Stockholm, 12-15 June.*

3. Un-printing toner: Early results. In *13th CIRP Intl. Conference on Life Cycle Engineering, Leuven, 31 May – 2 Jun 2006.* `http://www.mech.kuleuven.be/lce2006/122.pdf`.

1.5 Acknowledgements

The work was funded by the EPSRC through the University of Cambridge Department of Engineering doctoral training account. Although the work described in this document was all carried out by the author, he is grateful for the advice and help given by Julian Allwood, Ian Hutchings, Len Howlett, Wilhelm Huck, Catherine Smith, Jane Comrie, Barbara Bottrill, Bill Sampson, Peter Herdman, Les Tunna, Ali Kahn, Bill O'Neil, Quin Hu, the staff of the Bavarian Laser Centre (in particular Michael Schraut and Matthias Rank), and Catherine Will.

2 Reducing climate change

European environment ministers want to reduce European climate change gas emissions by 60–80% from 1990 levels by 2050[14]. Since 1990, emissions from the European paper industry have grown: increased consumption has offset lower emissions per tonne[7].

This trend could be reversed by:

- reducing consumption
- changing to carbon-neutral fuels
- improving the energy efficiency of each stage in the life cycle of paper
- cutting out stages in the life cycle of paper

Reducing consumption has been investigated by Hekkert *et al.*[15] They predicted that consumption of cut-size paper will increase at 5% a year in Europe between 1995 and 2015. They explored ways that the same needs could be met with less paper mass by: decreasing waste in the paper manufacturing process; decreasing waste in the printing process; reducing the average paper weight; 'good housekeeping' in offices; more double sided printing and copying; reducing the proportion of paper that is printed but not read. They predicted that double sided printing and copying would have the greatest effect on cut-size paper. They estimated that using all these technologies would reduce the climate change gas emissions from cut-size papers by 37% relative to their projection for 2015, although this would still represent a 74% absolute increase on 1995 emissions.

A change to carbon-neutral fuels is already well underway in the European pulp and paper industry. Biomass is used to generate half of the primary energy used in pulping and paper-making[7]. This has principally been achieved by using the waste wood and lignin from the pulping process to generate heat and electricity. Mannsbach *et al.*[16] analysed the potential for the Swedish chemical pulp industry to satisfy their entire power demand from biomass. They calculated that this could not be done by more efficient use of existing wood waste and lignin, but would be possible if extra biomass were to be supplied to the industry for use as a fuel.

The third approach relies on improving the energy efficiency of each stage of the pulping and paper-making processes. Martin *et al.* [17] analysed 45 technologies that might improve energy efficiency and predicted that they would allow the energy efficiency of the US pulp and paper industry to be improved by 31% on 1994 levels.

To date, studies of cutting out stages in the life cycle of paper have focused on whether to cut out landfill and replace it with incineration or with recycling. Surveys of this research, for example by Finnveden & Ekvall [18] and by Villanueva *et al.* [19], have explored the disagreement about whether to incinerate or recycle paper. They show that a significant factor in the choice is the mix of fuels that is assumed to be used by the paper industry and the mix of fuels that any energy created by incineration would be used to replace. There has not been a systematic comparison of the potential for climate gas reduction by cutting out transport through localising production, by cutting out forestry through the use of annual crops, by cutting out paper-making through the use of unprinting to allow paper to be reused or by cutting out printing through the use of electronic paper.

This chapter addresses two questions "What stages in the life cycle of office paper could be cut out?" and "What would be the impact on energy and on emissions of climate change gases?" The chapter focuses on cut-size paper used in office printers. It does not analyse economic constraints nor environmental impacts other than climate change gas emissions.

A quantitative assessment of the impact of cutting out different stages in the life cycle is made, but the numbers are rough estimates based on secondary sources. The estimates are believed to be correct relative to each other but should not be considered as absolute predictions or equivalent to life cycle assessments. The sensitivity of the conclusions to likely sources of error is considered in section §2.5.

The next section presents the typical stages in the life cycle of office paper together with the energy demand and climate change impact of each stage. Section §2.2 considers which stages could be cut out, section §2.3 analyses the potential impact on energy demand, section §2.4 examines the potential impact on climate change gas emissions and section §2.5 ranks the options and considers sources of error. The chapter ends with a discussion of directions for further research.

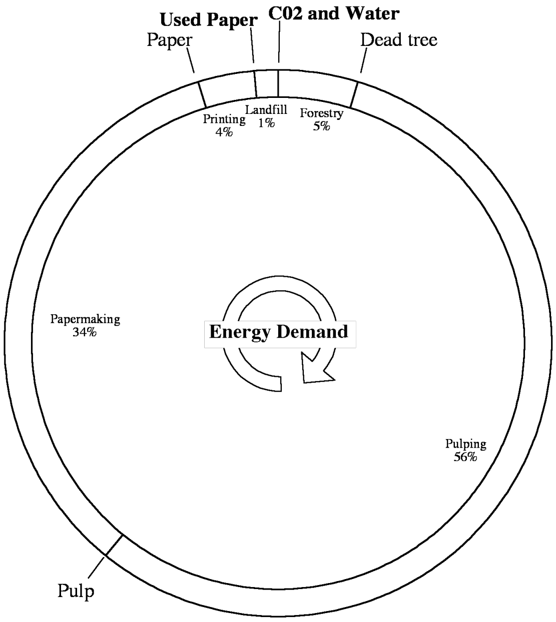
2.1 A typical life cycle

The energy demand and climate change impact of a typical life cycle of cut-size office paper is illustrated in figure 2.1 and discussed in this section.

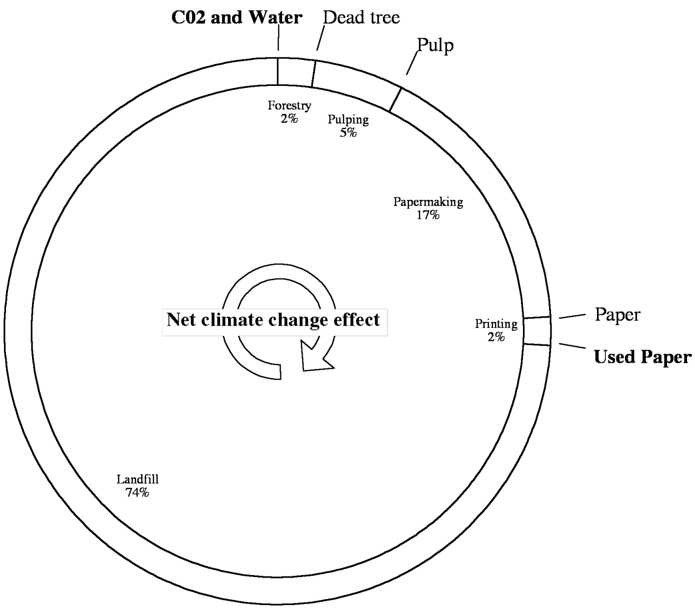
Cut-size office paper is formed principally from a web of fibres. These fibres are mainly cellulose, which is a glucose polymer of carbon, hydrogen and oxygen. The typical life cycle of office paper starts with carbon dioxide and water, which are converted by a tree into cellulose in its cell walls. The tree is felled, debarked, and pulped to separate the desired fibrous cells from the unwanted stiff lignin matrix that may constitute half a tree's mass. For cut-size office papers the pulping process normally uses solvents to dissolve the lignin. The un-dissolved fibres are then bleached to remove any remaining colour. The fibres are turned into paper by suspending them in water, pouring them over a fast moving mesh to form thin sheets, and then pressing and drying. In use most cut-size office paper is printed on or used for photocopying. It is then typically thrown into a mixed waste bin and taken with that waste to a landfill site. In a modern landfill site paper tends to decompose slowly into methane. Once in the atmosphere the methane is slowly transformed back into carbon dioxide and water, completing the cycle.

This is a description of the life of the majority of paper mass but excludes c. 15% of an office paper's mass that may be additives such as clays, binders or whiteners. These are incorporated at the paper-making stage and remain in landfill. The description also excludes variation across location: in some areas paper may be incinerated or recycled and at some landfills a proportion of the methane released may be captured and burnt. These variations are not considered here but are discussed in the following sections within a broader analysis of stages in the typical cycle can be cut out.

The typical energy demand for each stage in the life of office paper has been drawn from existing literature and is shown in table 2.1. The energy required to produce the chemicals used in pulping, to cut down and transport the trees, to transport materials and to finalluy print the paper has been incorporated. The solar energy used by the tree has been excluded. In practice the energy demand



(a) Source of c. 44 GJ/tonne energy demand



(b) Source of c. 6 tonne CO_{2e}/tonne climate change impact

Figure 2.1 An estimate of the relative contribution of different stages of a typical cut-size paper life cycle to energy demand and climate change impact.

Table 2.1 Approximate energy consumption and climate change gas emissions from a tonne of typical cut-size office paper.

	Energy Demand (primary GJ/tonne)	Climate Change Impact (tonne CO_{2e}/tonne)
Forestry	2	0.1
Pulping	25	0.3
Paper-making	15	1.0
Printing	2	0.1
Landfill	1	4.7
Total	44	6.3
of which transport	$\ll$1	$\ll$0.1

Based on data from Paper Task Force [20], EIPPCB [21], USEPA [22], Ahmadi *et al.* [23]

is likely to vary across products, across production sites and across time.

Translating the energy demand into emissions of climate change gases depends on the mix of fuel used, and on any non energy related greenhouse gas emissions. A likely set of emissions has been drawn from existing literature and is shown in table 2.1. This assumes energy generated from tree waste is carbon neutral. The largest greenhouse gas emission from the paper life cycle occurs during landfill. A recent survey by NCASI [24] suggests that greenhouse gas emission during paper decomposition in landfill is not entirely understood. A study by USEPA [22] suggests that office paper may release up to 398 ml of methane per dry gram of paper placed in landfill. The IPCC [25] estimate that methane is 23 times more potent in global warming potential than carbon dioxide over 100 years. This implies that landfill may contribute three quarters of the total climate change emissions of the typical paper life-cycle. The lowest value seen, from the Paper Task Force [26], allocates half of the total climate change impact to the landfill stage, but does not incorporate the lower lignin content (lignin tends to decompose to methane less readily) of most office papers.

2.2 Life cycle stages that could be cut out

There are fewer differences between waste and fresh sheets of office paper than there are between carbon dioxide, water and fresh sheets. Therefore, there may be opportunities to cut out stages in the life cycle of office paper. A range of options for doing this have been proposed. The ones considered in this chapter are illustrated

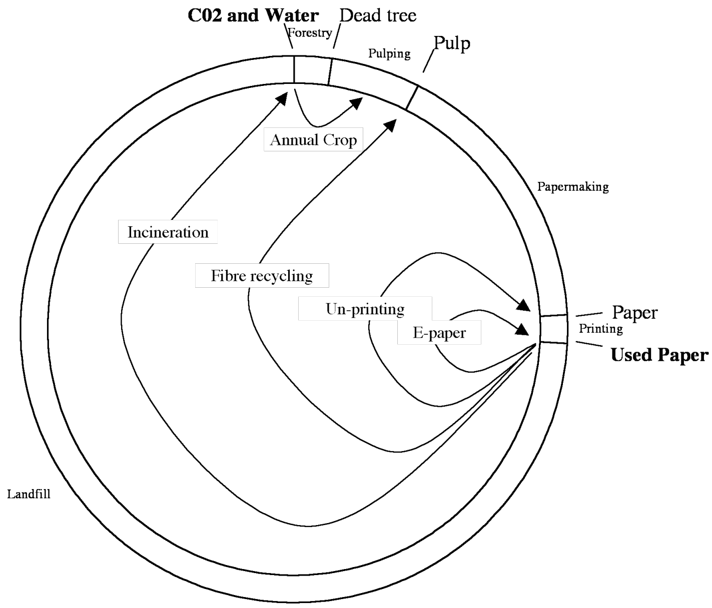


Figure 2.2 The options for eliminating stages in the life cycle that are considered in this chapter. (Localisation option not shown)

in figure 2.2. They will be discussed in order of the number of stages that they eliminate.

Incineration cuts out the landfill stage and transforms waste paper directly into carbon dioxide, without passing through methane. In some Western European countries up to 60% of municipal waste may be incinerated, much of it paper[27]. Incineration involves a change to the way that waste is transported. The heat generated by the incineration may be captured and used.

Localisation cuts transport by locating pulping and paper-making factories close to the point of paper consumption. The lack of forests close to urban centres means that localisation can rarely occur on its own, and is usually combined with a shift to a different fibre source[28], or to recycling[29]. It should be noted that localisation does not necessarily mean smaller scale as, for instance, New York consumes as much paper as Canada[30].

A shift to annual fibre cuts the need for forestry and replaces it with the unwanted bits of annual crops such as wheat, or made from crops grown specifically for paper-making such as Kenaf. Because these annual crops tend to contain less lignin, the scale of the pulping stage can be reduced. Transport may also be cut because annual crops tend to be grown over wider areas than forest. Annual fibres are used extensively for paper production in several countries, notably China. The pulping process may need adjustment, and new cleaning stages may need to be added to remove unwanted minerals from the crop.

Recycling cuts landfill, forestry and pulping by reusing the fibres from waste paper in the paper-making process. 54% of all European paper fibre is recycled[7], although only 7% of cut-size office paper is made from recycled fibre[3]. In order to reuse the fibres in office paper new collection, sorting and deinking stages may need to be added.

Reusing office paper would cut out all the stages except printing. This would require the effects of use to be un-done and print to be un-printed. One commercial un-printing system, the Toshiba 'e-blue', is on the market[31]. E-blue uses an altered toner formulation that becomes colourless when heated to 180°C for three hours.

Electronic-paper cuts out all the stages in the typical paper cycle and instead replaces many sheets of paper with a single electronic display. The displays of office computers and laptops have already replaced some use of office paper, particularly that used for archiving and communication purposes[5]. More paper-like displays have recently come to market e.g.[32].

2.3 Impact on energy consumption

Table 2.2 shows estimates of the potential impact on energy consumption of the options discussed in the previous section. This section discusses how these estimates were made.

Incineration does not eliminate any energy consumption from the life cycle. The heat energy from incineration may be used to do productive work or generate electricity. This is discussed in section §2.5.

Localisation does not have a significant effect on the energy consumed in the paper life cycle. Roberts & Johnstone[33] suggest that transport in the paper cycle typically uses 22 MJ per tonne of paper. This is less than one percent of the overall energy consumption. Localisation might significantly reduce the number of tonne kilometres of transport but the reduction in energy may be limited because long distance journeys are carried out by ship or other low energy mechanism.

Table 2.2 Potential reductions in energy consumed per tonne of office paper (Primary GJ/tonne)

	Energy saved from cut out stages	Energy added in replacement for cut out stages	Net energy saved	% saved
Incineration	≈0	≈0	≈0	0%
Localisation	≈0	≈0	≈0	0%
Annual Crop	25	15	10	22%
Recycling	27	5	22	49%
Reuse	42	5	37	86%
Electronic-paper	44	21	23	52%

Annual crops have a lower lignin content and therefore require less pulping. Data from the Paper Task Force [34] and Riddlestone [28] imply that the process energy used might be reduced by 10 GJ/tonne and this figure is used in table 2.2. The Paper Task Force [34] suggests that a greater volume of fertilisers may be required for annual crops compared with forests, which would reduce the net energy benefit.

Recycling fibre cuts out pulping, reducing energy demand by 27 GJ per tonne of paper. However the additional deinking process requires 5 GJ to remove the ink. Table 2.2 therefore shows a net saving in energy of up to 22 GJ per tonne. However, if the de-inked pulp is to be transported, 15 GJ of energy may be required to dry a tonne of pulp in preparation for transport (estimates based on data from EIPPCB [21]).

Reuse cuts out all the stages except printing, eliminating 42 GJ per tonne. This would be offset by the energy required to unprint. Tanaka *et al.* [35], who work for Toshiba, have carried out a life cycle assessment for their 'e-blue' system. They estimate c. 2 GJ of electricity is needed to de-colour a tonne of office paper. This would be equivalent to about 5 GJ of primary energy, so the net saving in energy may be 37 GJ per tonne.

Replacing paper with an electronic equivalent cuts out all the stages in the paper cycle, eliminating 47 GJ per tonne of office paper replaced. However, energy is required in the manufacture and use of e-paper. Quantifying this is difficult because electronic replacements are not well developed. One approach to making an estimate is to consider existing LCD technology. Socolof *et al.*[36] estimate that a 15 inch LCD display takes c. 2000 MJ to manufacture, c. 130 MJ a year to run and lasts 6.5 years. Determining how many sheets of office paper an e-paper would replace over 6.5 years is also difficult. Table 2.2 assumes that the screen replaces c. 20 kg of paper a year (estimate based on the average annual Western European consumption of cut-size paper per office worker from Cresswell[3]) In this case to 21 GJ of primary energy would be need to create and power enough electronic paper to replace a tonne of paper. A lower estimate might be produced by considering the recently released 'e-ink' display. Whereas LCD displays draw power continuously to display an image, this display only draws significant power when updating the page view. Based on the public specifications for this product[37] it would require 0.85 MJ of low voltage electricity to display the equivalent area of a tonne of A4 80gm paper. The primary energy efficiency of batteries ranges between 2.5% and 4.5%[38] implying a primary energy requirement of c. 20 MJ to be equivalent to a tonne of paper. There is no data on the energy required to make the product, so we cannot make a complete assessment of its energy consumption. If we assume it takes the same manufacturing energy as a current LCD display, then the device would consume 15 GJ of energy to present the same amount of text as that conveyed on a tonne of paper.

2.4 Impact on climate change gases

Estimates of the potential impact of each strategy on climate change gas emissions are discussed in this section and shown in table 2.3. The energy reductions from section §2.3 are converted into climate change gas reductions by incorporating the mix of fuel used to create the energy and non-fuel climate change gas emissions.

The main non-fuel climate change gas emission occurs in landfill. All the alternatives discussed above, except annual fibre and localisation, cut out this stage and with it 4.7 tonnes CO_{2e} per tonne of paper – about three quarters of the total climate change impact.

The pulping stage of the conventional paper life cycle is fuelled by waste wood which, if trees are replanted, is assumed to be neutral in climate change emissions. If the forestry and pulping are cut out and replaced by a deinking process as part of a conventional recycling process then a different fuel mix tends to be used,

Table 2.3 Potential reductions in climate change gases emitted per tonne of office paper (CO_{2e} tonne/tonne)

	CO_{2e} saved from cut out stages	CO_{2e} added in replacement for cut out stages	Net CO_{2e} saved	% saved
Incineration	4.7	≈0	4.7	74%
Localisation	0.1	0	0.1	1%
Annual Crop	0.3	0.1	0.2	3%
Recycling	5.1	0.3	4.8	76%
Reuse	6.2	0.2	6.0	95%
Electronic-paper	6.3	1.0	5.3	85%

usually including less renewable energy. This leads to a higher emission factor of perhaps 70 kg CO_{2e} per GJ of primary energy and means that deinking tends to add as much carbon dioxide as the pulping stage that it replaces.

Annual crops reduce the consumption of heat energy in pulping, but this is primarily provided from carbon-neutral fuels. Riddlestone [28] describes a straw based pulping process that uses half the electricity of conventional pulping, which could translate into a reduction in carbon dioxide emissions of 0.2 tonnes per tonne of paper. This figure is used in table 2.3. However, for Kenaf pulping, the Paper Task Force [34] analysis suggests that the lower lignin content of Kenaf means less waste is available for energy conversion, and therefore other fuel may be required, potentially leading to higher carbon emissions.

The reuse and e-paper alternatives both assume grid electricity is used as the energy source. The carbon emissions emitted to generate the power vary widely across time and country, ranging from almost zero in Iceland (where hydroelectric generation dominates) to c. 87 kg CO_{2e} / GJ of primary energy in Greece[39]. The calculations in table 2.3 use the standard emissions factor for the UK: 46 kg CO_{2e} / GJ[40].

2.5 Evaluation and Uncertainties

Table 2.4 compares the potential climate change gas reduction of each option. Reuse could make the largest reduction in climate change emissions, followed by e-paper, recycling and incineration. Switching to annual crops and localisation would appear to promise little reduction in climate change emissions. There are uncertainties in these results based on variation in: the ability of the options to effectively replace paper; what energy recovery is included; the fuel mix used; the level of methane emissions from landfill. These are discussed below.

The estimates in sections §2.3 and §2.4 assumed that the replacement for the cut out stages was perfect. For incineration, localisation and annual fibres this may be broadly true: they could completely replace the existing landfill, forestry and pulping stages. For fibre recycling, reuse and e-paper this is less certain. In both reuse and recycling a proportion of the old paper will become waste and a proportion of new paper must be added in order to obtain a tonne of useful paper from the process.

The fibre recycling option does not work well with short or damaged fibres; 40% of the waste paper mass that enters an office paper recycling process is rejected to landfill or incineration [21]. Smook [41] suggests that the process of paper-making damages paper fibres, so that they cannot be recycled more than five times. Together these imply that the fibre recycling process can only replace between 40% and 60% of paper. Similarly, to reuse paper using current un-printing technology waste sheets of paper must not be torn, crumpled, or printed with an incompatible ink. Furthermore, with the 'e-blue' system the build up of print may cause problems for further printing and use. Tanaka *et al.* [35] imply that their system can only reuse sheets five times. Electronic-paper is unlikely to replace all the uses of cut-size office paper in its current form.

The effect of these limitations is modelled in column two of table 2.4. This assumes that fibre recycling, un-printing and e-paper can only contribute half of the required paper demand, and therefore half of the paper is manufactured with the typical process. This causes incineration to become the most favourable option with a c. 74% reduction in climate change gases. The other options have reduced emissions savings of c. 45% for reuse, c. 35% for e-paper and c. 26% for recycling.

The estimates in the previous section excluded the potential for some stages of the paper life cycle to be used to generate power. This could occur by generating heat or electricity from landfill methane, from incineration, or from forest that is not being used under the recycling, reuse and e-paper alternatives. USEPA [22] suggest that 1000 BTU of energy is available from a cubic foot of methane. Bystrom & Lonnstedt [42] estimated 9 GJ of heat energy would be available from incinerating a tonne of office paper. A tonne of cut-size paper requires about two tonnes of wood to be cut down. If the wood was used directly as a fuel it could provide about 30 GJ of heat energy. Column three in table 2.4 therefore assumes that energy from incineration and wood burning is used to offset climate change emissions from grid electricity at the UK rate of 46 kg CO_{2e} per GJ. This does not alter the rank of the options, but if the trees saved by the reuse of paper or by e-paper were used to generate electricity, they might generate all the energy used in un-printing or electronic-paper.

In countries with high use of renewable or nuclear power the climate change gas emissions from grid electricity may be close to zero. This could make methane from landfill the only significant emission in the typical paper cycle. The amount of energy saved might then become the most important factor in choosing between the options. In countries with a high use of coal to supply grid electricity the climate change gas emissions from un-printing and electronic-paper would tend to be higher. Column four in table 2.4 assumes a higher emissions factor of 90 kg CO_2 per GJ of primary energy for e-paper and un-printing. Under these circumstances reuse would remain the preferable option. E-paper would be less attractive than recycling or incineration.

Landfill is the stage with the largest climate change impact in the typical paper cycle. This impact could be lower if, for instance, the landfill site chemistry favoured sequestering the carbon in the soil or turning it directly into carbon dioxide. Column five in table 2.4 assumes that landfill gas emissions are at the level predicted by the Paper Task Force [26] of 1.5 tonnes CO_{2e} per tonne of paper. This is a third of the level estimated in section §2.1. Reuse remains the most promising option under these circumstances.

2.6 Discussion

Cutting out stages in the life-cycle of cut-size office paper could reduce climate change gas emissions per tonne between 1% and 95%, depending on the steps that are avoided. Cutting out transport, by localising production, or cutting out forestry and some pulping by using annual fibres would have little effect on climate change gas emissions as those stages in the life of office paper emit little net CO_{2e}. Cutting out landfill, by incinerating, could reduce climate change gas emissions from the typical office paper life cycle by 48%–74% because landfill is the stage with the largest climate change gas emissions. Going further and cutting out pulping as well as landfill, by conventional fibre recycling, provides little extra reduction in climate change gas emissions because most of the energy in pulping is obtained from carbon-neutral fuels. Cutting out paper-making as well as landfill, forestry and pulping, by un-printing and then reusing sheets of paper, would reduce climate change gas emissions by 95% because paper-making is energy intensive and tends not to use carbon neutral fuels to the same extent as pulping. Cutting out paper altogether and replacing it with an electronic equivalent, could reduce climate change gas emissions by 85%.

The motivation of this chapter was to explore approaches to cutting absolute climate change gas emissions from cut-size office paper by 60% by 2050. Hekkert *et al.*[15] predicted that demand for such paper would grows by 5% a year to 2015. If we assume demand continues to grow at the same rate until 2050, then a 97% reduction in climate change gas emissions per tonne of paper use will be needed to achieve a 60% absolute cut. To deliver this, we will need to pursue all options in combination: reducing consumption, carbon-neutral fuels, improving the energy efficiency of each life-cycle stage and cutting out life-cycle stages.

The potential of reuse and of electronic-paper is uncertain. The proportion of office-paper use that they replace, and the environmental impacts they introduce are not well understood. To tackle this uncertainty about electronic paper we need to carry out fuller life cycle assessments of the new generations of electronic-paper and understand the interplay between electronic-paper's life-span, its functionality, and whether it cuts out other office products such as printers. To tackle this uncertainty about reuse we need to understand what prevents it, and whether these blocks can be overcome.

The next chapter reviews the state of research into un-printing, the first step towards office paper reuse.

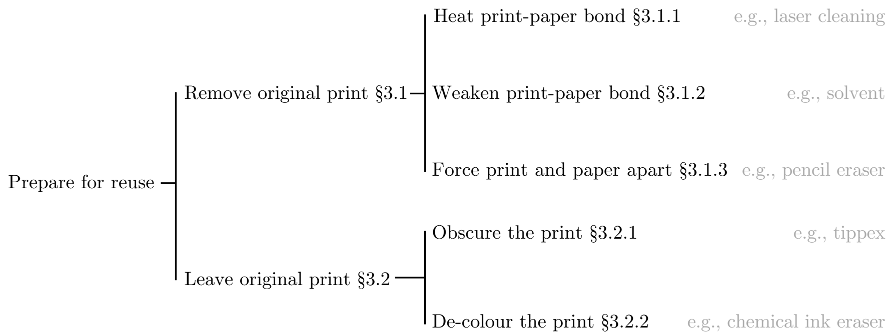
Table 2.4 Potential reduction in climate change gases for each option under the main scenario and with varying assumptions

		Rank under varying assumptions							
Rank under the standard set of assumptions described in sections 2,4 & 5		Rank when reuse, e-paper and recycling assumed to replace only 50% of paper		Rank when energy is assumed to be generated from incineration and un-used forest		Rank when electricity is assumed to have high CO_2 emissions		Rank when methane from landfill is assumed to be lower	
Reuse	95%	Incineration	74%	Reuse	117%	Reuse	92%	Reuse	90%
E-paper	85%	Reuse	45%	E-paper	106%	Recycling	76%	E-paper	69%
Recycling	76%	E-paper	35%	Recycling	98%	Incineration	74%	Recycling	53%
Incineration	74%	Recycling	26%	Incineration	81%	E-paper	70%	Incineration	48%
Annual Crop	3%	Annual Crop	3%	Annual Crop	3%	Annual Crop	3%	Annual Crop	6%
Localisation	1%	Localisation	1%	Localisation	1%	Localisation	1%	Localisation	2%

Percentage refers to the potential reduction in climate change gas emissions compared to the typical cut-size office paper life cycle. Percentages of more than 100% are the result of including the potential reduction in emissions from using some of the stages in the paper life cycle to generate energy for other industries.

3 Review of un-printing

Does the technology exist to un-print? Not completely. This chapter reviews and classifies existing technology according to its mechanism, as illustrated in this figure:

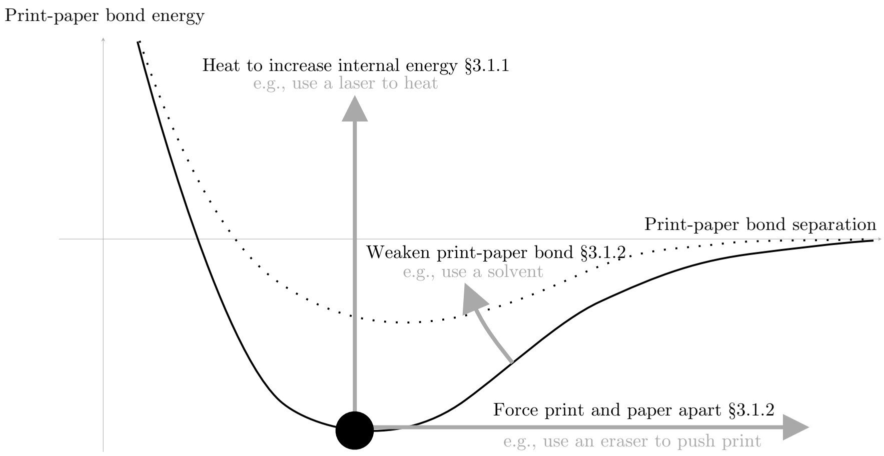


This is the first review of un-printing. An earlier iteration has been published[43] in a peer-reviewed journal. The principal sources for this chapter were patent applications that were filed between 1941 and 2005 and that were listed in the European Patent Agency database. Many of these patents have been published only in Japanese. Therefore a limitation of this review is that the author has relied upon translations for these patents and may have misrepresented or missed a body of research. Furthermore, most patents do not provide performance data or document their processes in a way that can be completely replicated.

This chapter has three sections. The first two follow the structure in the diagram above: section §3.1 reviews techniques that remove the original print, section §3.2 reviews those that leave the original print. Section §3.3 outlines five questions that may warrant further research and the final section sets out the quesions which will be answered in the remainder of this thesis.

3.1 Remove the original print

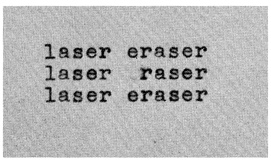
Approaches that remove print make up the largest category of published patents. They can be classified according to whether the bond between print and paper is: weakened; overcome by increased internal energy through heating; or overcome by external work done. This is illustrated in the diagram below based on the classic potential energy curve between two molecules.



The first group of approaches discussed in this section use heat alone, the second use solvents alone, the third force alone and the final group mix different approaches. Within each group, the strategies are organised according to the types of print that they can remove.

3.1.1 Heat the print-paper bond

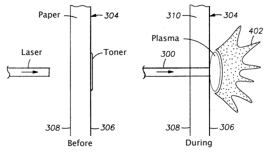
The bond between print and paper can be overcome by increasing the internal energy of the print, of the paper or of both the print and paper. The increase in energy can be created by heating with radiation, conduction or convection.



Performance data from Schawlow [44]. Image © Science.

Ink. The earliest report of using ablation to remove print is a brief mention in a 1965 review article by Schawlow [44]: 'A flash of laser light can vaporize carbon ink pigment from the surface of paper without noticeably affecting the underlying paper (page 19)'. The article did not specify the type of laser used, nor the type of print that was vapourized, but did provide a single image (left) that implies that the technique has the potential to completely remove a single letter of print.

Toner. Two patents have been filed that use the principle of focusing laser radiation onto toner print in order reuse the sheet of paper. The first was filed in 1992 by Niikura *et al.*[45] It proposed scanning a ND:YAG laser across the top of a toner-printed surface, dwelling where it was blackest, causing the toner print to vaporise. This patent does not provide any performance data. A variation, reported by Tankovich[46], is to fire a laser through the paper to strike the underside of the toner. This, he suggests, causes a plasma to be formed between the toner print and paper. The plasma expands rapidly, mechanically ejecting the remainder of the toner print from the paper surface. They specify the laser and settings that they used and report that it takes about 15 seconds to clean an A4 sheet. He does not specify how well his approach works, but hints that 'for enhanced document cleaning' the sheet may need to be placed in a hydrogen peroxide (bleach) bath after laser processing.



Tankovich[46] remove toner by firing a laser through a sheet of paper, hitting the underside of the print.

Modified ink. One patent has proposed using convective heating of the print and paper and one has proposed conductive heating. Both require a modified ink to be used. The earlier 1980 patent[47] proposes a modified ballpoint pen ink that uses an anthraquinone as its source of colour. This sublimes when blown with air heated to 450 K. No data on its performance is provided. The later 1994 patent[48] proposes an integrated printing and un-printing system. This system uses a print that sublimes at low temperatures. The print sublimes when the paper surface is heated by contact with hot rollers and the gas is collected. The gas is then condensed and reused in the printing mechanism. No performance data is provided.

3.1.2 Weaken bond

In theory the print-paper bond can be weakened by a chemical reaction that changes the structure of the print or paper, or by a change in the medium between the print and paper. In both cases, the focus is on reducing the cohesion of the print, the strength of the bonds between the print and paper, or the cohesion of the surface of the paper. Of these possibilities, only changing the medium to a solvent to reduce print cohesion have been documented*. These documented approaches are considered below, divided according to the type of print they remove.

Ink. Two fields study how solvents can be used on to remove ink: conservators and frauds. Banks [49], a paper conservator, briefly mentions using solvents to remove print marks, although not ink-jet print, and his main focus is on removing stains, lacquers and dirt. For instance, he recommends dimethyl formamide for the removal of ball-point pen. Unfortunately he does not provide any performance data, but he does emphasise the importance of laying an absorbent material on the surface of the paper when applying the solvent, so that the stain is drawn out rather than redistributed across the sheet. Frauds have also used solvents to remove inks. Patents on cheque security technologies, such as by Laxer [50], suggest that many cartridge pen inks can be removed by careful application of water and many ball-point pen prints by certain alcohols and ketones.

Toner. There are three patents[51–53] that suggest using solvents to reduce the cohesion of toner-print† so that it separates from paper. The process described in the two earlier patents[51;52] involves placing the paper in a bath containing a solvent and a surfactant, agitatating the bath with ultrasound and then removing the paper, before heating and pressing it to remove the solvent. In addition, the later patent[53] uses mechanisms, such as suction jets and electrostatic plates to try to ensure that the pigment in the toner does not re-deposit on the paper when the toner-print resin loses its cohesion. This later patent[53] uses chloroform as its solvent. It is difficult to discern the solvents used in the earlier patents. The earliest patent, by Orita & Chikui [51], uses an 'extender agent' which is 'implanted on the paper surface to bleach the paper'. It is not clear what chemicals were actually used. Higuchi & Takahashi [52] report a little detail on the relationship between time, temperature and the rate of toner removal. More substantial performance data is available for the patents that mix solvents and abrasion. This is discussed later in this review in section §3.1.4.

* It could be argued that the conventional fibre recycling process uses water as a solvent to reduce the cohesion of paper and hence dislodge the print particles.

† The middle patent, by Higuchi & Takahashi [52], claims that their approach could be used on other print types but does not provide any examples.

Modified ink or paper. Other patents modify the ink to make it less resistant to a solvent, or the paper to make it more resistant to a solvent. Asahina *et al.* [54] propose altering the toner resin to be biodegradable and therefore using enzymes to remove it. A patent filed by Takama & Yoshie [55] uses solvents to remove toner-print from sheets of overhead transparency. Other patents [56–61] propose treatments or replacements for paper to make it resistant to a particular solvent. The solvent is then used to remove the print. In these patents the solvent is often water.

3.1.3 Force apart

In theory, print can be separated from paper by either an externally applied force or an internally generated stress. The force can be applied in tension, compression or shear across the print-paper bond. An external force could be created by direct pressure, or by an electric, magnetic or electromagnetic field. An internally generated stress can be created by expanding or contracting the print, the paper or both. The expansion or contraction can be activated by a change in temperature, by a chemical reaction, by a piezoelectric effect, or by the diffusion of another material into or out of the print or paper.

The majority of the techniques that have been documented use an external force created by direct pressure. They vary in the type of print that they abrade, the extent to which the force is abrasive or adhesive and, in the case of patents on toner-print removal, the use of a second, internally generated, stress.

Pencil and ink. The pencil-eraser is the commonest embodiment of abrasive print removal. Pencil-erasers tend to be classified according to their hardness. The earliest ‘non-abrasive’ erasers were made from bread[49]. Today they tend to be made of vinyl or of natural or synthetic rubbers and can abrade pencil marks without visible abrasion of the underlying paper. Pigment and dye inks tend to penetrate further into the paper, requiring ‘abrasive’ erasers embedded with a fine grit (often pumice[62]) that removes the top layers of the paper together with the print . Some pigment and dye inks have been designed to be ‘erasable’ by remaining in the top layers of paper rather than penetrating deeply. Erasers that are softer than the underlying paper (known as ‘putty erasers’) are used to remove soft pencil marks, charcoal, chalks and other soft artistic prints from paper without damaging the surface. The

20th Century reuse: The 1980 IBM Correcting Selectric III, with built in correction system that could lift its own print back off of the page. Image © Martin [65]

typical composition of putty erasers is not known, but it has been reported[63] that professional cartoonists and artists use blu-tack to remove graphite pencil marks through a purely adhesive action.

Typewritten print. In 1916 Baldwin[64] patented a mechanism for using adhesive tape to correct typewritten mistakes: 'narrow strips of the well known surgeon's plaster being preferably employed (page 1, line 76)' to strike against the paper around the print to be erased and then lift-off a layer of paper fibres together with the print. Later embodiments, such as the 1973 IBM Correcting Selectric II typewriter, sought to leave the paper intact and just remove the print. The Selectric system used a 'correctable' print that did not penetrate into the paper surface and a 'lift-off' correcting ribbon that, at the touch of a key, would be pressed against recently printed characters, stick to them and lift them back off of the page, allowing the text to be re-typed[66]. The mechanism for accurately positioning the removing tape over the unwanted print was disclosed in a 1973 patent[67] but the formulation of the print and adhesive were kept secret. The approach continued to be developed until the 1990s, with the emphasis on creating adhesive formulations that preferentially bond to print over paper[68–71].

Toner print. Approaches to removing toner-print vary according to whether they use abrasion or adhesion and whether they introduce a second internally generated stress to weaken the print-paper bond before removal.

Mitsuhashi[72] proposes a purely abrasive approach to removing toner print: He heats the print and paper and then uses a diamond abrasive wheel to grind off the top 10 µm of the paper and with it the print. He does not discuss the effect of that level of removal on the quantity of print remaining, or on the ability of the paper to be re-printed. Yamazaki[73] proposes a less abrasive approach to removing toner print. He heats the printed paper and then rubs the surface with a counter-rotating felt roller. His patent filing provides little extra detail, and no performance data. Obata & Tanaka[74] use adhesion rather than abrasion to remove toner print. They heat the paper, then press it against a tacky belt that moves at the same speed as the paper and sticks to the toner print. The belt then moves away from the paper, pulling the toner print away from the paper surface. This is perhaps the closest equivalent to the 'lift-off' correction system on the IBM typewriters discussed on page 30.

A common extension, seen only in approaches that apply to toner-print, is to generate a shear force between print and paper by causing the paper fibres to swell. A patent filed by Sugawara [75] and ten very similar patents (mostly filed by Ricoh) listed in appendix table in appendix table B.1 describe a technique that causes the paper fibres to swell by placing the printed paper in a bath of water and surfactant. This weakens, but does not overcome, the toner-paper bond. The patents then all use some form of tacky surface to lift the print from the paper in a similar fashion to Obata & Tanaka [74]. The patents vary in the choice of surfactant and in the material, shape and configuration of the adhesive component. None of the patents provide performance data.

A short paragraph published in the Financial Times in 1993[76] and a slightly longer article published in the New Scientist in 1994[77] report that Ricoh had a prototype 'recycle copier' that could remove conventional black toner print from office paper at a rate of 3 A4 pages per minute. Based on patent filings of the time, it is likely that this used swelling and adhesion as described in the previous paragraph. At the time they were considering building the technology into their photocopiers but were 'still evaluating the market'. No further reports on this technology have been found.

Modified print. Tsuneo *et al.* [78] propose using a toner print that bonds less strongly to paper, making it easier to force apart. Similarly Kuramoto *et al.* [79] propose using a more viscous toner, so that it does not penetrate into the paper and is therefore easier to remove.

Modified paper. Tsukamoto *et al.* [80] use an erasable paper, to which toner-print bonds less forcefully, and a complementary abrasive eraser[81] to rub the print off. Thirty patents (listed in table B.9) change the paper so that the bond between print and paper can be weakened on demand. The majority of these add a coating to the paper that swells when immersed in water. This swelling reduces the bond between the toner and the paper making separation easier.

3.1.4 Mixed approaches to removal.

All of the approaches listed above could be mixed. Some of the patents detailed above mention that their performance could be improved by the additional use of heat, solvents or abrasion, but the only group that appear to rely on two mechanisms are those that weaken the print-paper bond with a solvent and then force the print and paper apart. Below, historic examples of using this mechanism are discussed first, then more recent patents and finally the experiences of a start-up that developed and marketed a prototype that used this approach to remove toner-print.

Palimpsests. Ancient writing materials that were reused are known known as palimpsests, a word whose etymology is the ancient Greek for 'again rub smooth'[82]. They writing materials were papyrus or parchment and they were prepared for reuse by a combination of washing and scraping to remove the original ink.

Papyrus was used as a writing material in Egypt and parts of Europe from the 6th century BC until at least the 6th century AD[83]. It was formed by hammering flat a mesh of strips of the pith of papyrus plants, and then rubbing the surface smooth[83]. It was usually marked with a carbon-gum based ink[84]. In some cases this print could be removed by gentle sponging with water and the papyrus reused[85]. A later, more complex, process was described in a 3rd century AD text, the 'Papyrus Grecus Holmiensis':

> By the following procedure one likewise makes papyrus sheets, which are written upon, clean again so that they appear as though they never had been written upon. Take and dissolve natron in water. Then put in, when the soda solution has formed, one part of raw earth, one part of Cimolian earth, and cow's milk in addition so that all of it comes to a glutinous mixture. Then mix in oil of mastic and daub it on with a feather. Let it dry and then scale it off and you will find the pearls [papyrus] white.[‡]"

Parchment was widely used during the middle ages as a writing material. It was formed by a complex process of scraping, then simultaneously stretching and drying animal skin[87]. Due to the high cost of manufacture it was frequently reused: "They can be considered wax, even though they are called parchment: you can destroy the text every time you wish to renew them[††]". Initially

‡ English translation of the original Greek by Caley [86].

†† Translated from a 1st century BC Latin quote "Esse putas ceras, licet haec membrana vocetur: delebis quoties scripta novare voles." reported by the European community 'Rinascimento Virtuale [88]' project that is cataloguing Greek palimpsests.

parchment was written upon with the same carbon-gum ink as papyrus, allowing it to be easily sponged off[85]. Later metallic inks required a more complex removal processes. Reed [87] relates that the print could be weakened by rubbing with an acid, and provides four medieval recipes for the acids. A slightly more involved process is described in a Latin quote reported by the Rinascimento Virtuale [88] project:

Medieval reuse: parchment cleaning. Image © Fotoscientifica di Parma [89]

> Anytime a writer wishes to write on parchment a second time, soak the parchment in milk for a night. Then, when removed, sprinkle with coarse bread and, to avoid wrinkles when you lift it out, press until dry. When that is done, polish with Cretian pumice stone to restore the previous white brilliance‡‡.

A modern equivalent of the palimpsests was proposed in two patents by Hibi *et al.* [90;91]. They proposed that paper be replaced with a polyester sheet. This can be soaked in water and rubbed to remove the original print.

Toner print There is evidence of using solvents and abrasion in combination to remove toner-print from standard office paper in four patents by Minolta[92–95] and two by DeCopier Technolgies[96;97]. DeCopier technologies developed and publicised prototype products based on this principle.

The processes described in the patents all swell, rather than completely dissolve, the toner print. This, they claim, weakens the bond between print and paper, and allows the print to be rubbed off by a rotating brush or web. The patents all recommend a mixture of water (to swell the paper fibres, weakening the bond), a solvent or acid (to swell the toner print, weakening the bond) and a surfactant (to retain the print when it has been separated). They differ only in the choice of chemicals.

The earliest Minolta patent, awarded in 1996 to Yamamoto *et al.* [92], lists a large number of chemicals that might be used to swell toner "includ[ing] dihydric organic monoesters, glycol ether and the like" and a standard set of laboratory solvents. The next

‡‡ An 11th century Medieval Latin quote "Quicunque in semel scripto pergameno necessitate cogente iterato scribere velit, accipiat lac imponatque pergamenum per unius noctis spacium. Quod postquam inde sustulerit, farre aspersum, ne ubi siccari incipit in rugas contrahatur, sub pressura castiget quoad exsiccetur. Quod ubi fecerit, pumice cretaque expolitum priorem albedinis suae nitorem recipiet." again reported by the Rinascimento Virtuale [88] project.

Table 3.1 Performance of solvents, as reported by Machida *et al.* [93]

Solvent	Surfactant	Cleaning efficiency
Toner made from a styrene-acryl copolymer:		
50% Toluene	1% $C_{18}H_{29}NaO_3S$	83.5%
60% Toluene	2% Eleminol ES-20	82.0%
30% Xylene	1% Eleminol JS-2	80.4%
10% Dichloromethane	2% Pelex NB-L	79.3%
100% Xylene	-	13.4%
50% Toluene	-	6.2%
Toner made from polyester resin:		
40% Dichloromethane	2% Pelex NB-L	81.7%

Percentage by volume, with balance made up of water.

Minolta patent, awarded to Machida *et al.* [93], is unusual in that it reports limited performance data on using five different solvents on two different toner formulations (reproduced in table 3.1). They measure 'cleaning efficiency' which is the percentage increase in the amount of light reflected from the sheet before and after unprinting. It is not clear how their highest reported cleaning efficiency of 84% translates into real-world usefulness, but they claim that an efficiency of above 70% results in usable paper. The key implication from their data is that the use of a surfactant is critical. That patent is not specific about how the 'rubbing' of the printed paper is carried out but two subsequent Minolta patents[94;95] provide some detail on a possible embodiments such as using rotating nylon brushes.

A US start-up initially called ImageX Technologies and later DeCopier Technologies was founded in 1996[98] and appears to have ceased trading towards the end of 2001. During this period it promoted a system that it claimed could completely remove toner print from sheets of office paper or from sheets of overhead transparency.

The DeCopier Technologies approach, is fairly well specified in two patent filings[96;97]. The earlier patent[96] filed in 1999 states that the waste paper is heated to 330K and then sprayed with a deinking solution. The solution is left for three or four seconds, to allow the toner print to swell. The paper is then passed under two low density polypropylene bristled rollers that scrape away the swollen toner. The paper is then air dried at 340 K before passing under a set of compression rollers that heat and press the paper to remove any remaining deinking solution. The deinking solution is collected and may be re-circulated, although it is not cleaned to remove any dissolved resin.

A range of deinking solutions are proposed, but the preferred embodiment has four or five components: water; an aliphactic solvent such as diethylene glycol n-butyl ether; an aromatic solvent such as ethyl-4-methoxybenzoate; a surfactant such as Triton X-305 (a product of Buckman Laboratories) and potentially a proprietary enzyme. The second patent published a year later[97] proposes approximately the same process and chemicals, but exchanges sodium stearate (common soap) for the Triton surfactant, and suggests that either the aliphatic or the aromatic solvent can be used alone as well as together.

A deinking solution	
Water	75-87%
Aliphactic solv.	15-20%
Aromatic solv.	3-5%
Surfactant	1-3%
Enzyme	1-3%

Source: Bhatia *et al.* [96]

The earlier patent claims[96] that 100% of the toner is removed by the process and that the cost of this removal is 0.3 cents per sheet. The removal claim was investigated by two FBI agents, Frost & Dwyer [99], who appeared concerned about the potential to use the device to commit fraud. To test the potential for complete removal of print they printed sample paper and overhead transparency with a range of combinations of toner, ink-jet, type-writer, pen and pencil print. The DeCopier prototype was not working at the time of their test, so they asked a DeCopier employee to manually apply the deinking solution, brush and heat and dry the samples. The employee was permitted to vary the proportions of the chemicals in the deinking solution and the time and pressure of the brushing according to optimise the process for each sample. The results might therefore be expected to be better than might be achieved by an automated machine. A qualitative evaluation of the state of the paper was then conducted, principally using an optical microscope. The level of paper damage and quantity of readable text was qualitatively tabulated. The authors found no readable text on the toner-printed overhead transparency nor on five other samples out of thirty-nine. The only samples where there were no traces of toner print visible when examined by microscope were those printed on transparency. In all cases of printing on standard paper a change in texture of the paper was visible after de-copying. The agents therefore suggested that the patent claim to remove 100% of toner was not true, that success was limited to a few formulations of toner-print, and that the process worked best on transparency. They no longer seemed worried about the potential to use the device to commit fraud.

The reason for DeCopier Technologies failure is not well documented. A case study of the company written by Friar & Kinnunen [98] for management students in 2001 reported that the firm needed an investment of $2.25 million to commercialise their prototype. A 2001 newspaper article[100] briefly reports that the company did not launch because the technology was still too expensive (perhaps $45000 a unit according to Friar & Kinnunen [98]). The firm appears to have marketed their product as a more secure way of erasing documents than paper shredders rather than for its environmental benefit[101].

3.2 Leave the original print

An alternative to removing the original print is to leave it in place and instead prevent it from interfering with a subsequent re-print. In theory, this could be done by obscuring or by de-colouring the original print.

3.2.1 Obscure the original print

An obscuring process could take place before or after re-printing. If it took place before, it could be applied to the entire sheet or just to the printed areas. If it took place after, then it would need to be restricted to the areas that need to be white in the new text. In addition to the approaches that obscure print in order to correct minor mistakes, two patents have been filed on obscuring existing print to allow whole sheets of paper to be reused.

In the UK and Germany, 'Tipp-Ex' is almost synonymous with obscuring print*. There are usually four major components to correction fluids like Tipp-Ex: a very opaque material (usually titanium dioxide[102]); a pigment to match the paper colour; a polymer to bond the opaque material and pigment to the paper surface; a solvent to keep the paint fluid until it is dispensed (e.g. naptha[103]). When dispensed onto the paper, the solvent evaporates leaving a thin layer of pigment.

The pigment can also be mixed with an adhesive and applied from a polymer backed tape[104] or a solid stick[102]. Again, this approach was used in the IBM Correcting Selectric II typewriter. It

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∗ 'White-out' is the equivalent US brand could be loaded with a 'cover-up' tape that could be used to obscure mis-typed text when the typewriter was using a conventional print ribbon[66] rather than the 'correctable' ribbon mentioned earlier in section §3.1.3.

The first patent on obscuring existing print to allow whole sheets of paper to be reused was filed during the second world war by Mayhew [105]. It proposes silk-screening the surfaces of used paper with a white paste. A much later patent, filed in 2001 by Boyce *et al.* [106], proposes that waste paper be scanned, and a white or coloured toner printed over the black areas to obscure existing print. Neither patent indicates what the white obscuring material would be. Nor do they indicate the ability of the approach to hide the print, to match the paper colour, or to act as a good base for further printing.

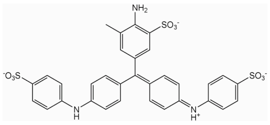
3.2.2 *De-colour the original print*

Print is readable due to the contrast between its colour and that of the underlying paper. De-colouring the print would remove one obstacle to re-printing. Approaches to de-colouring are grouped below according to the type of print that they de-colour.

Washable blue ink. For the dyes and pigments conventionally used in print, colour is created when electrons within the dye molecule absorb light at a visible wavelength. The parts of molecules which cause electrons to have energy levels which absorb visible light are known as chromophores. The colour of a molecule can therefore be changed by changing the energy levels of the outer electron orbitals of the chromophores. If it is changed to a colour outside of the visible range, it will appear colourless.

A correction product that makes use of this property is the 'ink corrector pen' (also known sometimes as 'ink eradicator') that can be used to wipe a chemical over some 'washable blue inks' and make the inks appear colourless. The area can then be re-written with a different ink that doesn't react with the chemical. This limits the process to one cycle of reuse and reprinting. Patent filings suggest the de-colouring pens were known in the 1940s[107] and reached their current form in the late 1970s[108;109] but today their use is largely confined to some schools.

From patent filings[110–112] it seems that the conventional mechanism used by the de-colouring pens is to change the acidity of the paper around the print. The triarylmethane dyes used in some



The molecular structure of acid blue 22, a common triarlymethane dye that can be de-coloured. Image public domain and © WikiMedia commons.

blue inks are naturally acidic (i.e. they tend to accept electrons). When they are neutralised in a base solution (often an amine) the electrons change structure, altering their energy levels so that they no longer absorb light in visible wavelengths, and so the dyes appear colourless. Other approaches mentioned in patents include using an oxidising agent to remove electrons and therefore 'bleach' a coloured molecule[113]. Patent filings suggest that more recent research has focused on developing new inks that can be de-coloured[113;114] and ink-eradicator combinations where the original ink can be used to write again over the eradicated ink without it immediately reacting with the de-colouring chemical and becoming colourless[109–112].

Modified print. There are 17 patents (listed in table B.7 in the Appendix) that propose new ink formulations that can be made colourless on demand. They vary in the exact formulation of the print, the corresponding trigger used for the colour change (heat, chemicals or specific frequencies of light) and whether the change is reversible.

Figure 3.1 21st century reuse: The Toshiba 'e-blue' system (Image © Toshiba[115])

A print developed by Toshiba is of particular interest because it is commercially available. Toshiba have been selling their proprietary de-colourable toner-print in Japan since December 2003 under the name of 'e-blue'[31]. The e-blue mechanism, its environmental and economic performance and its operational challenges are reviewed below.

The e-blue system has three components[115]: a modified laser printer, photocopier or pen; a toner or ink containing a modified colouring agent; and an un-printer. The printer or photocopier (labelled 1 in figure 3.1) is conventional but must be loaded with a special toner-print and a modified photoconductor drum†. The special toner-print contains modified dyes that are proprietary to Toshiba and have a blue colour. Toshiba have also partnered with other companies[117] to launch pens that use similar modified pigments (labelled 2). The un-printer (labelled 4) heats a 400 sheet batch of A4 paper to 420 K for three hours causing the modified print to become colourless (labelled 5). The sheet can then be reused.

The special toner appears to have been patented by Tokyo Shibaura Electric Company who are now part of Toshiba[118;119]. The patents, together with two conference articles[117;120] report that the toner contains a dye, a developer and a de-colouring chemical. The dye is a leuco dye, such as crystal violet lactone, which is initially colourless. Under the heat and pressure from printing the dye reacts with the developer (propyl gallate) to become coloured. By heating at higher temperatures (400–420 K) the de-colouring agent (cholic acid) reacts with the developer to neutralise it. This allows the dye to return to its original colourless state. This is similar to an ink eraser patented earlier by Iwata *et al.*[121] and, according to Takayama *et al.*[120], is the reverse of some thermal printing processes.

The e-blue system is likely to be environmentally preferable to the alternative of using fresh sheets of virgin or recycled paper. The system was used as the basis of the analysis of reuse in the previous chapter (§2). The analysis described in that chapter suggested that it might use 80% less energy and emit 90% less climate change gas than the conventional paper-making or paper-recycling processes. The conclusions of that chapter were based on the energy analysis of Tanaka *et al.*[35], Toshiba employees, which has at least two limitations: it does not investigate whether any extra energy is to create the modified print; nor does it consider other

† The photoconductor drum is the part of a laser printer or photocopier to which the print attaches before it is transferred to the paper. It was the critical invention which allowed the process of xerography to be created[116]

environmental impacts beyond climate change gases. There is no reason to believe either limitation would be significant compared to the paper-making or paper-recycling processes.

The system appears to have an acceptable cost. Price data from Toshiba [122] suggests that the modified printers, photocopiers, pens and toner are being sold at close to the price of their conventional equivalents. The cost of the un-printer is not specified by Toshiba, but the New Scientist [123] reported a launch price of £1600 including an unspecified quantity of the special toner. The simplicity of the un-printer's operation implies it may cost substantially less to make. The un-printer uses 2 MJ of electricity per batch of 500 sheets [124] which suggests an electrical running cost of below 0.02 pence per sheet, which is perhaps a twentieth of the cost of a new sheet of paper.

The operational performance of the e-blue system is mixed. On the positive side, its speed is acceptable. The printers and photocopiers can run at their usual speed. The stated speed is three hours to de-colour 500 sheets. Based on an average daily consumption of five to thirty sheets per person (discussed in section §1.2.1) this could be run overnight to provide the daily needs of 15 to 100 people. On the negative side, the original text is faintly visible, the modified print fades rapidly in bright sunlight and the un-printing process causes the paper to yellow [125] after a few cycles. Recent publications by Toshiba employees [126–128] reveal that Toshiba are tackling the operational performance difficulties of their process, potentially by combining the de-colouring with an abrasive process or by requiring a special paper to be used.

One of Toshiba's competitors, Xerox, are working on a similar un-printing processes. In 2006 they were reported [6;129] to have developed a print that fades to invisibility within 16 hours, allowing the paper to be reused. It is interesting to speculate whether Xerox are making a virtue out of the problem that Toshiba are facing with the rapid fading of their ink in sunlight.

Modified papers. An alternative to modifying the print to allow de-colouring is to modify the paper. The ancient Greeks and Romans used beeswax covered wood as a temporary writing material [130]. They wrote on the tablets by scoring with a sharp point. The score would reflect ambient light differently from the surrounding surface, creating a visible mark. The text could be made invisible by removing the scored mark, either by smoothing the wax or by adding a second layer of wax[131]. This allowed the tablet to be reused.

A series of patents are listed in table B.8 propose altered papers with an embedded de-colourable pigment. In 2001 Ricoh demonstrated a system based on this principle that used a special paper and printer[132]. The paper contains a pigment that becomes transparent when heated to 450 K and cooled rapidly, and coloured when heated to $290 - 450$ K and cooled slowly. The printer first heats and then rapidly cools the whole sheet to erase any previous print, then heats selected parts and allows them to cool slowly to create new text and images. In mid-2006 Toshiba launched the 'SX8R', which appears to be an almost identical product[133;134].

3.3 Does the technology to un-print exist?

This chapter has reviewed four systems for un-printing that are on sale, three that have been used historically, two that were prototyped and many whose only record is patent filings. This implies that the technology to un-print only partially exists, and leaves five questions that warrant further research.

The four systems for un-printing that are on sale all require a change to conventional office printing. The e-blue system requires a special toner print. The SX8R system requires special paper and a special printer to be used. Ink eradicators require everyone to print with washable blue inks. Erasers require pencil to be used.

The three systems for un-printing that have been used historically are wax tablets, parchment or papyrus palimpsests, and perhaps the correcting typewriters of the 1980s. Neither wax tablets, nor parchment, nor papyrus are used in modern offices. The un-printing facilities of typewriters were used to correct mistakes rather than to allow entire sheets of paper to be reused and are now rarely seen in offices.

The two prototype systems were similar: the DeCopier and the Ricoh toner removal systems both used a combination of solvents and abrasive brushes. There is little evidence to explain why the Ricoh system did not go on sale. The single independent evaluation of the DeCopier system implied it had, at best, mixed performance.

Approximately 120 patent documents have been found that relate to un-printing. A full list of those studied is contained in appendix §B. The majority are duplicates, re-issues and extensions. Most of the remainder do not provide any performance data. Many do not describe the critical components or operating parameters of the processes that they propose. Some patents imply that other patented approaches do not work, but do not present evidence as to why. These suggest that there are at least five opportunities for further research:

3.3.1 *Can conventional toner be de-coloured?*

The review of de-colouring approaches identified seventeen patents that use a modified print that is decolourable. This implies that the conventional colouring (carbon-black and iron oxide pigments) cannot be reasonably de-coloured.

3.3.2 *Can toner be rubbed off without excessive damage to paper?*

The review of approaches that remove print by force identified two patents that modify toner print to bond less forcefully to paper, thirty patents that modify paper to be able to bond less forcefully to toner-print and two patents that modify paper to be more resistant to abrasion. This implies that conventional toner-print cannot be removed from paper without excessive damage to the paper.

3.3.3 *Can toner be dissolved without also dissolving the paper?*

The review of approaches that remove print by solvents identified five patents that modify paper to be more resistant to solvents, and one that modifies the toner-print to be less resistant to certain classes of enzyme. This implies it may be impossible to find a combination of water, solvent and surfactant that removes print without also harming the paper.

3.3.4 *Can toner be ablated without charring the paper?*

All that use heat to remove print required the laser radiation to be tightly focused on the print, or for the print to be altered to sublime at a lower temperature. This implies that it is difficult to ablate toner without damaging the paper.

3.3.5 *Could other approaches to un-printing work?*

The final implication of the patent record is that research into un-printing has been carried out independently and secretly. This has resulted in a large number of duplicates in the patent record and provides little confidence that all possible approaches to un-printing have been researched.

3.4 Experimental Focus

This final section summarises which of the five questions are answered in the remainder of this thesis.

The first question, "Can conventional toner be de-coloured?" is not answered. It required too great a knowledge of chemistry.

The questions on rubbing, ablation and dissolution are addressed in the three following chapters. These three approaches to removing print form an interesting set because they each take a fundamentally different approach to breaking the intermolecular bond between print and paper: abrasion does work to overcome the bond, ablation changes the internal energy of the molecules and dissolution shields the electrons in the molecules and therefore weakens the bond.

The original focus of this thesis was the last question "could other approaches to un-printing work?" No satisfactory answer was developed. A structured search for all possible approaches was carried out using the morphological analysis method of Zwicky [135]. In the words of French [136] this requires that researchers "take all the possible elements that might enter into a solution, combine them in all possible ways, and then select the best combination." Critics of the morphological method suggest that it produce to many approaches for them to be appropriately tested [136;137], and that the results are likely to be sensitive to assumptions that were made about the problem [137]. A series of morphological tables of un-printing techniques was developed and both criticisms were valid in this case. Furthermore, it was difficult to balance specificity with comprehensiveness: any morphological table that inspired confidence that all possible approaches to un-printing had been captured was generally too abstract to implement. Conversely, any table that described approaches in enough detail to test did not inspire confidence that no approaches had been missed.

The effort spent on the morphological analysis was not successful enough to be included in this thesis, but did guide the structure of the literature review, inspire some of the conclusions drawn in the final chapter of this thesis, and help clarify the author's thoughts when carrying out the more successful experiments on abrasion, ablation and dissolution of toner-print that are reported in the next three chapters.

4 Abrasives

This chapter answers two questions:

1. Under what conditions can toner-print be removed from office paper by abrasive wear?
2. Under conditions that remove toner-print, is the paper re-usable?

The first section reviews previous work in this area. The second and third and fourth sections report on experiments to quantify the influence of abrasive size, speed, distance, pressure, direction and repetition on the amount of toner removed. The fourth section evaluates the re-usability of the paper under the best toner-print removal conditions. The final section discusses the potential for improving the performance.

4.1 Previous attempts to wear toner-print

Most tribological studies have focused on how to minimise wear. In this case the wear of one material (the toner) is to be maximised while the wear of a substrate (the paper) is minimised. The closest well studied operation might be abrasive paint stripping – both processes face the challenge that the surface has been designed to withstand a certain level of abrasion. However paint stripping and toner-removal are not comparable for two reasons: the first is that the toner penetrates into the paper; the second is that the paper, and to a lesser extent the toner, have complex heterogeneous structures.

The small body of research into using a wear process to remove toner-print can be divided into two groups: those studies that imply success and those studies that imply failure – neither group makes conclusive statements. In particular, some reports imply that the surface of a sheet of paper needs to be completely removed in order to remove the toner.

4.1.1 Two patents imply success

The reports of success are restricted to two patent applications that were mentioned briefly in section §3.1.3. Neither report performance data. Mitsuhashi [72] provides the most detail on his mechanism. He heats the printed paper to 40 to 90°C and then removes the top 10 μm of the paper surface using a diamond abrasive coated roller. The abrasive has a particle size of 150 μm, and the 25 mm diameter roller rotates at 1200 rpm with a pressure of 200 g/cm^2. He states that the paper can then be reused as if it were brand new, although he does not claim that these are the optimal set of operating parameters. The earlier Japanese patent filed by Yamazaki [73] seems to imply heating to a higher temperature (up to 200°C) before rubbing with a felt roller. The patent does not describe the other operating parameters or the performance acheived. The language of the patent is also not entirely clear as to whether the paper must be pre-treated before printing for the removal process to work.

4.1.2 Many more patents indirectly imply failure

A large number of patent filings use wear as a small part of a larger toner-print removal process. This implies that wear does not work alone. As mentioned in section in section §3.1.3, the simplest extension, as proposed by Atarashi *et al.* [94] and Machida *et al.* [95], seems to be to soak the waste paper in a solution to weaken the paper to print bond before rubbing. Other approaches change the paper or the print. Tsukamoto *et al.* [80] propose an erasable paper, to which toner-print bonds less forcefully, and a complementary eraser [81] that uses abrasion to rub the print off. Other patents [138;139] change the paper so that the bond between print and paper can be weakened on demand. The majority of these add a coating to the paper that swells when immersed in water. This swelling reduces the bond between the toner and the paper making separation easier. Other groups propose changing the print. Tsuneo *et al.* [78] propose a toner print that bonds less strongly to paper, making it easier to force apart. Similarly Kuramoto *et al.* [79] propose a more viscous toner that does not penetrate into the paper and is therefore easier to remove. The work of Gotanda *et al.* [128] is of particular interest, because they report the impact of varying the roughness, speed and (implicitly) duration of rubbing printed paper with a belt sander. However they are not trying to completely remove toner because they have developed a toner that can be triggered to lose its colour and therefore become almost invisible.

4.1.3 Do the surface layers of the paper need to be removed?

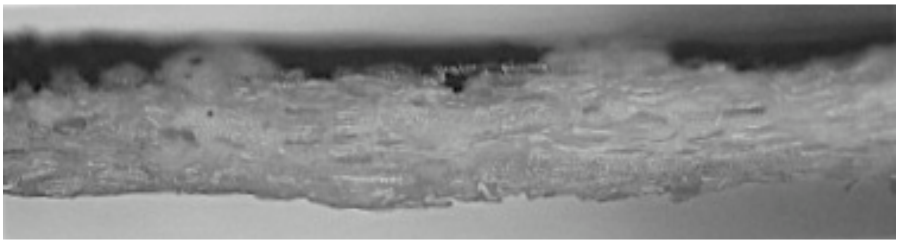


Figure 4.1 Cross section of printed paper. Toner is visible as black surface layer, and penetrates into the paper surface

A cross-section of a sheet of toner-printed paper suggests that toner penetrates up to 10 μm into the surface of the paper (see figure 4.1). A critical question for the feasibility of an abrasive reuse process is whether this means that the top 10 μm of paper must be completely removed in order to remove the print. A typical sheet of $80\,g/m^2$ office paper ($70 - 100\,\mu m$ thick) would, in this case, lose $10 - 15\,\%$ of its volume. The minimum weight paper accepted by many office printers is $60\,g/m^2$, suggesting that at most two layers of print could be removed before it was unusable.

Mitsuhashi [72] and Gotanda *et al.* [128] both imply that a complete surface layer of paper does need to be removed. Mitsuhashi [72] removes the top 10 μm from the surface of paper, presumably by setting the gap between the abrasive roller that removes the print and the elastic roller on which the paper rests. Gotanda *et al.* [128] similarly set a gap between abrasive and paper.

If would be preferable to extract toner-print from between the paper fibres without damaging them. The experiments reported in the following section seek to clarify whether this is possible and therefore whether the optimistic or pessimistic abrasion patents are closer to reality.

4.2 Method: Abrasive drum

The ability of abrasion to remove toner-print was tested by towing samples of text past a spinning abrasive drum under a constant load, illustrated in figure 4.2. The drum consisted of small pieces of abrasive sheet that were wrapped around the brass drum on a layer of double-sided adhesive tape. The drum was brass, with a diameter of 8 mm and a depth of 10 mm. The text was directly

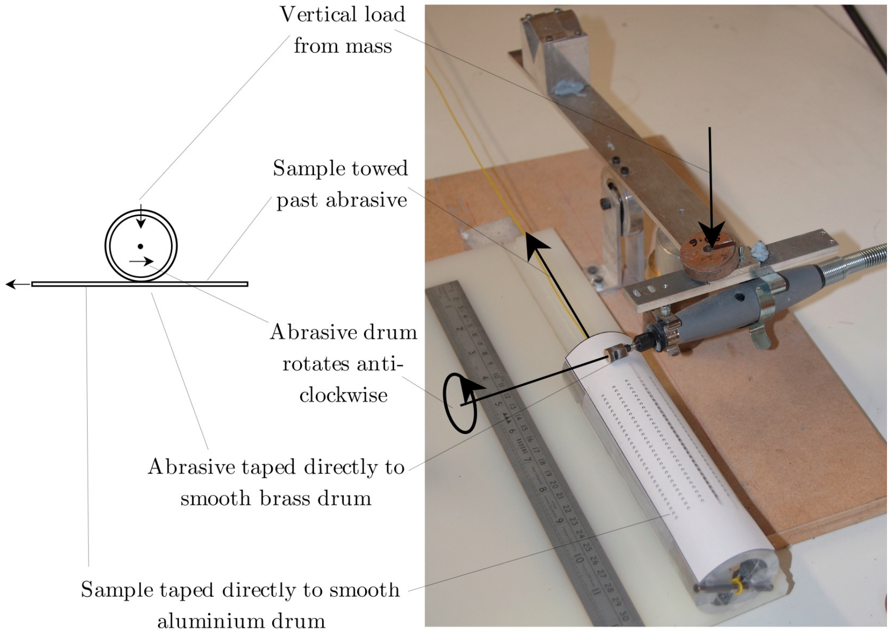


Figure 4.2 The apparatus

attached to a larger 5 cm aluminium drum with tape at each end. The samples were mounted on a drum so that several tests could be carried out in sequence by rotating the sample under the abrasive. The nominal contact area between the drum and the sample was 2 by 6 mm. The abrasive drum was spun by a 'Dremel' power tool with an integrated speed control with feedback. The sample was pulled past the abrasive on a nylon track using a second motor. This second motor did not have feedback on its control system but had sufficiently high torque to maintain a constant speed. Once the abrasive drum and the sample had reached the desired speed the abrasive drum would be lowered against the sample and held against it using a dead weight.

The tests were carried out on samples printed with thirty letter 'e' characters in a 12 point Times font spaced over 10 cm:

e e e e e e e e e e e e e e e e e e e e e e e e e e e e e e

For each test the abrasive drum was run over the sample of 30 characters. The level of print removal and the level of damage to the paper were both assessed qualitatively and relative to fresh sheets of paper. This assessment was made against a white background to gauge print removal and against a light box to gauge any changes to the thickness and opacity of the paper. In the results below, the images are of the last few characters in the row of thirty.

Table 4.1 The range of parameters tested

	Low	Default	High
Grit size (μm)	2	22	125
Load (N)	0.2	0.5	2.0
Abrasive speed (m/s)	2.3	6.0	11.5
Sample speed (cm/s)	0.3	1.4	3.0
Repetition (passes)		1	10
Abrasive life (mrubbed)		0.1	3.3
Grit material	Silicon Carbide	Aluminium Oxide	Diamond

There are a large number of parameters that might influence wear. Viswanath & Bellow [140] have used dimensional analysis to develop a formula for the rate of wear of polymers that was based on the load, speed and duration of rubbing, the roughness of the abrasive counterface and the thermal conductivity, and heat capacity, surface energy and Young's modulus of the sample. The properties of the sample are fixed in our case, and therefore the experiments have focused on the load, speed and duration of rubbing, together with the roughness of the abrasive.

Table 4.1 shows the full range of parameters tested and the 'default' values that were used. The abrasive material was varied as a proxy for surface energy, the abrasive grit was varied as a proxy for surface roughness. The duration of rubbing was adjusted by varying the speed at which the sample was pulled past the abrasive. The temperature was not varied and the experiments were carried out at room temperature (21 to 23 °C) and humidity (46 to 53%). The abrasive was replaced for each test.

4.3 Results

The results of the tests are split into two parts. In the first part each of the six parameters are varied alone to explore their basic relationships with print removal and paper damage. In the second part the three main parameters – grit size, load and duration of rubbing – are varied together to explore how they interrelate. The main findings are then summarised. The next section evaluates overall performance on a larger sample.

4.3.1 Basic relationships

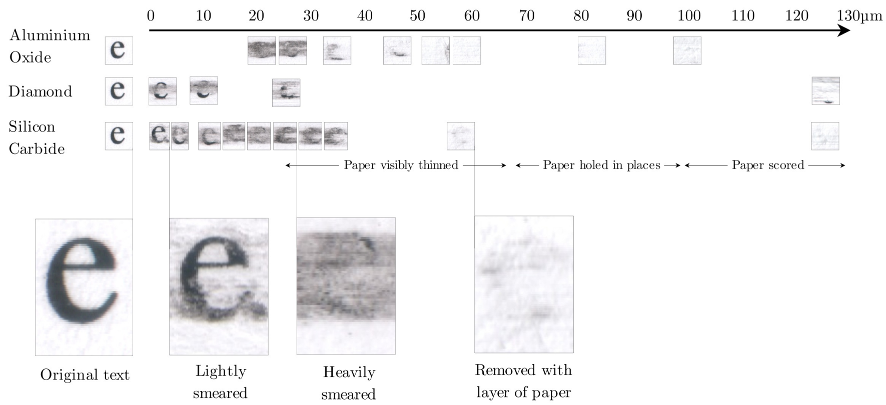


Figure 4.3 Effect of abrasive material and grit size

Figure 4.3 shows a letter 'e' that has been rubbed with different sizes and types of abrasive. The original sample is on the left, and the size of the abrasive grit increases towards the right. The row indicates which of the three types of abrasive was used – aluminium oxide, silicon carbide or diamond. The type of abrasive material does not appear to influence the level of print removal significantly. Increasing grit size leads to increased print removal, starting by having little effect, then increasingly smearing the text until it is eventually entirely removed. There appear to be two thresholds, the first at a grit size of 10 µm where the print becomes smeared on the surface of the paper to the extent that the text is no longer legible and a second at a grit size of 35 µm where the letters are entirely removed, leaving a white surface. The grit size also influences the level of damage to the paper. At very large grit sizes (100 µm and above) the paper develops score marks that penetrate through its depth, leaving long holes. At smaller grit sizes of 60 to 100 µm entire layers of paper fibres appear to be removed, leaving a very rough and uneven surface with holes in places. At grit sizes below 60 µm the thinning of the paper becomes gradually less severe and gradually more even and consistent. At grit sizes below 25 μm there is little visible thinning of the paper.

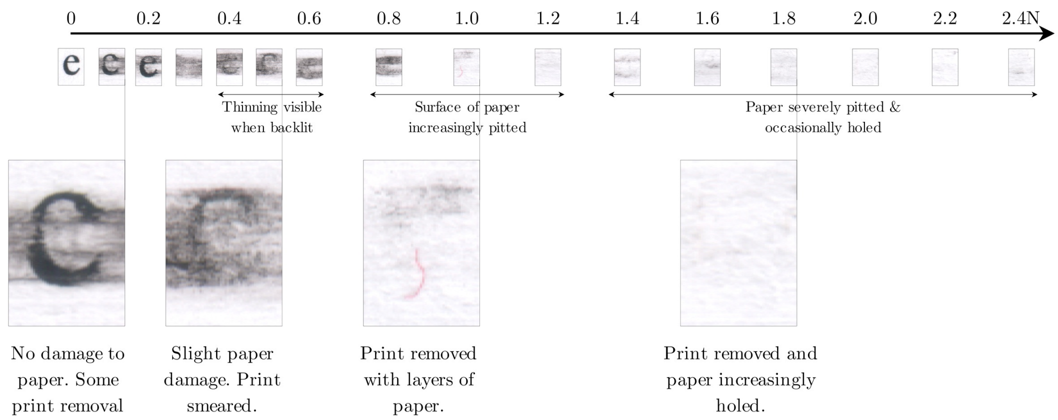


Figure 4.4 Effect of load

Figure 4.4 shows the effect of rubbing under increasing loads. Both the amount of print removal and of damage to the paper increase with increasing load. There are two interesting thresholds in load with respect to print removal. Even at the lightest tested load (0.1 N) there is some visible removal of print. At a load of 0.3 N the print is smudged and removed enough for it to be difficult to read the text. At a load of 1.0 N and above the text is entirely removed along with a layer of paper.In erms of paper damage, no damage is visible up to loads of about 0.3 N. Slight thinning is visible on close inspection for loads up to 0.6 N. Gross damage is clearly visible from loads of 1.0 N and this increases with load until the paper becomes occasionally holed at 1.6 N. At the highest load tested (2.4 N) the paper is torn in a channel for the first few centimetres of rubbing, and then the abrasive becomes blunt and damage decreases. Measuring the size of the worn areas on the paper suggests that the apparent contact area increases slightly over this range of loads from 6 to 8 mm in height and from 2 to perhaps 3 mm in width. This implies that as the load is varied from 0.1 to 2.4 N, the pressure varies between approximately 5 and 100 kPa.

Figure 4.5 shows the effect of increasing the time spent rubbing each character. This is achieved by reducing the speed at which the sample passes underneath the abrasive wheel. The general relation seems to be that the more time that is spent rubbing a

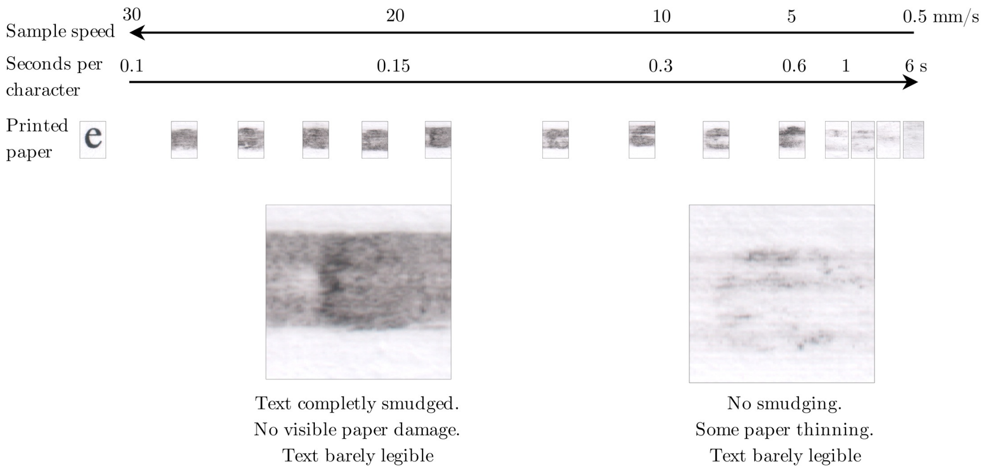


Figure 4.5 Effect of the time spent rubbing each character

sample, the less smudged it appears. There is also a threshold at about 1 s of rubbing per character, above which the character is almost completely removed without smudging. The same speed threshold also applies to paper damage. If the character is rubbed for less than 1 s then there is very little damage to the paper. If it is rubbed for more than that amount then some thinning is visible. At the extreme, if the sample stops moving past the abrasive, then the abrasive will wear through the paper.

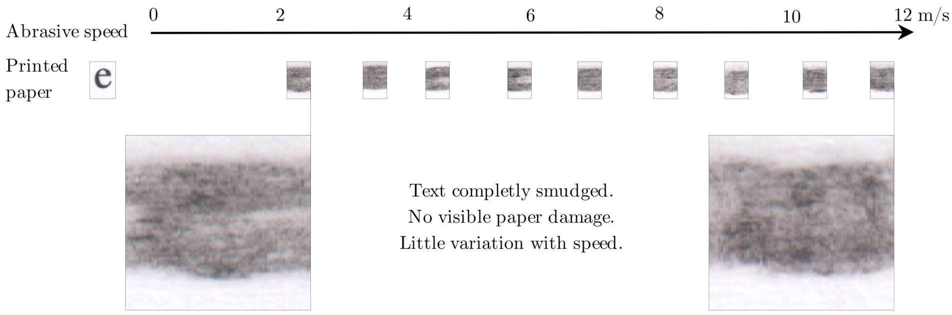


Figure 4.6 Effect of the speed at which the abrasive is rubbed

Figure 4.6 shows the effect of increasing the speed with which the print is rubbed. This is achieved by increasing the speed at which the abrasive drum rotates. As the abrasive speed is increased, the sample speed is reduced in proportion. This is in order to maintain a constant number of rotations of the abrasive drum as it passes over each character – otherwise increasing the speed would also increase the amount of rubbing each character received. Given this adjustment, there does not seem to be any link between abrasive speed and print removal. In all the cases tested the text was entirely smudged and the paper was not visibly damaged.

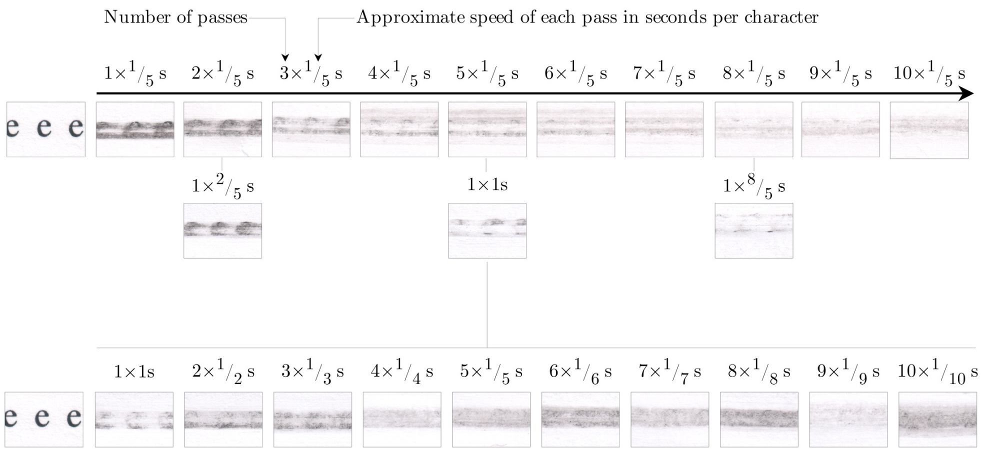


Figure 4.7 Effect making more than one pass with the abrasive

Figure 4.7 shows the effect of carrying out several passes with the abrasive over the same print. On the top row each pass is carried out at a constant speed and the effect of increasing numbers of passes is shown moving to the right. For comparison, the row below shows samples that have been rubbed for an equivalent length of time, but in one pass. This implies that repeated high speed passes may remove slightly more print than the one pass at a lower speed, however the effect is slight. This is explored in further detail in the third row where the speed of each pass is increased in proportion to the number of passes to maintain a constant length of time spent rubbing each character. The implication of this set of results is that greater removal is achieved by making more than one pass, but that the effect disappears after four passes and the level of removal then appears quite variable. There does not appear to be a relationship between repetition and damage to the paper. The damage increases with the time spent rubbing each character, irrespective of the number of passes made.

Figure 4.8 shows how the removal of print changes over the life

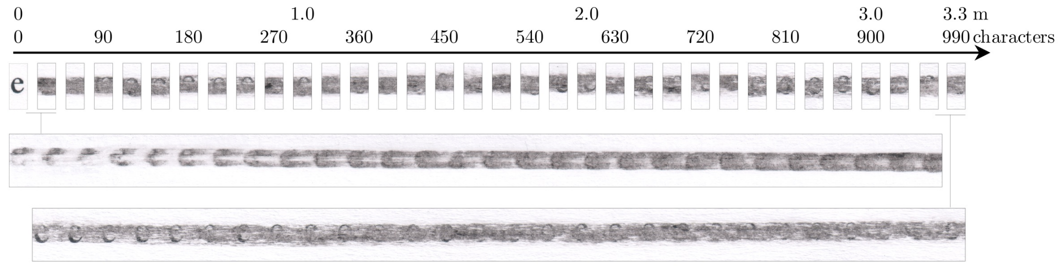


Figure 4.8 Variation in removal over the life of an abrasive

of a piece of abrasive. The measurement at the top is the number of characters abraded (there are 30 characters every 10 cm). There is some variation in removal of the toner but this does not appear to be correlated with the stage in the abrasive's life. An exception is the effect on the first few characters that are rubbed. These are shown in the middle image on the left. The first ten characters are different from the remaining characters and from any other character in the test. Although not correlated with the stage in the abrasive's life, there does appear to be a rhythm in the removal. For example, the bottom image on the right shows characters 960 to 988 and it can be seen that first few characters have a different pattern of removal from the last few. This is probably because the samples are printed in blocks of 30 characters, with blank paper to either side and the blank paper has an effect on the removal of the next few characters. There is no visible damage to the paper except for the first five characters. This is presumably correlated to the increased level of removal of those characters.

4.3.2 *Interplay of parameters*

Three parameters appear to be critical: force, grit size and duration of rubbing. Three sets of experiments were carried out to find out the critical combinations of these parameters.

Figure 4.9 shows the combinations of load and time spent rubbing that remove just enough print for it to be illegible. Higher loads require less time to be spent rubbing. In all cases, to achieve illegible print there is some damage to the paper, but the level of damage varies considerably. For loads of up to 0.4 N the damage is not visible in general use, although it is clear that some thinning has taken place if the paper is backlit. For loads up to 0.7 N

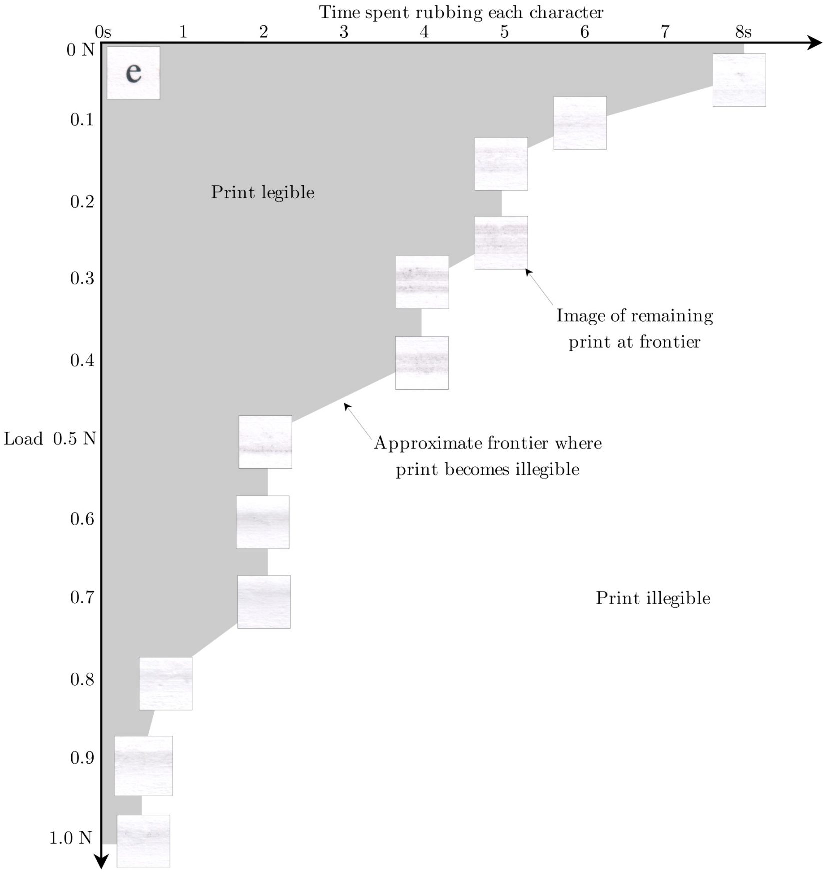


Figure 4.9 Relationship between load and time spent rubbing each character

the damage to the paper is visible as thinner and rougher paper. For loads above this the paper becomes increasingly pitted and occasionally holed.

Figure 4.10 shows the combinations of abrasive grit size and time spent rubbing that remove just enough print for it to be illegible. Larger grit sizes require less rubbing. At one extreme, the large grit sizes are very sensitive to the time spent rubbing and at the other extreme it appears that grit sizes of 10 µm cannot be used to entirely remove print at the 0.5 N load used. These abrasives did not appear to remove any further print after 5 s of rubbing (the tests were halted at 15 s of rubbing per character). For these grit sizes no damage to the paper was visible. Some thinning and surface roughness was visible for the grit sizes below 30 µm. Severe damage and large holes were visible for abrasives

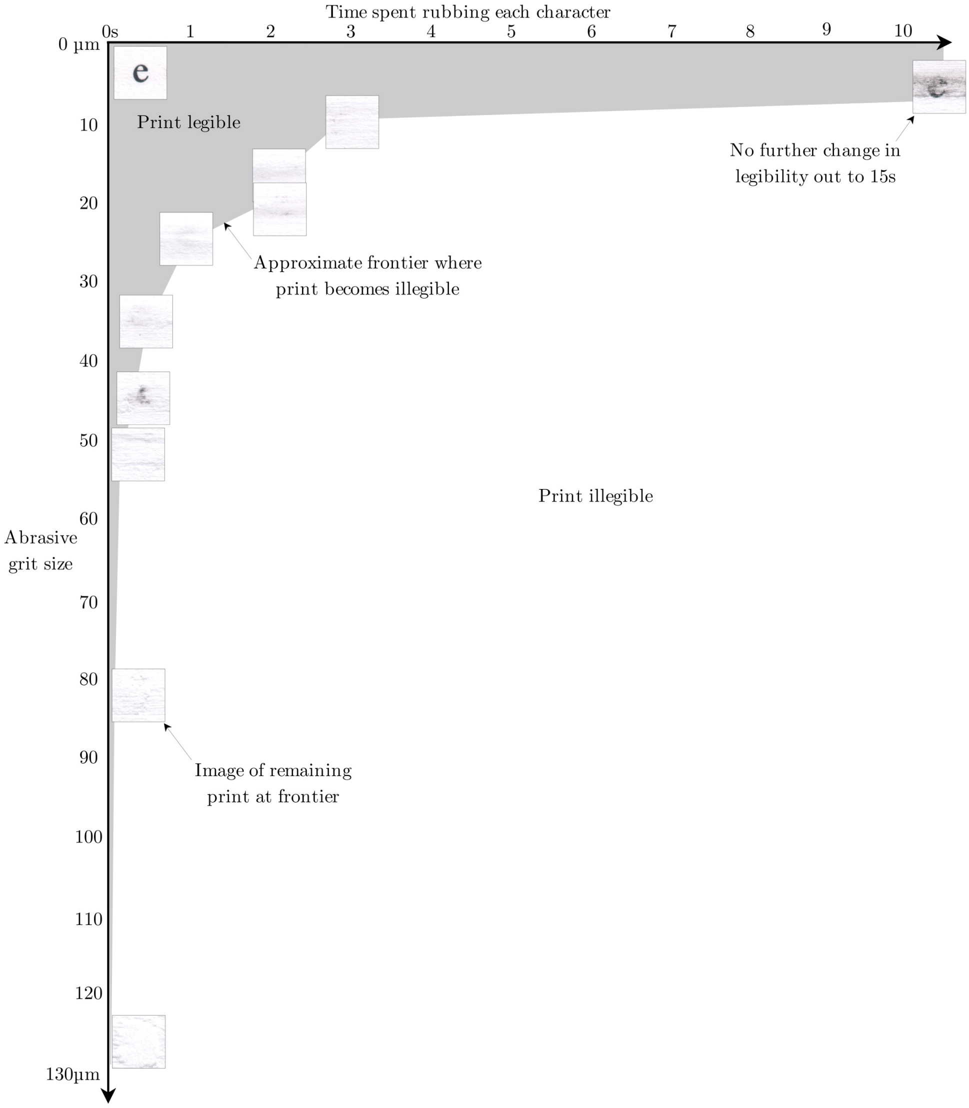


Figure 4.10 Relationship between abrasive grit size and time spent rubbing each character

with larger grits.

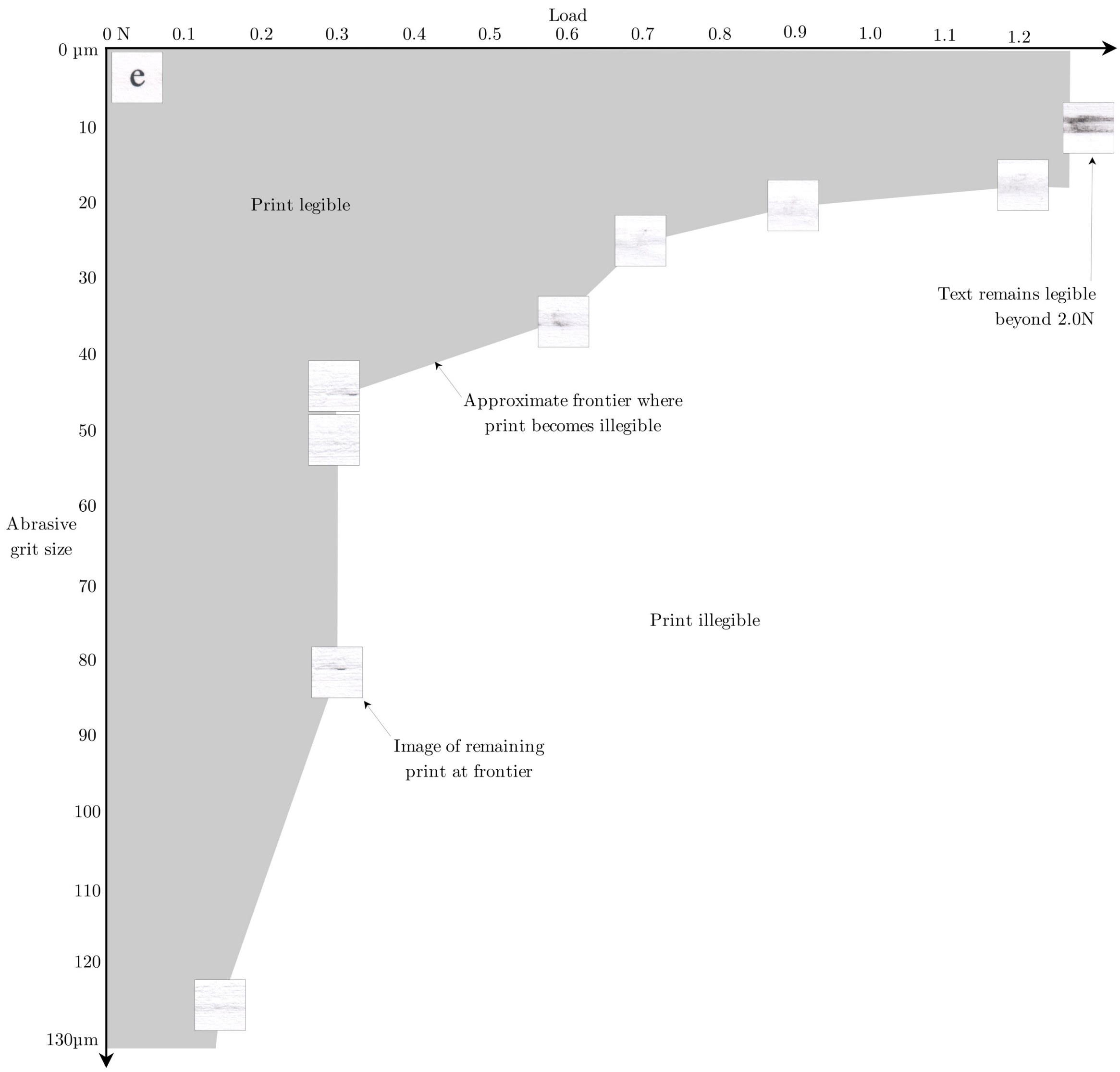


Figure 4.11 Relationship between abrasive grit size and load

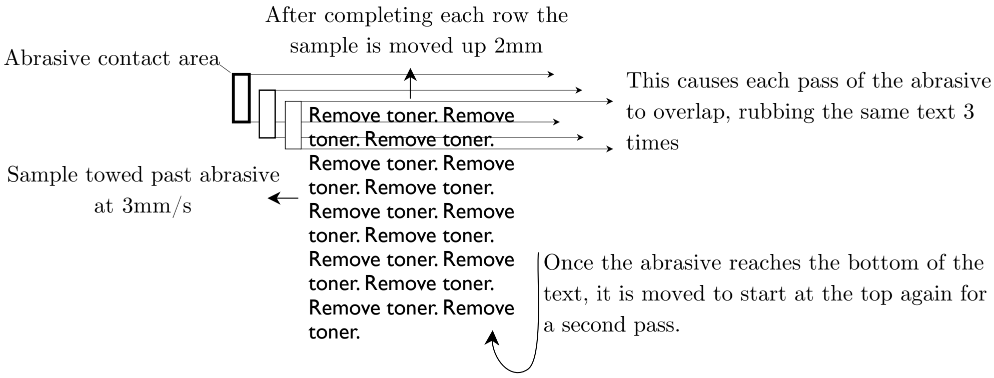
Figure 4.11 shows the combinations of abrasive grit sizes and load that remove just enough print for it to be illegible. The smaller the grit size the more load is required. As with the relationship to time spent rubbing, the larger grit sizes are very sensitive to the level of load and the smallest grit sizes (below 10 µm) cannot be used to entirely remove print. The paper is severely damaged and holed for grit sizes above 30 μm and mildly damaged at levels below.

4.3.3 Summary of relationships identified

- Increasing the size of the abrasive grit increases the damage to paper and the removal of print (because the print is removed with the damaged paper). The damage increases significantly for grits that are larger than 30 μm and decreases significantly for grits that are smaller than 10 μm.
- Increasing load increases the damage to both print and paper. Below 0.6 N the damage is rarely visible when using the smaller grit sizes.
- Increasing the time spent rubbing only slightly increases damage to the paper when using smaller grit sizes and light loads. If the time spent rubbing is increased above 1 s per character then a significant increase in print removal is seen.
- Rubbing several times quickly rather than once slowly does not alter the damage to the paper but may slightly increase print removal.
- The rubbing speed was tested over the range 2 to 12 m/s and did not seem to influence the level of paper damage or print removal.
- The damage to the paper and the level of print removal reach a steady pattern after rubbing a few characters (perhaps 3 cm in distance) and remain at similar levels up to the limit tested (roughly 1000 characters or 3.3 m).

4.4 Evaluation: Two reuses at 'draft' quality

To evaluate overall reuse a larger 3 x 3 cm sample was tested. This necessitated a slightly more complicated motion for the abrasive:



To minimise damage to the paper a grit size of 22 µm and a load of 0.3 N was chosen. To completely render the print illegible with these settings requires approximately 6 s of rubbing per character. This rubbing was carried out in six passes as shown in the figure above.

The results are shown in figure 4.12. Starting at the top left of the figure, the first image shows the sample with the printed text (labelled a). The image to its right shows the sample after the abrasive process (b). As can be seen, there is no legible print but the paper appears significantly greyer. The sample was then re-printed with the text in the left-most image on the second row (c). The image to its right shows the sample with this second layer of print (d). The text appears equally legible, but close examination reveals that there are small spots of white (at the top of the 'I' and 'f' in the first 'if' for instance) where the second layer of print has not adhered. The image below on the third row shows the same paper but viewed from the reverse (e). By comparing it to the reverse of the original print, it can be seen that the rubbed paper is thinner, allowing the print on the other side to be viewed more easily (f).

This second layer of print was then abraded with the same settings and the result shown in the image at the top of the third column (g). It was noticeable that the print was removed much more rapidly on this pass and left a whiter surface. This sample was re-printed and the result shown in the second row (h). Once again the text is legible but there are a slightly larger number of white spots where the print has not taken. Viewing the reverse of the sample shows that the paper has thinned quite significantly, to the point where the text is readable through the paper (i).

The third layer of print was then abraded with the same settings and the result shown in the image at the top of the fourth

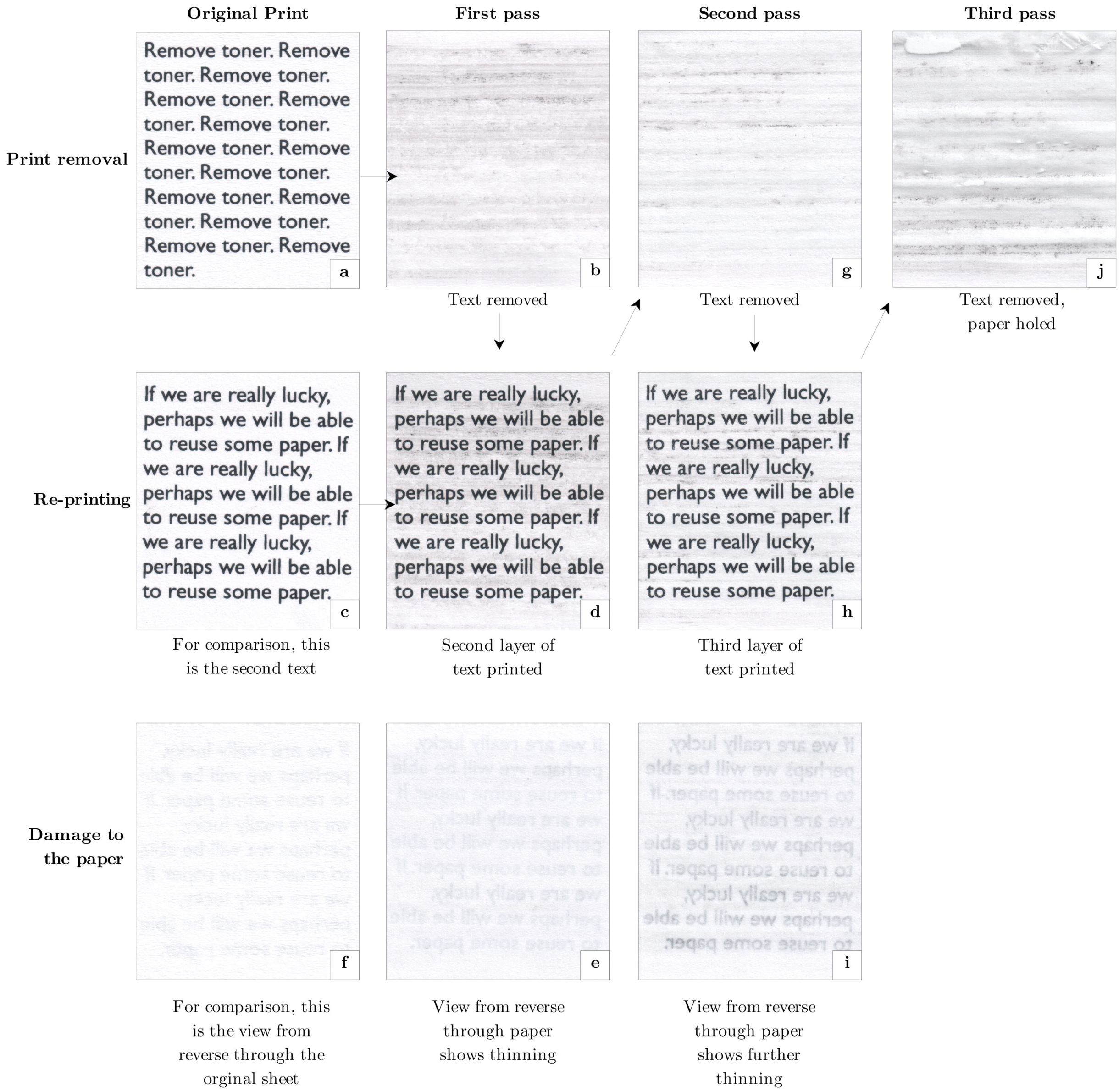


Figure 4.12 Evaluation of overall performance

column (j). Once again the print appeared to be removed much more rapidly than the first pass. Unfortunately on this pass the abrasion left holes in the paper, ending its useful life.

The answer to the questions posed at the start of this chapter might therefore be that under the conditions that remove toner-print, the paper will be left in a state that allows reuse where the quality of presentation is not critical (for example internal documents and early drafts of work). However the surface layers of the paper will be removed. This limits reuse to two cycles of abrasion before the paper is holed.

The next section will discuss the possible mechanisms behind the abrasion and therefore scope for improvements to this performance.

4.5 Discussion: Exploiting adhesive wear

Wear is not a single process. A mixture of mechanisms are usually involved in the break-off and removal of particles. These mechanisms are commonly split into 'adhesive' and 'abrasive' wear. In adhesive wear the worn material first sticks to the abrasive forming a 'transfer layer'. This transfer layer may then gradually fragment to form wear particles. In abrasive wear the abrasive cuts or gouges the worn material turning it directly into wear particles. Both mechanisms can be seen in the results above.

Figure 4.13 illustrates the two mechanisms in the removal of print. The top row shows the original printed text. The second row shows the text after being rubbed with a 22 μm grit. As can be seen, the effect of the abrasive varies as it moves across the letters, gradually increasing the smudging of the letters as time passes. In contrast, the 35 μm abrasive on the third row results in a relatively even level of removal. The former, finer, abrasive is presumably working through a mainly adhesive wear mechanism while the latter, coarser, abrasive is working through a mainly abrasive wear mechanism. Examining the abrasive sheets after the rubbing supports this conclusion – the 22 μm abrasive has the remains of a black transfer layer, while the 35 μm abrasive does not.

In contrast, the wear of the paper appears to be purely abrasive. The abrasion appears to take four different forms. The largest grits tested are of the same order of size as the paper thickness (approximately 100 μm) and therefore appear to cut through the paper as if it were a homogeneous material. As the grit size

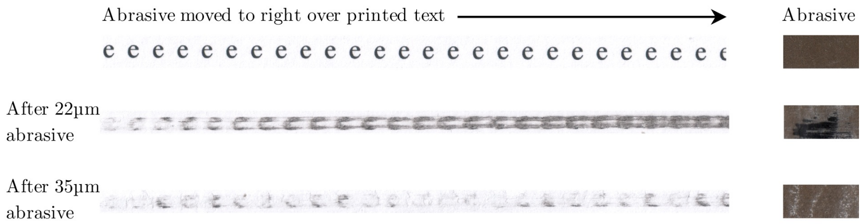


Figure 4.13 The two types of wear mechanism that are visible

reduces, the rough uneven surface of the worn paper suggests that the wear mechanism at least partially shifts to a 'plucking' mechanism, where abrasive particles capture and pull layers of paper fibres away from the bulk. As the grit size drops below 60 µm the surface becomes smoother, implying a change in mechanism: possibly away from plucking individual fibres and back to a more conventional cutting mechanism. As the grit size drops below 25 µm the damage to the paper drops considerably and the paper becomes glossier and smoother. This suggests a further change in mechanism. The surface looks similar to that of paper after it has been pressed between high speed smooth rotating drums (a process known as calendaring that paper makers use to create a smoother surface finish on paper). This implies that in some cases instead of cutting the paper fibres, the abrasive may be crushing them flatter. It may also be possible that at this scale, the contact area of the abrasive particle on the paper fibre is smaller than the average spacing between fibres in the paper, which means that the fibres might be deforming elastically and therefore wearing less.

An ideal process would remove the toner-print without damaging the paper. One way to do this would be to design a very localised wear process, combined with a sensing and control system that would wear only where there was print. An alternative approach would be to use a bulk wear process to which paper and toner-print respond in different ways. The potential for adhesive wear in toner but not in paper is one such difference that might be exploited and is discussed next.

To maximise the potential from adhesive wear, several issues would need to be overcome in the formation, fragmentation and removal of the transfer layer.

There are four issues related to the formation of the transfer layer.

- Until the transfer layer is formed, wear of the paper is more severe. This is visible as the greater level of removal of the first few characters in figure 4.8. It is also visible in the image of the third pass of the abrasive in figure 4.12 where the first and largest hole is formed over the first few characters of text.
- Once the transfer layer is formed removal is uneven and depends on the relative distribution of print and white space. This is again visible in figure 4.8 where there are variations in removal over time and in particular, in the bottom row of that figure which shows the typical situation where the first few characters after a blank space are more legible.
- Once the transfer layer is formed it may inhibit further removal. In the experiments, all abrasives with a girt size below 40 μm formed a transfer layer. Unfortunately figure 4.10 shows that the duration of rubbing required to remove print increases rapidly as the grit size drops, to the point where it is difficult to make print illegible with grit sizes of 10 μm or less.
- The transfer layer does not form over the entire abrasive. The middle row of figure 4.13 shows a typical abrasive after adhesive wear. The transfer layer usually starts at the join in the abrasive sheet and extends anticlockwise. It rarely extends in width beyond 2 mm and length beyond 15 mm. The width might be expected to be limited to the height of the text in these tests. The length may similarly be related to the width of an average character. It is not clear whether the mixture of transfer layer and abrasive area helps the wear process or whether it hinders the process by leaving an area of abrasive that does not adhesively wear the print and may abrasively wear the paper.

Once formed, the next stage in adhesive wear is for parts of the transfer layer to fragment and be removed as wear particles. If, as might be the case with the finer abrasives, the presence of the transfer layer inhibits further removal of print then the overall rate of removal may be inhibited by the rate at which the transfer layer breaks up and forms wear particles.

The formation of large wear particles seemed to occur every twenty characters or so during the abrasive life tests in section §4.3.1 and at variable times after a blank space. This suggests that the wear particles are triggered by the build up of print on the transfer layer rather than external influence. In the pauses while the apparatus was shifted to a new row of characters in the abrasive life tests a 'tail' of toner-print was visible on the anti-clockwise end of the toner print that was sticking out tangentially from the abrasive and appeared to be about to form a wear particle.

The repetition tests implied that slightly better print removal might be achieved by making several faster passes with the abrasive rather than one slow pass. It can be supposed that frictional heating will lead to higher average temperatures in the print on the paper during slower passes and this may influence the way that print is moved to and from the transfer layer. There might also be differences in the break up of the transfer layer due to differences in the frequency and amplitude of fatigue cycles as the abrasive moves from letter to letter.

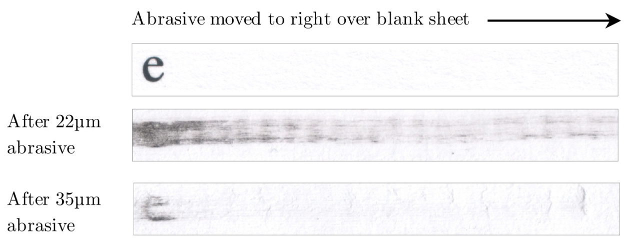


Figure 4.14 The adhesive wear tends to redeposit print back onto the paper

The pigment in the toner used in these experiments, magnetite, has a high hardness. This is likely to influence the way that the transfer layer forms and is broken, but it is not known how. The point of the process is to remove this pigment from the surface of the paper. Unfortunately when it breaks from the transfer layer it may simply move back onto the paper surface. This is particularly visible in figure 4.14 which shows the impact of the abrasive on the blank paper that is just after the end of the letters that are being removed. In the case of the 25 µm adhesive sample there is a clear trail of black print that has been redeposited on the surface. During the course of the repetition experiments different patterns of re-deposition were visible depending on whether the abrasive was moved slowly or in several quick passes. In the quick passes the first pass would tend to smear the print into a continuous black streak with occasional large black fragments pressed into the surface. Subsequent passes would then gradually reduce the blackness of the paper surface, presumably by re-abrading the pigment and depositing it elsewhere. The slower passes tended to deposit less pigment onto the paper during the first pass. Instead, the print was visible as a spray of fine wear particles projected from the contact point between the abrasive and paper. A similar spray of fine white particles of paper is also occasionally visible in these lower speed cases.

Taken together, these issues suggest that the mechanisms of toner wear are complex. Because of this complexity it is unlikely that the abrasive approach used in the evaluation section of this chapter is optimal. The issues create some interesting directions for research. These will be discussed according to whether they relate to the formation, fragmentation or removal of the transfer layer. The possibility of including a feedback and control system to locally vary the abrading characteristics will then be considered.

The issue of increased abrasion of paper while the transfer layer forms at the start of an abrasive run leads to the hypothesis that the abrasive should be pre-coated with a transfer layer before first use. This in turn leads to the hypothesis that a conventional grit based abrasive may not be optimal type of material with which to wear printed paper. It might be worthwhile to explore rubbing with smooth layers of other materials that would not abrade the paper but might have a similar enough surface energy for the toner print to wet against after some frictional heating has occurred (rubbing with a layer of polymer similar to those in the toner might be an interesting candidate). Given the observation that the transfer layers tend to start at or near the join in the abrasive paper where it meets after wrapping around the drum, it might also be worthwhile exploring how the shape of the surface promotes the formation of transfer layers.

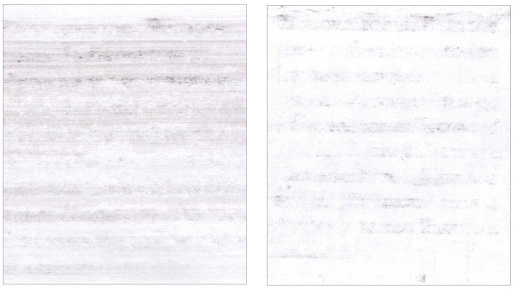
Adhesion between materials is related in part to the local true area of contact between them. The conformity of the sample and the abrasive may influence this contact area and in turn might be influenced by inserting a more compliant backing material under the sample or abrasive. The contact area may also be influenced by the local heating and melting of the toner polymer.

The conventional toner printing process uses a hot press to fix the toner to the paper. To allow the toner to be fixed quickly, toner polymers are usually designed with glass transition temperature in the range 60 to 80 °C and good wetting properties at temperatures just above this point. Pre-heating the abrasive or sample to these temperatures might have a significant effect on the way the wear process operates. Another approach to exploiting this glass transition temperature would be to use friction heating to flash melt the toner-print and remove it by squirting it away from the paper as a liquid. It seems probable that the first stages of flash melting were reached when testing sub 10 μm abrasives at loads of above 2 N for the grit-size against load tests reported in the results above. In these cases after abrasion the abrasive and sample were found to be much hotter than usual and the print had been smeared and embedded in the paper in a glossier and more solid looking way. Unfortunately the test also revealed two potential obstacles in increasing the temperature and viscosity of the print – the paper had yellowed due to the heat in the areas where it had been rubbed and the print had been embedded deeper into the paper rather than being removed.

Pre-cooling the abrasive or sample may also alter the way that the wear process occurs by encouraging brittle fracture in the toner-print. This may alter both the way that the transfer layer forms and the way that it fragments. The fragmentation of the layer may also be influenced by varying the stress cycles to which it is subjected. This could be done by altering the stiffness of the abrasive or its surface roughness. It could also be done on a larger scale by periodically altering the speed, direction and load of the rubbing. Wire meshes have been used as abrasives in order to explore the influence of fatigue in wear. It might be interesting to explore what impact they have on print removal.

A wire mesh might also be advantageous in ensuring that wear particles are removed from the paper surface by trapping them in the pockets between the mesh. Varying the contact area may also influence the way that wear debris is formed and removed. If, as in the case of the tests involving several passes at high speed, the particles are smeared across the paper surface during the first then it seems plausible that subsequent passes might be more effective if they were carried out with a different set of operating parameters (grit size, load, speed) than the first. This would require a basic control system.

A general issue with the adhesive wear of toner print is variability in the removal related to the variation in the amount of print at different points on paper. In the evaluation above, this was overcome by using a set of abrasive parameters that ensured that the worst areas of print were removed. This meant that time was wasted rubbing areas of paper that had already had their print removed, or were blank from the start. It may also mean that more damage to the paper was caused than necessary. Introducing a feedback and control system that could monitor the state of the paper, levels of print and the state of the abrasive might mitigate this. As an example, by using the same abrasive parameters as in the evaluation section but giving the operator the freedom to manually move the sample past the abrasive as desired allowed a cleaner looking sample to be produced in about a third less time (shown in figure 4.15). It should be noted that the sample was still holed on the third abrasive cycle.



The best result using steady abrasion

The best result using manually varied abrasion

Figure 4.15 Adding a manual feedback and control system to concentrate rubbing on the print

Several interesting directions have been discussed. It seems likely that only abrasive situations that occur outside of everyday use (e.g., high speed, high frequency, using sharp contact areas) would need to be considered, as the printer manufacturers have actively sought to ensure that their toner-print remains stuck to the paper in normal use.

4.6 Conclusions

The effects of varying abrasive grit size, material, speed, pressure, duration and number of passes on the removal of toner from office paper were explored. This analysis suggested that grit size, pressure and duration were the most significant parameters. In particular, the damage to paper increases significantly for grits that are larger than 30 µm and decreases significantly for grits that are smaller than 10 µm.

The chapter identified a wear process that removes enough toner-print from a sheet of waste paper for a new layer of print to be clearly legible and that leaves the paper in a condition to survive re-printing. The second layer of print is legible, although the paper is greyer, which may mean it is only suitable for use for draft or internal documents. A second cycle of abrasive print removal can be performed and a subsequent reprint of text is again legible. Unfortunately at this point the paper has been significantly thinned so that any text printed on its reverse will be visible. A third cycle of abrasive print removal will cause the paper to be holed.

The final section of the chapter discussed the mechanisms behind the removal achieved and focused on the potential for encouraging adhesive wear in the toner-print while avoiding abrasive wear in the paper. The mechanisms of this adhesive wear are complex and it is likely that the process identified in this chapter could be improved upon, particularly by considering whether the abrasive grit used could be replaced by a smoother material.

5 Lasers

This chapter answers two questions:

1. Can toner-print be removed from office paper by a laser?
2. Under conditions that remove toner-print, is the paper re-usable?

This chapter is a technical feasibility study. The first section reviews previous work in this area. The second section reports on experiments to quantify the influence of different laser settings on the amount of toner removed. The third section evaluates the re-usability of the paper under the best toner-print removal conditions and the final section discusses the main obstacle encountered.

5.1 Previous attempts to lase toner-print

The four previous attempts to lase print as part of a paper reuse process have not been reported in sufficient detail for the removal performance or damage to the paper to be judged. Related work on the use of lasers in paper conservation and in printing does not allow the performance to be predicted.

5.1.1 *Laser erasing of print*

The review in section §3.1.1 mentioned the early report by Schawlow [44] on using a laser to remove print. The three subsequent patents on lasing toner-print do not provide much performance data.

Niikura *et al.* [45] filed the first patent on the principle of focusing laser radiation onto toner print in order reuse the sheet of paper. It proposes scanning an ND:YAG laser across the top of a toner-printed surface, dwelling where it was blackest, causing the toner print to vaporise. It does not provide any performance data. A variation reported in a patent by Tankovich [46] is to fire a laser through the paper to strike on the underside of the toner. This, the patent suggests, causes a plasma to be formed between the toner print and paper. The plasma expands rapidly, mechanically ejecting the remainder of the toner print from the paper surface. The patent uses a Q-switched ND:YAG laser operating at 1.064 µm for white paper or 0.355 µm for coloured paper, with an energy density of 1.5 to 2.8 J/cm^2. In the example given in the patent the laser beam is shaped into a rectangle 50 by 5 mm and applies 3 pulses on each spot of paper at 200 Hz before stepping on to leave a 50% overlap (i.e., each spot of paper is lased twice). The patent does not report whether the settings work, but hints that 'for enhanced document cleaning' the sheet may need to be placed into a hydrogen peroxide bath after laser processing. This approach has been named 'verso cleaning' and explored in an chapter by Barone *et al.* [141], although it does not present any results for toner-print and the results for ink and pigment based inks suggest only partial removal.

5.1.2 Indirectly related work

Although not aimed at paper reuse, there are reports on lasing printed paper as an approach to paper conservation and as a printing process. However none of these remove toner-print.

The use of lasers to clean objects as part of the conservation process is well established – a recent textbook by Fotakis *et al.* [142] reports their use on stonework, paintings, parchment, textiles and paper. The aims of the conservators differ from the aims of this research in that they wish to leave the original print. For instance Szczepanowska & Moomaw [143], an artwork conservator and a research chemist, used a laser to remove stains created by fungi as they ate paper. They removed certain colours of stain and suggested that the wavelength of the laser was the critical parameter. They also reported that the laser energy rate needed to be kept low so that is was entirely dissipated in the vaporisation of the stain rather than damaging the surface of the paper. They used a 532 nm ND:YAG pulsed laser operating at 1.6 W and 10 Hz. They found that when the laser was used without a focusing lens a 4 mm spot burnt the paper burnt after 1.5 seconds. Rudolph *et al.* [144] further explored how paper is damaged under laser conservation treatments and found greater damage with UV lasers than with those operating towards the infrared.

Lasers are also well-established as a printing process where paper is printed with solid areas of colour, and the print is then selectively removed by a laser to leave white text. For instance Domino Printing [145] market a 10 to 20 W carbon dioxide laser for scribing barcodes, batch numbers and dates onto plastic, metal and paper packaging. Few details are provided by Domino, but they appear to operate their laser continuously rather than in a pulsed mode. More detail is provided by Stewart *et al.*[146] who used a ND:YAG laser to remove layers of print from the surface of a sheet of paper in order to create a 'tactile surface' that could not be be forged using a colour photocopier. They printed four 10 μm layers of print onto the paper using offset and screen printing processes (i.e., not the toner-print widely used in offices). The bottom and third layer were white, the top layer was black and the other layer was cyan. They irradiated the paper at a 1.06 μm wavelength and frequencies of 1 to 30 kHz with a spot size of 0.35 to 0.4 mm diameter. They found relatively good correlation between volume of print removed and energy input. They were unable to ablate the bottom white layer without charring the paper.

5.2 Method

This section describes toner removal experiments that test the ability of a variety of lasers and laser settings to remove print and leave the underlying paper undamaged.

The tests were carried out on samples that had been printed with black text in a 12 point Times font using the printer and paper described in §1.2.4.

In each test the sample was placed at the focal point of the laser, and the laser beam was steered in a series of horizontal lines across the surface. In doing so the laser beam was scanned across both printed text and blank paper, allowing the effect of the laser on each to be gauged. For the basic parameter tests, the scan was restricted to the area around a single printed character. For re-usability tests a larger 9 cm^2 area of text was scanned.

The parameters tested were wavelength, power, pulse frequency, scan speed, line spacing and number of times that the scan pattern was repeated. These represent the principal settings that can be varied on most lasers. Only one parameter was varied at a time over the range shown in table 5.1 and the other parameters set a reasonable default value (also shown in table 5.1). The exception was the tests of varying frequency. In this case the scan speed was also varied in order to maintain a constant spacing of the laser pulses on the sheet.

Removal of print was gauged qualitatively by comparing scanned images of the different samples. The level of damage to the paper was assesed using an optical microscope. To test the overall re-usability of the process the larger samples were lased and then

	Low	Default	High
Wavelength	193 nm	1064 nm	10600 nm
Power	0.5 W	1 W	10 W
Pulse frequency	0.5 kHz	10 kHz	60 kHz
Scan speed	5 mm/s	400 mm/s	
Line spacing	1 µm	40 µm	50 µm
Number of passes		1	32
Spot size		40 µm	

Table 5.1 The range of parameters tested.

re-printed. This cycle of lasing and re-printing was repeated up to five times.

5.3 Results

The results for each parameter are now presented, starting with wavelength.

The laser wavelength was varied by using four different single wavelength lasers: an AR:FR Excimer laser with a wavelength of 193 nm, a frequency tripled ND:YAG laser with a wavelength of 355 nm, a standard ND:YAG laser with a wavelength of 1064 nm and a CO_2 laser with a wavelength of 10600 nm. In each case the full range of each laser's settings were tested to find the optimal performance for that particular laser.

196 nm 355 nm 1064 nm 10600 nm

Figure 5.1 Best result with a laser of a given wavelength.

Longer wavelengths remove more print than paper. Figure 5.1 contains magnified images of the letter 'a' with laser wavelength increasing from left to right. All the print has been removed at 1064 nm and 10600 nm without visible damage to the surrounding paper. However, for the paper area that was covered by text it seems that the paper surface has been altered. For the shorter 355 and 193 nm some print has been removed, but only with significant damage to the surrounding blank paper. The results suggest that there is a greater difference in laser absorption between print and paper at the two longer wavelengths than at the two shorter.

The remainder of this section reports results for the ND:YAG laser. Similar tests were carried out with the other lasers but are not interesting: no parameters were found that removed more print than paper for the UV lasers, and the results for the CO_2 laser were very similar to those of the ND:YAG laser.

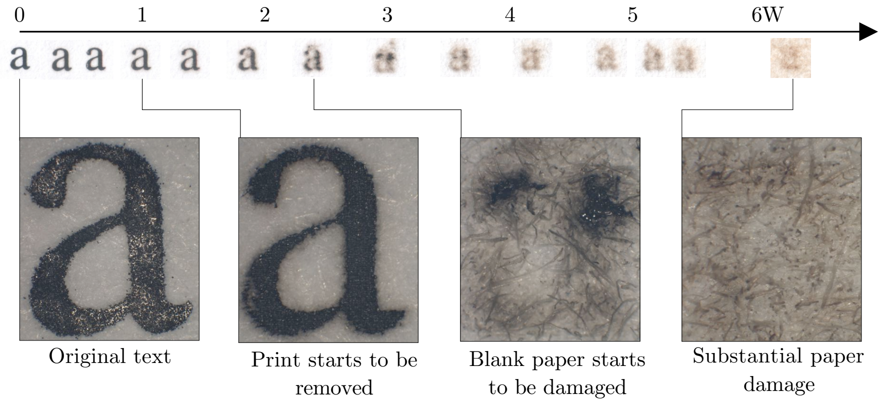


Figure 5.2 Relation between laser power and removal.

There are two relevant power thresholds. Figure 5.2 contains magnified images of the letter ‘a’. The power increases towards the right. There appears to be a minimum power threshold for there to be any visible removal of print. Above this threshold an increasing level of print removal is visible. Above a second threshold there is visible damage to the paper. In the case of the ND:YAG laser the minimum power for removing print is 0.5 W and the minimum for damaging paper is 2.4 W. These are equivalent to power densities of 0.4 and 1.1 GW/m^2 respectively.

Lower laser frequency results in greater damage to the paper. Figure 5.3 contains magnified images of the letter ‘a’. The frequency decreases towards the right. There appears to be a trend of increasing print removal and increasing paper damage with increasing frequency. With this laser, no print appears to be removed when operating the laser in continuous mode. Print starts to be removed at frequencies below 40 kHz. Blank paper is visibly damaged at frequencies below 2 kHz. The area of paper under the

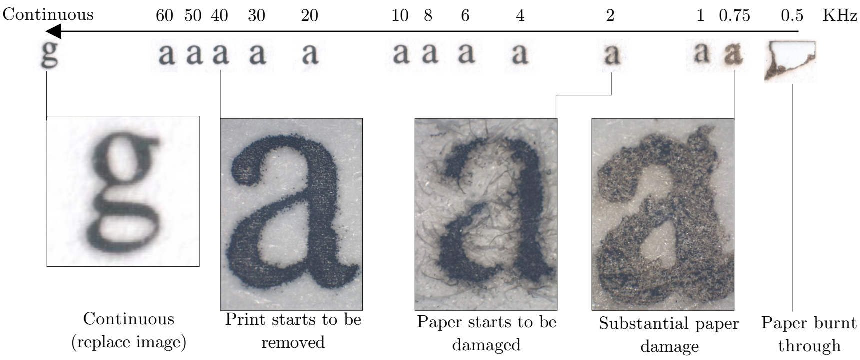


Figure 5.3 Relation between laser frequency and removal.

print generally suffers greater damage than the surrounding blank paper. At 2 kHz charred paper fibres are visible around the remaining print when viewed under a microscope. As the frequency drops further the damage to the paper under the print becomes increasingly severe until the paper burns through at a frequency of 500 Hz.

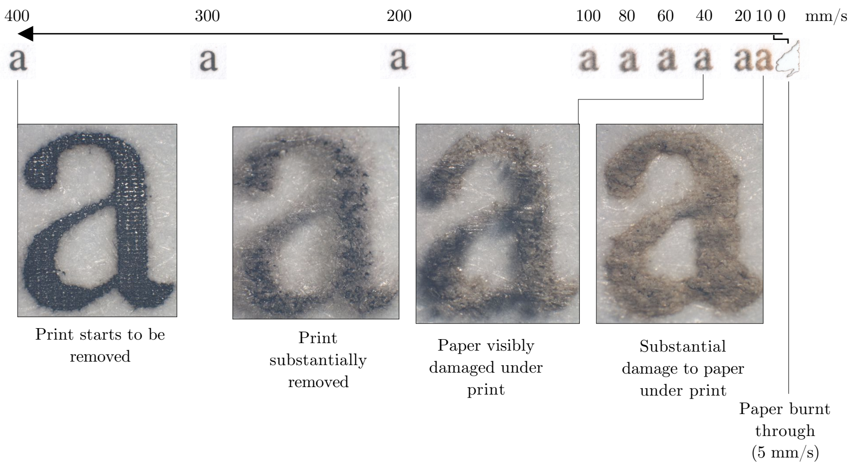


Figure 5.4 Relation between laser line speed and removal.

Decreasing line speed removes print and starts to damage the underlying paper. Figure 5.4 contains magnified images of the letter ‘a’. The line speed decreases towards the right of the graph. There appears to be a trend of increasing print removal and paper damage as line speed decreases. At 400 mm/s some removal of print is visible under a microscope, but not by visual inspection of the text. The text becomes visibly removed once the speed drops below 200 mm/s. Once the speed drops below 50 mm/s the text appears to become blurred and, under a microscope, the paper underneath the print can be seen to be yellowed and burnt. At this point no damage to blank areas of paper was visible. As the speed decreased further the area of paper damage spread out from around where the print was removed. At a speed of 5 mm/s the paper burnt through over an area a few millimeters larger than the printed letter.

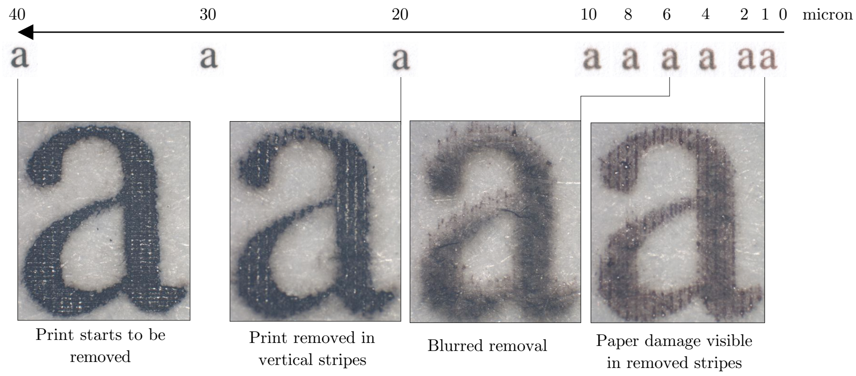


Figure 5.5 Relation between laser line spacing and removal.

Decreasing line spacing removes print and damages paper. Figure 5.5 contains magnified images of the letter ‘a’. The line spacing decreases towards the right. As the line spacing decreases, more print is removed. At a spacing of 10 µm and below the spots of removed print join so the removal appears to take place in vertical stripes (i.e., perpendicular to the direction of the laser scan). As the spacing decreases further the width of these vertical stripes increases, although they do not join. This implies that although the spot size is 40 µm, the laser power is substantially higher in the middle of the spot. Also worth noting is that on occasion (such as the whole of the 6 µm spacing result in the figure and the bottom left of the 1 µm result) the paper is left with a blurred and even coat of black. The cause of this is not known, but it could be linked to the way that the print blocks the laser as it is vaporised.

Repetition removes more print with less paper damage. Figure 5.6 contains magnified images of the letter ‘a’. The repetition increases towards the right. The level of toner removal increases up to the 8th pass with the laser. After that point no extra removal

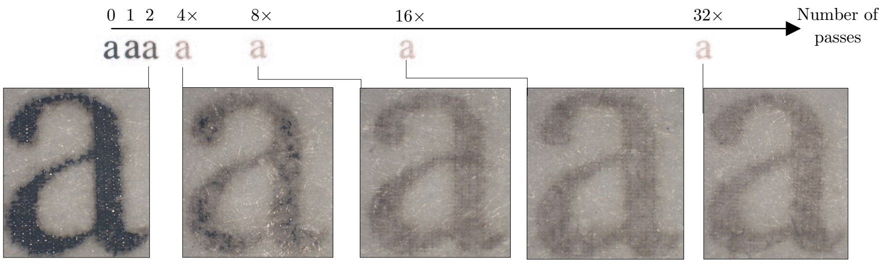


Figure 5.6 Relation between repeating laser passes and removal.

of print is visible. No paper damage is ever visible on the blank areas of paper. The area under a microscope the area under the print appears discoloured rather than damaged and has a slight hint of yellow.

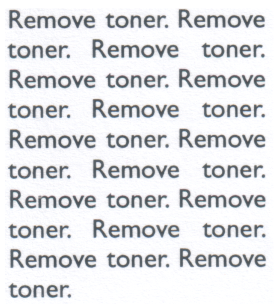
In summary, Longer wavelengths remove print before they damage blank paper but still damage the paper below the text. Print removal and damage to the paper both increase with power, decreasing frequency, decreasing speed and decreasing line spacing. Less damage to the paper takes place during removal if a larger number of passes at a lower power are used.

These tests are limited in three ways: they test only one toner-paper combination – varying the print or paper may yield different results, particularly if the print or paper were designed for the purpose of easy removal; they do not test wavelength entirely independently of other laser properties; the results are presented qualitatively. Furthermore, the results have not been used to test any of the models and theories of laser ablation.

The following section discusses what the tests suggest about the feasibility of using a laser to remove toner and allow paper to be reused.

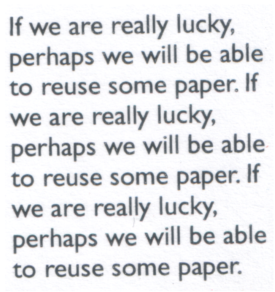
5.4 Evaluation: Print removed but paper is yellowed

To evaluate overall feasibility, the best performing laser parameters from the section above were applied to a larger sample. These were to use an ND:YAG laser operating at a wavelength of 1064 nm with a power of 1.4 W and a frequency of 10 kHz. The laser produced a 40 µm spot that was focused on the paper and rastered across at 400 mm/s eight times. The sample was then re-printed. This print, un-print cycle was then repeated to test the impact of repeated reuses of the same paper.

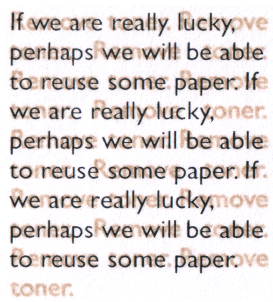


(a) For comparison, sample before first removal

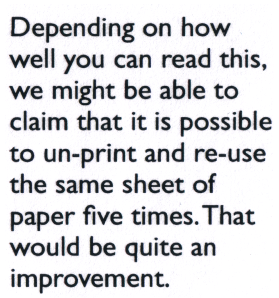
(b) Sample after first removal



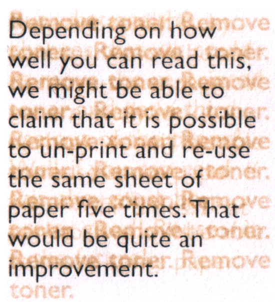
(c) For comparison, this is the text used in re-printing



(d) Sample after re-printing



(e) For comparison, this is the text used in the fifth printing



(f) Sample after and four removals and five printings

Figure 5.7 Removal and subsequent re-printing of office paper

Figure 5.7 shows the results. The images are arranged in order of time, with the left hand column containing images on fresh paper for comparison with the un-printed and re-printed results in the right column.

The results show that the print is always entirely removed. The first question set in the introduction to this research can therefore be answered positively: "Can toner-print be removed from office paper by a laser?". The answer to the second question "Under conditions that remove toner-print, is the paper re-usable?" is more equivocal. The conditions that remove toner-print do not need to damage blank paper but the area of paper under the text is always yellowed. The implications, possible causes and possible solutions to this yellowing are discussed next.

5.5 Discussion: The yellowing effect

The yellowing under the text does not appear to interfere significantly with the quality of the re-printed text, or with subsequent removal passes, but does means that the original text remains readable even after the print has been removed. Furthermore after re-printing it is less comfortable to read the new text because of the reduced contrast with the yellow background and the distracting contrasts between the yellowed and white areas of the paper. This is an obstacle to reuse. The source of the yellowing will be discussed and then possible solutions presented.

The blank paper was not yellowed by laser irradiation, but the paper under the print was. This suggests that the yellowing is a result either of thermal conduction from the toner-print to the paper causing the paper to reach higher temperatures under the print than it did under direct irradiation, or of a light or heat activated reaction between a component of the toner-print and a component of the paper.

Kolar *et al.*[147] and Strlic *et al.*[148] who have sought to understand the origins of yellowing of paper when lasers are used to remove dirt as a conservation technique. Their results seem to imply that the effect is due to higher temperatures under the print rather than a specific chemical reaction between print and paper. This would suggest that a form of paper ageing is taking place. This has been studied by paper conservators and occurs due to oxidation reactions amongst a range of the components of paper. These reactions can be accelerated by heat, moisture, UV light and metallic cations[149]. UV induced yellowing is most relevant for paper that contain lignin. Most newspapers contain lignin but most modern office papers do not (the ones tested in this chapter do not). The iron-oxide pigment in the toner used in these tests is likely to be a source of cations. Furthermore, as the laser passes over the print white sparks are visible which implies that the iron-oxide is being heated to temperatures of perhaps five or six thousand degrees. It is difficult to predict or observe how heat flows from these high temperature pigments into the paper. At the lowest laser pulse frequency tested in section §5.3) the heat flow was large enough to cause the paper to ignite (which suggests a temperature above 230 °C). The yellowing appears visually very different from this burnt paper, which suggests that this is a more complicated chemical reaction than straightforward burning of the surface layer of paper and that the temperature of the surface remains below 230 °C.

There are two generic approaches to the yellowing obstacle: prevent the yellowing, or remove the yellowing after it has occurred. It may not be necessary to prevent or to remove all of the yellow. For the purposes of reuse it may be sufficient to blur the yellowed area so that the original text is no longer readable. The yellowing might be prevented by changing the environment to inhibit the chemical reaction, or by reducing the temperature reached by the paper surface.

Operating in a lower oxygen environment may reduce the ability for the paper to oxidise. A brief experiment where the lasing was carried out in a stream of Argon did not result in any reduction in yellowing. It is possible that more thorough removal of oxygen might result in better performance, but it seems more likely that the yellowing does not require oxygen to occur.

Reducing the temperature reached by the print or the ability of the print to transfer energy into the paper or increasing the cooling of the paper might all result in a lower peak temperature on the paper surface and therefore less yellowing.

If the removal of print operates purely through a process of vaporisation then there is little potential to reduce the temperature reached by the print below that at which its components vaporise. If, however, the removal can be made to take place through a process of ablation or a through a process of ejection then the temperature might be lowered further. Ablation begins to dominate as the laser wavelength is reduced towards the UV. Unfortunately the experiments in this paper have shown that there is not enough difference in absorption between print and paper at UV wavelengths for print to be removed without damaging blank paper.

The print could, instead, be ejected from the surface of the paper by pressure waves created by the laser in either the print, the paper or a third medium (such as water) added to the paper surface. The patent by Tankovich [46] that was discussed in section §5.1.1 is an extreme case of this – the laser was fired through the paper to hit the underside of the print, reportedly projecting it away from the paper. Firing through the paper was attempted in this research, but no removal was achieved. Particles of print were visibly ejected at the lower pulse frequencies reported in section §5.3 but unfortunately at these frequencies the laser also damaged blank paper. Further work on angling the laser and introducing a layer of water over the paper surface might yield more positive results.

The amount of energy transferred from the print into the paper will be a function of the rate of conduction between the two materials and of the time available to conduct. The rate of conduction depends on the printing process and will be difficult to alter. It might be possible to reduce the time available to conduct by shortening the pulse length. This was not explored for this chapter, but femtosecond pulse duration lasers have been proposed as potentially useful in avoiding heat damage when cleaning artworks [142].

Increasing the cooling of the paper relative to the heating could be achieved by reducing the energy in each pass of the laser over the paper and increasing the number of passes. Direct cooling of the paper may also be possible by, for instance, soaking in cold water, although it is unclear whether this would be able to operate effectively against the power of the laser heating.

If these approaches to preventing the yellowing of the paper do not work, a pre- or post-treatment of the paper may prevent or remove the yellowing. Chemical treatments have been developed to reduce the propensity of paper to age for example [150]. It may be worth investigating whether pre-treating with one of these chemicals is sufficient to prevent yellowing. As reported by Strlic *et al.* [148], and confirmed in the experiments in this paper, post-treatment by additional laser passes do not seem to reduce the yellow. Carter [149] identifies a range of chemicals that may be used to ‘bleach’ yellowing.

5.6 Conclusions

The effects of varying the laser wavelength and the frequency, power and repetition of laser pulses on the removal of toner from office paper were explored.

This research suggested that:

- The four tested wavelengths all remove print and the two longer wavelengths can do so without damaging blank paper.
- For a ND:YAG laser with a 40 µm spot and at 10 kHz, toner print is removed at powers above 0.5 W. Blank paper is damaged by powers above 2.4 W.
- For the same laser operating at 1.0 W, print is removed at frequencies below 40 kHz and paper is damaged at frequencies below 4 kHz.
- For the same laser, there is both greater damage to the paper and more print removal if the line speed and spacing are such that more than one laser pulse lands on the same location (in this case if it is less than 400 mm/s speed and 0.04 mm line spacing).
- If the power is kept at 1 W and frequency at 10 kHz in order to prevent damage to blank paper, then it takes eight passes with the laser to remove an entire printed character.
- The area of paper under a printed character is yellowed during the process of removing the character.

The main conclusion of this chapter is that there are a set of laser parameters that entirely remove toner-printed characters and do not damage blank paper.

Unfortunately the results also show that, although blank paper is not damaged, the paper under printed characters is yellowed during removal. This yellowing does not interfere with subsequent re-printing or laser removal cycles. The yellowing does, however, mean that the original printed text remains legible. This has two implications: it makes subsequent layers of re-printed text less legible as the eye is distracted by the original text; it may create concerns about privacy and confidentiality.

The final part of this chapter proposes that this yellowing might be avoided by adjusting the parameters to reduce the time available for heat conduction from the toner-print to the paper.

6 Solvents

This chapter answers two questions:

1. Are there solvents that will dissolve toner-print but not paper?
2. Will dissolving the toner enable office paper reuse?

In answering these questions, the effect of varying three parameters is studied:

1. What is the effect of agitation on toner removal?
2. What is the effect of mixing solvents on toner removal?
3. What is the effect of the volume of solvent on toner removal?

The next section of this chapter briefly reviews the Hansen approach to selecting solvents. Section §6.2 appraises the evidence of previous attempts to remove toner from paper using a solvent. Section §6.3 describes the experimental method used in this research. Section §6.4 reports and section §6.5 evaluates the results of these experiments. There are two important limitations to this research: only a single toner-paper combination has been tested and not all the factors that influence solubility have been investigated. These limitations are discussed in the final section.

6.1 The Hansen approach to selecting sovlents

A simple model of our problem would have three components: toner*, paper and solvent. Either the toner, the paper or both may be soluble in the solvent. The objective is for only the toner to dissolve. This would require that the Gibbs free energy of mixing toner and solvent be negative while that of mixing paper and solvent to be positive. The entropy and enthalpy components of the Gibbs free energy of mixing will be considered in turn to identify what options exist for ensuring a difference of sign when

* The remainder of this chapter will use the short-hand of 'toner' to refer to the toner-polymer (the acrylic or polyester) and 'paper' to refer to the paper-polymer (cellulose).

mixing the same solvent in the same conditions with both toner and paper.

The equation for the Gibbs energy of mixing is:

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{6.1}$$

Where:

ΔG_m is the change in Gibbs free energy upon mixing. A negative value means that mixing is likely to be spontaneous.

ΔH_m is the change in enthalpy upon mixing. A smaller or negative value means that mixing more likely to be spontaneous.

T is the temperature. A larger value means that mixing is more likely to be spontaneous (assuming that the other parameters do not change with temperature).

ΔS_m is the change in entropy upon mixing. A larger positive value means that mixing is more likely to be spontaneous.

Next the change in enthalpy and in entropy are considered in more detail.

6.1.1 *Entropy of mixing*

Considering first the entropy term $-T\Delta S_m$, Flory[151] developed an approximate formula for calculating its value when a polymer is mixed with a solvent:

$$-T\Delta S_m = T\,k(n_s \ln \phi_s + n_p \ln \phi_p) \tag{6.2}$$

Where:

k is the Boltzmann constant.

n_s & n_p are the number of solvent and polymer molecules.

ϕ_s & ϕ_p are the fractions of the total volume occupied by the solvent and by the polymer respectively.

From this it can be seen that higher temperatures and more solvent molecules will tend to increase the entropy term (and therefore the probability of solubility) for both toner and paper. Pragmatically, the number of toner and paper molecules are likely to be variable and unknown. However, if they were not it might be possible that the relative proportions of toner, solvent and paper could be adjusted to minimise the entropy term for the paper-solvent mixture and maximise that of the toner-solvent mixture and therefore bias the solvent to dissolve the toner but not the paper.

6.1.2 *Enthalpy of mixing*

Turning to the enthalpy term ΔH_m, Flory-Huggins approximate formula for polymer-solvent systems is:

$$\Delta H_m = kTn_s\phi_p\chi_{ps} \tag{6.3}$$

Where χ_{ps} is the Flory parameter that depends on temperature and the particular combination of solvent and polymer.

From this it can be seen that a smaller Flory parameter, fewer solvent molecules and a smaller fraction of the total volume occupied by the polymer will all tend to result in a smaller enthalpy term and therefore increased likelihood of spontaneous mixing. The Flory parameter depends on the number, strength and nature of intermolecular forces that arise between the polymer and solvent. It is inversely related to temperature (countering the temperature term in the enthalpy formula above). This implies that the choice of solvent will have an influence on solubility through the types of inter-molecular bonds it will tend to form and through its relative size.

6.1.3 *Practical estimates from material properties*

Taken together the enthalpy and entropy terms imply that a solvent needs to be found that has a smaller Flory parameter χ_{ps} with toner than with paper. It may then be possible to adjust the temperature and volume of solvent so that the Gibbs free energy of mixing is positive for the solvent-toner and negative for the solvent-paper combinations.

Hildebrand *et al.*[152] developed an approximation for χ_{ps} that can be calculated from the properties of the materials alone:

$$\chi_{ps} = \frac{V_p}{RT}(\delta_s - \delta_p)^2 \tag{6.4}$$

Where:

V_p is the volume of a unit of the polymer.

δ_s & δ_p are material-specific Hildebrand parameters and depend on the strength of the material's intermolecular cohesion.

This approximation is based on the assumption that the energy of an intermolecular bond between two substances is the geometric mean of the intermolecular bonds within each substance. It implies that the mixing is most likely when the strength of a solvent's inter-molecular bonds are close to those of a solute. Removing toner is therefore predicated on toner and paper having distinct inter-molecular bond strengths and being able to identify a solvent with an intermolecular bond strength close to that of toner. Hildebrand *et al.* acknowledged that this assumption does not hold when the intermolecular forces are created by polar or hydrogen based bonds. To address this shortcoming, Hansen [153–155] proposed that the Hildebrand solubility parameter could be treated as the sum of three components:

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{6.5}$$

Where:

δ_t is the Hildebrand parameter.

δ_d is the square root of the energy of any dispersion type intermolecular bonds in the substance.

δ_p is a similar measure for any dipole-dipole (polar) bonds.

δ_h is a similar measure for any hydrogen bonds.

The Hanesen parameters, δ_d δ_p δ_h, can be plotted on a three dimensional chart with individual substances appearing as points. The closer two substances are in the space this creates, the more likely they are to be soluble. Hansen suggested a measure, Ro of the distance between two solvents in this space:

$$Ro^2 = 4(\delta_{dA} - \delta_{dB})^2 + (\delta_{pA} - \delta_{pB})^2 + (\delta_{hA} - \delta_{hB})^2 \tag{6.6}$$

He also suggested that a solvent and polymer did not need to match parameters exactly. The polymer-solvent Ro need only be less than some polymer specific distance Ra. This is presumably connected to the entropy term in equation 6.2 above. From this Hansen defined a measure of whether a solvent would dissolve a polymer $RED = \frac{Ro}{Ra}$. If RED is less than one, then the solvent will dissolve the polymer. The Hansen parameters of many common solvents have been published[156;157]. Hansen suggests that mixtures of solvents tend to have Hansen parameters equal to the volumetric average of those of the solvents.

This section has considered the influences of Gibbs free energy of mixing. The level of mixing that actually occurs is likely to be influenced by the availability of routes to mixing, in particular the rate at which the solvent and toner can inter-diffuse. Furthermore, a more accurate prediction of solubility would require consideration of the other components of toner and paper, the way that they interact with each other as well as with the solvent, and the complexities of the resulting changes to enthalpy and entropy.

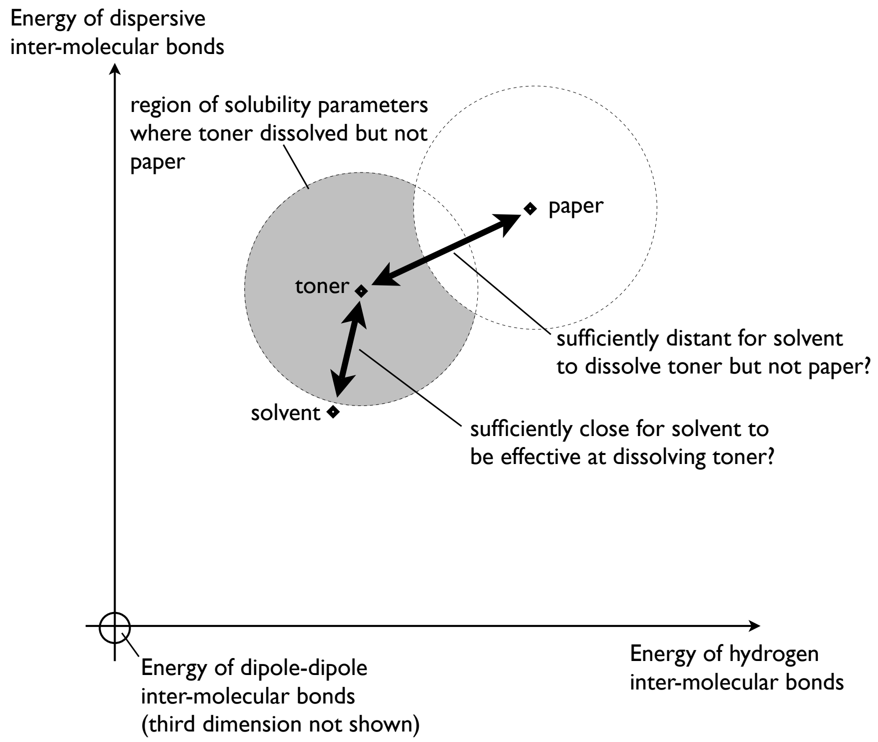


Figure 6.1 Summary of research question, using Hansen model of solubility.

The Hansen plot allows the research problem to be neatly illustrated. Using the Hansen model of solubility, the research question that this chapter addresses is illustrated in figure 6.1: The toner, paper and solvent will each have a set of hansen solubility parameters based on their inter-molecular forces. If they have the same solubility parameter they will be mutually soluble. If they have different solubility parameters, but the difference is less significant than the *Ra*, then they will still be soluble (this is illustrated in the figure by the radius of the circles). The research question is first to establish the solubility parameters that are within circle A, but not in circle B. This will require defining the solubility parameters and *Ra* for the toner and the paper. From the desired solubility parameters, a set of possible solvents and solvent mixtures can be identified that are likely to be able to remove toner without damaging print. Once these solvent and solvent combinations are identified, the potential for improving performance by varying operating conditions such as the volume of solvent, level and type of agitation and local temperature can be explored. From this the practical potential of the process can be gauged.

6.2 Previous work on removing toner with solvents

One academic paper and nine patents provide evidence of previous work in this area. Their implication for each of this paper's research questions are discussed.

6.2.1 Reports on the choice of solvent

The solubility parameters of cellulose have been defined. Those of typical toners have not. Consequently the quantitative difference in solubility, *Ra* has not been estimated. However there is qualitative evidence that the solubility of toner is distinct from the solubility of paper. The evidence of this is reviewed below in chronological order.

The earliest report of removing toner with a solvent was in a case study on the hazards of using photocopiers in a conservation environment: Nicholson [158] mentioned that she was able to use toluene and dimethylethane to remove toner from some valuable historic documents that had accidentally been fed into a photocopier instead of fresh paper.

As reported earlier in sections §3.1.2 and §3.1.4, each of the nine patents that have been filed on using solvents to remove toner propose a different set of solvents, to be used either alone or in combination. None suggest a principal by which to select which solvent would work best. None indicate how the mixing affects removal performance.

6.2.2 *Reports on overall effectiveness*

Section §3.1.4 reported two claims that solvents can remove toner sufficiently for paper to be reused. Machida *et al.*[93] presented a table of six organic-solvent–water–surfactant combinations (reproduced earlier in table 3.1) and claimed that four of the six mixtures resulted in usable paper. Their data does not allow the separate effects of mixing solvents or of adding surfactants to be understood. DeCopier Technologies Ltd claimed that some of their de-inking solutions could entirely remove print. This claim was contradicted by an independent analysis by FBI agents.

6.2.3 *Reports on other operating parameters*

The patents do not specify potentially important operating parameters, such as the volume of solvent used. The patents all suggest agitation but they do not indicate how agitation influences removal performance. Higuchi & Takahashi[52], Orita & Chikui[51] and Yasumasa[53] use ultrasound. Yamamoto *et al.*[92], Machida *et al.*[93;95], and Bhatia *et al.*[96;97] brush or rub the paper surface. Nicholson[158] places the paper on a suction table.

In summary, existing reports give some confidence that toner can be removed using solvents but doubts remain as to how useful the results are, what the most effective operating parameters are, how the parameters relate to performance and whether the processes have been optimised.

6.3 Methods

Six sets of experiments were carried out on the single toner–paper combination described in section §1.2.4. The first set were designed to estimate the solubility parameter of the toner, the second to investigate mixing solvents to vary the solubility parameter and the third to investigate the re-usability of the paper once the toner was removed. The final three sets of experiments explored the influence of mechanical agitation, ultrasonic agitation and the volume of solvent. This section describes the experiments, the next section reports their results.

6.3.1 *Measuring toner removal performance*

Three performance measures were used: a relative and a quantitative measure of toner removal, and a relative measure of reusability.

1. During the early tests, the visible effect of the solvent was slight and uncertain, so a relative measure of removal was used. A 1 cm^2 square of paper, printed 100% black was used as the test sample. After carrying out the test, the sample and solvent were poured onto a piece of filter paper. The solvent was allowed to soak and pass through the filter paper, before both the filter paper and sample were air-dried. The sample was visually inspected for traces of white, and the filter for traces of back. The results were then qualitatively compared with each other rather than placed on an absolute scale.

2. The quantitative removal was based on the resulting whiteness of a black sample. A 1 cm^2 square of paper, printed 100% black was used as the test sample. After carrying out the test, the sample was air-dried and a 600 dpi optical scan of the black surface taken on a conventional flatbed scanner. The level of toner removal was quantified by calculating the mean whiteness of the sample (on a scale of 0-255) of the resulting image. On this measure it was found that an untouched black printed sample has a mean whiteness of 42, and a fresh sheet of paper has a mean whiteness of 252. The whiteness results were then linearly converted into a percentage, with a black printed sample given 0% and a white sheet of paper 100%.

3. Re-usability is closely tied to readability, and was therefore measured qualitatively using a larger 9 cm^2 square of paper that was printed with black text. After the test, the sample was air-dried and a 600 dpi optical scan of the printed surface taken as for the quantitative method above. The sample was then attached to a backing sheet of paper and re-printed with a different text. A scan of the re-printed sample was then taken. The un-printed and re-printed text were then qualitatively compared to freshly printed sheets of the original and new texts.

The re-usability performance is measured using paper printed with black text, representing the typical state of used paper. The tests of the effects of varying operational parameters are done with paper that is completely covered on one side with black print because this makes differences between performance levels more visible and quantifiable. In this way both the typical and extreme states of paper can be explored.

6.3.2 *Test 1: Hansen solubility parameters*

The exact formulation of the toner resin is not known so its solubility parameters were estimated using a variation of the experimental method proposed by Hansen [156]. This interpolates a polymer's solubility parameters based on which solvents cause it to dissolve. In this case, a 1 cm^2 sample of 100% black printed paper was placed in 50 ml of each of the 16 solvents listed in table 6.1 for twenty-four hours at room temperature. The effectiveness of the solvent was then evaluated using the qualitative measure 1 explained in section §6.3.1 above. The solubility parameters of the solvents and their ability to dissolve the toner were fed into a custom program†. The program followed the method described in Hansen [156] and made iterative estimates of the solubility parameters and solubility radius (Ra) of the toner, seeking to maximise the number of tested solvents whose performance would be correctly classified using those values.

The approach used varies from that of Hansen [156] in that a direct measure of solubility is not being made. Hansen recommends that the interaction of the solvent and polymer be examined under a microscope to spot signs of dissolution or swelling. This method looks for an indirect result of the dissolution: black pigment will become detached from the paper when polymer dissolves. However this assumes that the pigment becomes suspended in the solvent once detached from the paper.

6.3.3 *Test 2: Mixing solvents*

Once the Hansen parameters of the toner were estimated, a series of tests were carried out with mixed pairs of solvents in varying propotions in order to explore the effect of varying the effective Hansen parameters of the solvent. The first pair was chloroform and acetone. The second pair was chloroform, and dimethylsulfoxide. In both cases six tests were carried out on 1 cm^2 samples of 100% black printed paper that were placed in 5 ml of solvent, of which between 0% and 100% was chloroform, and then agitated for 10 s with ultrasound.

The level of toner removal was analysed with the quantitative method 2 outlined in section §6.3.1 above. The results were compared to the estimated Hansen solubility parameters of the solvent mixture. These parameters were calculated as the volumetric av-

† A listing of the program is available from the author on request.

erage of the parameters of the component solvents, as suggested by Hansen.

6.3.4 *Test 3: Overall performance*

Overall performance was measured using larger 9 cm^2 square samples of paper printed with black text. These were placed in 10 ml of solvent and agitated for 240 seconds. The solvents tested were water, dimethylsulfoxide, chloroform, dicrloromethane, acetone and mixtures of each. The results were scanned and visually compared to the original sample. The samples were then re-printed with a second layer of black text and compared.

6.3.5 *Tests 4, 5 & 6: The effects of Agitation and Volume*

Once overall performance had been established, three further sets of tests were carried out to explore the effect of ultrasonic and mechanical agitation and of varying the volume of solvent used. In each case the solvents were chosen from those tested above, using one that had been found to be bad at removing toner, two that had been found to be indifferent and one that had found to be good. Performance was measured using the quantitative method 2 outlined in section §6.3.1 above.

To measure the effect of ultrasound, 1 cm^2 samples of 100% black printed paper were placed in 4 ml of solvent for 4 minutes. The jar containing the solvent and sample was placed in an ultrasound bath, operating at 40 kHz and 80 W. The ultrasound was switched on for the final 0 to 240 s of the four minute soak.

To explore mechanical agitation, 1 cm^2 samples of 100% black printed paper were placed in 4 ml of solvent for 60 s. The sample was then removed and rapidly placed face down on a piece of fresh white tissue paper. It was then dragged across the tissue paper until the solvent had dried. This process was repeated on the same sample between one and five times.

To measure the effect of varying the volume of solvent on toner removal, 1 cm^2 samples of 100% black printed paper were placed in acetone for 60 s and agitated with ultrasound. The volume of solvent was varied from $\frac{1}{2}$ ml to 9 ml.

6.4 Results

This section presents the results of each test. The next section uses the results to answer the five research questions. The final section of this chapter discusses the limitations and opportunities of the method and results.

6.4.1 Test 1: Hansen solubility parameters

Table 6.1 Solubility of toner in 16 solvents.

White flecks visible on the sample and black flecks on the filter paper
Acetone
Dimethylformamide
Tetrahydrofuran
Black flecks on the filter paper
Dichloromethane
Diethylether
Ethylacetate
Toluene
Traces of black on the filter paper
1-butanol
Acetonitrile
Chloroform
No visible effect
Dimethylsulfoxide
Ethanol
Hexane
Isopropanol
Methanol
Water

The results of the tests to estimate the Hansen solubility parameters of the toner are shown in table 6.1. In this table the solvents have been grouped according to the visible effect they demonstrated in these experiments, and then organised alphabetically. Of the 16 solvents tested, 3 dissolved the toner polymer and 6 did not. The remaining 7 solvents appeared to have some influence on the toner.

Table 6.2 Best estimates for solubility parameters of toner-polymer

	Fit	δ_d	δ_p	δ_h	Ro
Cellulose*		8.3	8	13.9	17.4
Best guess for toner polymer based on					
10 solvents	1.0	15.3	8.5	6.2	10.5
7 solvents	0.9	16.9	10.1	3.1	9
3 solvents	1.0	16.6	9.9	8.8	5

* Estimate for amorphous cellulose from Hansen [156].

From these results, the estimated Hansen solubility parameters for the toner are $\delta_d = 15.3 - 16.9$, $\delta_p = 8.5 - 10.1$, $\delta_h = 3.1 - 8.8$ and $Ro = 5 - 10.5$. The range is based on whether the best 3, 7 or 10 solvents are counted as being solvents for the toner and is detailed in table 6.2.

No solvents had a significant impact on the paper, therefore the Hansen solubility parameters for cellulose are taken from Hansen [156]. From this Ra, the difference in solubility between the paper and toner was estimated as $16.0 - 20.4$.

The Hansen parameters based on 10 solvents are used for the remainder of this chapter.

6.4.2 *Test 2: Mixing solvents*

Table 6.3 contains the two-component mixtures that are calculated to have Hansen solubility parameters closest to those estimated for the toner above in test 1. The left hand column contains the composition, the middle column contains the estimated solubility parameters, and the right hand columns contain the estimated solubility of the mixture with respect to toner and to paper.

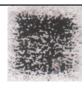
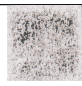
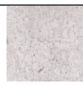
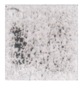
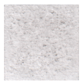
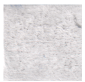
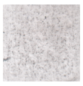
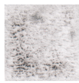
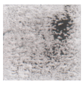
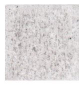
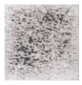
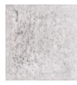
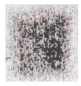
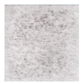
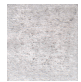
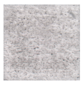
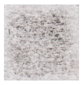
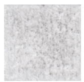
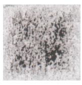
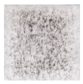
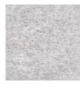
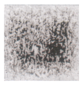
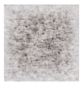
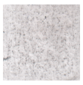
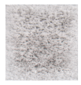
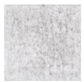
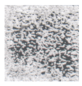
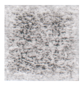
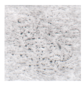
The results of the tests to investigate the influence of mixing pairs of solvents are shown in table 6.4 for chloroform–acetone mixtures. Table 6.5 shows the results for chloroform–dimethylsulfoxide mixtures. The left column lists the proportion of chloroform used in the mixture, with the balance made up of the other solvent. The middle columns list the predicted solubility parameters and solubilities with respect to the toner and cellulose. The right columns

Table 6.3 30 two-solvent mixtures with estimated solubility parameters close to those of the toner, with the constraint that the mixture should not be expected to dissolve the paper.

				RED_e	
Mixture	δ_d	δ_p	δ_h	toner	paper
22% toluene + acetone	16.0	8.4	5.9	0.1	1.0
31% chloroform + acetone	16.2	8.1	6.6	0.2	1.0
57% dimethyl.formamide + hexane	16.3	7.8	6.4	0.2	1.0
30% acetonitrile + tetrahydrofuran	16.4	9.4	7.4	0.3	1.0
49% dimethyl-sulfoxide + diethyl-ether	16.4	9.5	7.6	0.3	1.0
52% hexane + dimethyl-sulfoxide	16.6	7.9	4.9	0.3	1.1
70% tetrahydrofuran + acetone	16.4	7.1	7.7	0.3	1.0
44% acetonitrile + chloroform	16.7	9.7	5.9	0.3	1.1
52% acetonitrile + toluene	16.6	10.0	4.1	0.3	1.1
17% chloroform + ethyl-acetate	16.1	4.9	6.9	0.4	1.0
73% tetrahydrofuran + diethyl-ether	16.2	4.9	7.2	0.4	1.0
49% hexane + acetone	15.2	5.3	3.6	0.4	1.0
25% dimethyl-sulfoxide + acetone	16.2	11.9	7.8	0.4	1.0
36% acetonitrile + dichloromethane	17.2	10.5	6.1	0.4	1.1
18% dimethyl.formamide + tetrahydrofuran	16.9	7.1	8.6	0.4	1.0
88% tetrahydrofuran + dimethyl-sulfoxide	17.0	7.0	8.3	0.4	1.1
53% dimethyl.formamide + ethyl-acetate	16.6	9.8	9.4	0.4	1.0
10% hexane + tetrahydrofuran	16.6	5.1	7.2	0.4	1.0
48% dichloromethane + diethyl-ether	16.3	4.5	5.6	0.4	1.1
2% methanol + tetrahydrofuran	16.8	5.8	8.3	0.4	1.0
99% tetrahydrofuran + dichloromethane	16.8	5.7	8.0	0.4	1.0
99% tetrahydrofuran + isopropanol	16.8	5.7	8.1	0.4	1.0
99% tetrahydrofuran + toluene	16.8	5.7	7.9	0.4	1.0
99% tetrahydrofuran + 1-butanol	16.8	5.7	8.1	0.4	1.0
2% ethanol + tetrahydrofuran	16.8	5.8	8.2	0.4	1.0
2% chloroform + tetrahydrofuran	16.8	5.6	8.0	0.4	1.0
99% tetrahydrofuran + water	16.8	5.8	8.3	0.4	1.0
28% hexane + ethyl-acetate	15.5	3.8	5.2	0.5	1.0
56% dimethyl.formamide + toluene	17.7	8.3	7.2	0.5	1.1
74% dimethyl.formamide + diethyl-ether	16.6	10.9	9.7	0.5	1.0

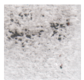
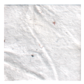
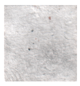
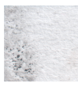
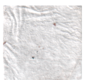
contain a scanned image of the sample and a corresponding measure of the whiteness of the sample.

Table 6.4 Effect on toner removal of mixing chloroform and acetone.

% chloroform	δ_d	δ_p	δ_h	*RED* Toner	*RED* Paper	Ultrasound duration 5 s		10 s		60 s	
100%	17.8	3.1	5.7	0.7	1.2	49%		71%		79%	
90%	17.6	3.8	5.8	0.6	1.2	75%		82%		83%	
80%	17.3	4.6	6.0	0.5	1.2	79%		78%		80%	
70%	17.1	5.3	6.1	0.5	1.1	65%		80%		80%	
60%	16.9	6.0	6.2	0.4	1.1	65%		80%		79%	
50%	16.6	6.8	6.3	0.3	1.1	61%		78%		78%	
40%	16.4	7.5	6.5	0.2	1.0	72%		72%		81%	
30%	16.2	8.2	6.6	0.2	1.0	65%		74%		76%	
20%	16.0	8.9	6.7	0.1	1.0	61%		68%		77%	
10%	15.7	9.7	6.9	0.2	1.0	79%		72%		81%	
0%	15.5	10.4	7.0	0.2	0.9	67%		68%		80%	

Mixtures of two solvents generally had an increased ability to remove toner compared to the solvents alone, but this did not appear to correlate with the increase in solubility predicted by the Hansen solubility parameters. Nor did the removal vary smoothly as the proportion of each component varied. Mixtures of chloroform and acetone resulted in sample whiteness of around 80%,

Table 6.5 Effect on toner removal of mixing chloroform and dimethyl-sulfoxide.

				RED_e		Ultrasound duration	
% chloroform	δ_{de}	δ_{pe}	δ_{he}	toner	paper	60 s	
100%	17.8	3.1	5.7	0.7	1.2	86%	
90%	17.9	4.4	6.1	0.6	1.2	85%	
80%	17.9	5.8	6.6	0.6	1.2	76%	
70%	18.0	7.1	7.0	0.5	1.2	90%	
60%	18.0	8.4	7.5	0.5	1.2	86%	
50%	18.1	9.8	7.9	0.6	1.2	89%	
40%	18.2	11.1	8.4	0.6	1.2	88%	
30%	18.2	12.4	8.8	0.7	1.2	94%	
20%	18.3	13.7	9.3	0.8	1.2	79%	
10%	18.3	15.1	9.8	0.9	1.2	85%	
0%	18.4	16.4	10.2	1.0	1.3	85%	

while some mixtures of chloroform and dimethylsulfoxide resulted in sample whiteness of above 90%.

6.4.3 *Test 3: Overall effectiveness*

Figure 6.2 shows the effectiveness of solvents for removal of toner print and figure 6.3 shows the usability of subsequent re-prints on the cleaned paper.

The best performance of a single solvent appeared to be with chloroform. However, this leaves the original text faintly visible. Better performance was achieved by the two mixtures of solvents, with a 40% chloroform 60% dimethlysulfoxide mixture being particularly effective.

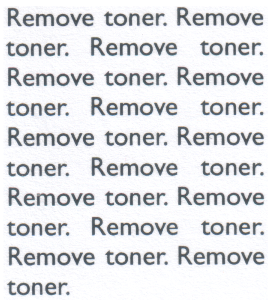
6.4.4 *Tests 4,5 & 6: Agitation and Volume*

The results of the tests to investigate the influence of ultrasonic agitation are show in table 6.6. This table has the four solvents tested across the top organised in increasing order of solubility as estimated in the test 1. Vertically the table is organised according to the duration of ultrasound, increasing downwards. Each cell in the table contains an image of the scanned sample and a number indicating the average whiteness of the sample as specified in section §6.3.1 above.

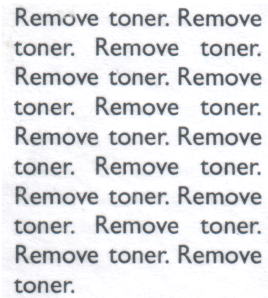
The use of ultrasound improved whiteness. The best removal performance without ultrasound was 12%. The best performance with ultrasound was more than 80%, achieved by using chloroform and 240 s of agitation.

The results of the tests to investigate the influence of mechanical rubbing are shown in table 6.7. Similar to the ultrasound results table, this table has the four solvents tested across the top organised in increasing order of solubility as estimated in the test 1. Vertically the table is organised according to the number of times the sample was soaked in the solvent and then rubbed, increasing downwards. Each cell in the table contains an image of the scanned sample and a number indicating the average whiteness of the sample as specified in the method section above.

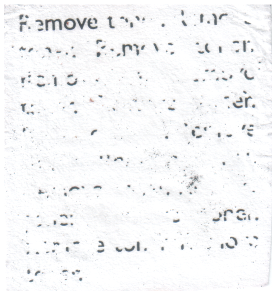
One mechanical rub improved whiteness, but subsequent rubbing did not necessarily result in improvement. The best performance, with a whiteness of 68%, was achieved by rubbing an acetone soaked sample once. Rubbing samples that had been soaked in chloroform or dichloromethane was much less effective, possi-



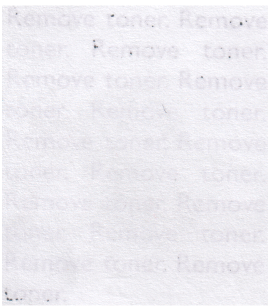
(a) For comparison: original sample.



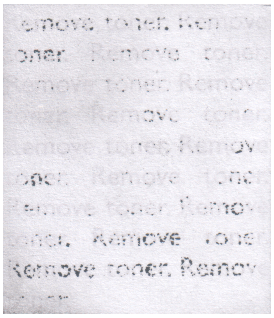
(b) Water



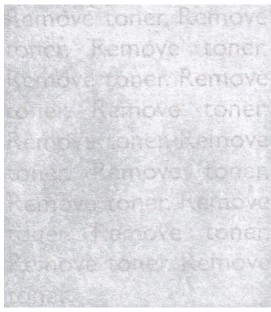
(c) Dimethylsulfoxide



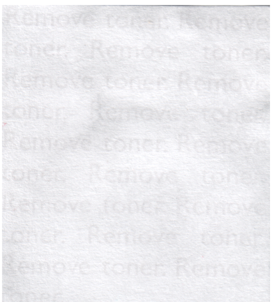
(d) chloroform



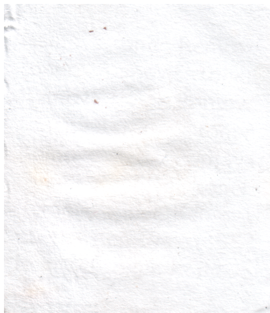
(e) dichloromethane



(f) acetone

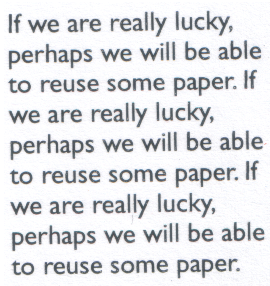


(g) 80% acetone + 20% chloroform

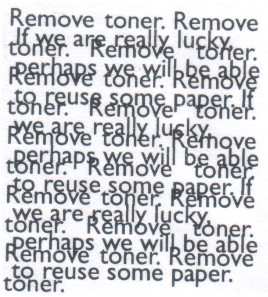


(h) 40% chloroform + 60% Dimethylsulfoxide

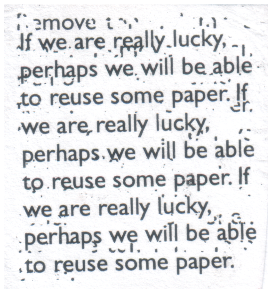
Figure 6.2 Un-printed office paper. b,c non-solvents; d,e,f solvents; g,h mixtures



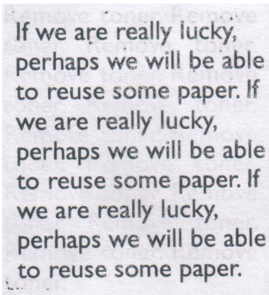
(a) For comparison: text on fresh paper.



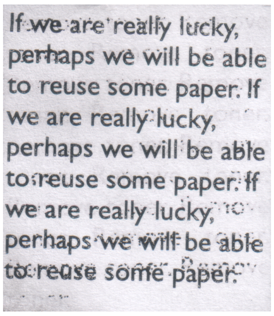
(b) Water



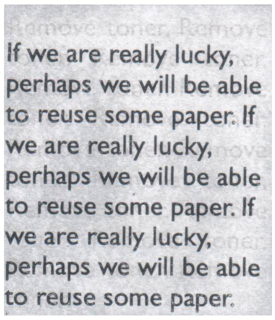
(c) Dimethylsulfoxide



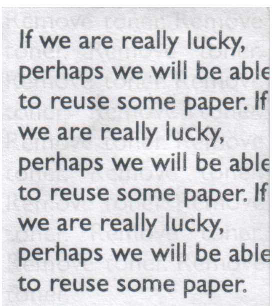
(d) chloroform



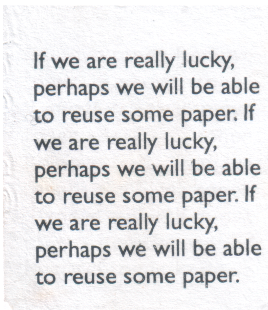
(e) dichloromethane



(f) acetone



(g) 80% acetone + 20% chloroform



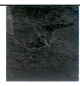
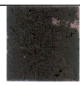
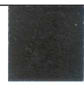
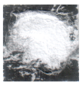
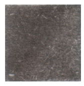
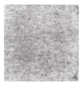
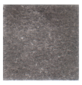
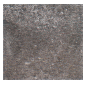
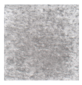
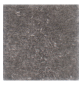
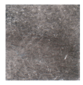
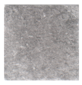
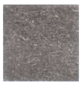
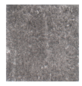
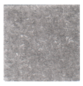
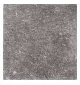
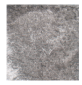
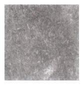
(h) 40% chloroform + 60% Dimethylsulfoxide

Figure 6.3 Re-printed office paper. b,c non-solvents; d,e,f solvents; g,h mixtures

Table 6.6 Effect on toner removal of ultrasound duration.

Ultrasound	Water	chloroform	dichloromethane	acetone
None	3%	3%	5%	12%
1s	12%	33%	43%	40%
3s	4%	40%	64%	44%
5s	4%	64%	43%	37%
7s	4%	58%	62%	56%
10s	2%	77%	52%	64%
15s	7%	80%	53%	56%
30s	10%	83%	66%	71%
60s	4%	86%	83%	74%
120s	4%	83%	75%	74%
240s	2%	82%	83%	78%
For comparison:	Black sample	0%	White paper	100%

Table 6.7 Effect on toner removal of rubbing with tissue.

Number of rubs	Water		chloroform		dichloromethane		acetone	
0	3%		3%		5%		12%	
1	58%		20%		24%		68%	
2	.	*	32%		34%		65%	
3	.	.	31%		34%		55%	
4	.	.	37%		40%		52%	
5	.	.	42%		49%		50%	
For comparison:	Black sample		0%		White paper		100%	

* All subsequent rubs destroyed the sample.

bly because these solvents evaporate from the paper more quickly than the other solvents.

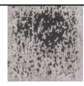
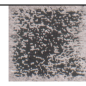
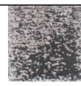
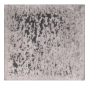
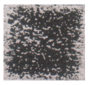
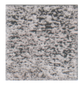
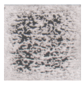
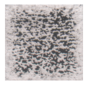
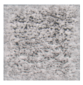
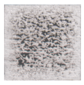
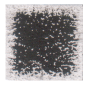
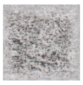
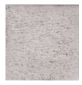
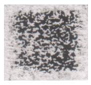
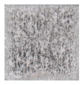
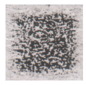
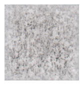
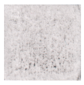
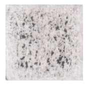
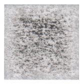
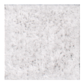
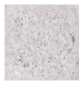
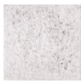
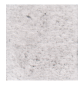
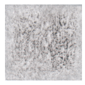
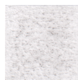
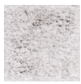
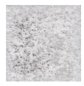
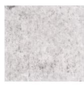
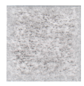
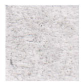
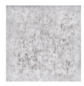
Close inspection of the sample after rubbing suggests that the paper may have been damaged – individual paper fibres were much more visible than when not using agitation or when agitated with ultrasound. The extreme case was water, where one rub was sufficient to remove a layer of paper fibres and subsequent rubs destroyed the paper.

The results of the tests to investigate the influence of solvent volume is shown in table 6.8. The volume of solvent used increases down the table. The cells of the table contain scanned images of the sample and a corresponding whiteness measure.

For chloroform, whiteness of 80% was reached using 3 ml of solvent, for dichloromethane 5 ml was required. A peak whiteness of 78% was also reached at 5 ml for acetone.

The result was checked by repeating some of the tests with a half-size sample. The results of these checks implied that the results above were due to solvent volume rather than influence of

Table 6.8 Effect on toner removal of the volume of solvent used.

Volume of solvent	chloroform		dichloromethane		acetone	
$\frac{1}{2}$ ml	47%		40%		40%	
1 ml	56%		31%		53%	
$1\frac{1}{2}$ ml	63%		58%		62%	
2 ml	65%		40%		62%	
$2\frac{1}{2}$ ml	69%		58%		59%	
3 ml	80%		54%		69%	
4 ml	80%		76%		66%	
5 ml	86%		79%		78%	
6 ml	85%		80%		70%	
7 ml	88%		79%		77%	
8 ml	85%		80%		73%	
9 ml	84%		82%		75%	
For comparison: Black sample	0%			White paper	100%	

a change in volume on the way that the ultrasonic agitation was transmitted into the sample.

6.5 Evaluation

This section will use the results to answer the five questions set out in the introduction, starting with the big questions of whether it is a useful process and then discussing the effect of varying the operating parameters. The next and final section will discuss the overall limitations of this research.

6.5.1 Useful, but not perfect, removal can be achieved

In answer to the first two questions posed in the introduction to this chapter: there are solvents that dissolve toner-print but not paper and useful, but not perfect, removal can be achieved.

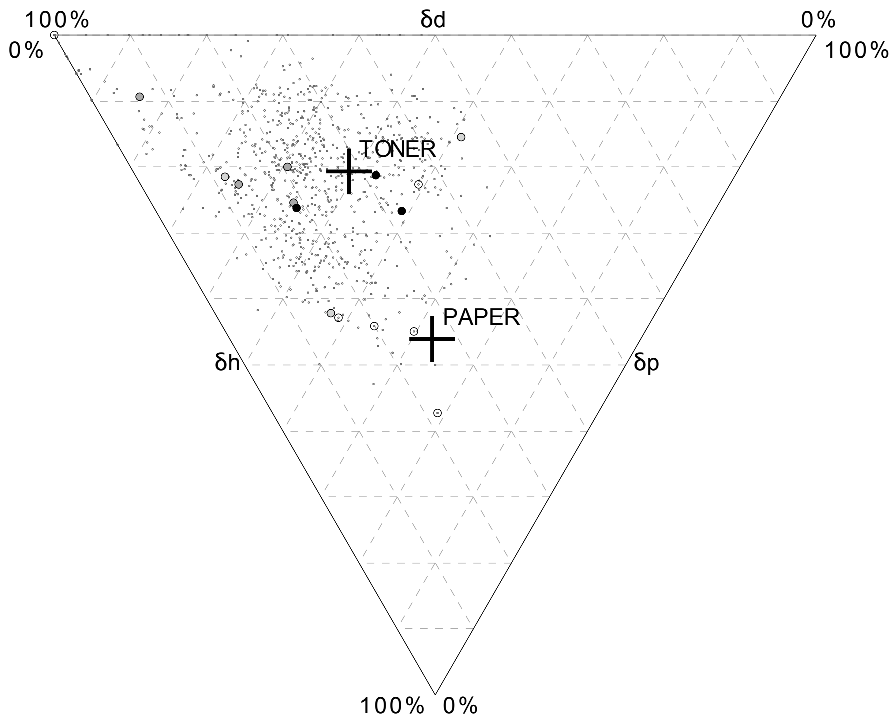
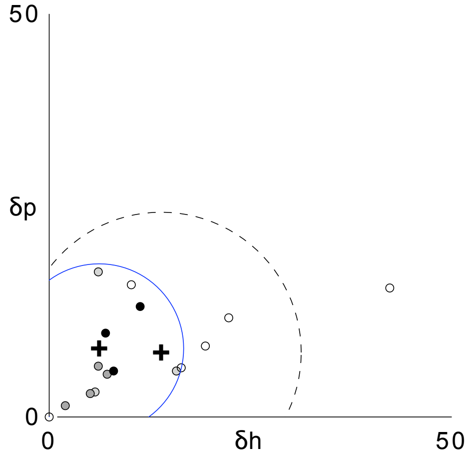
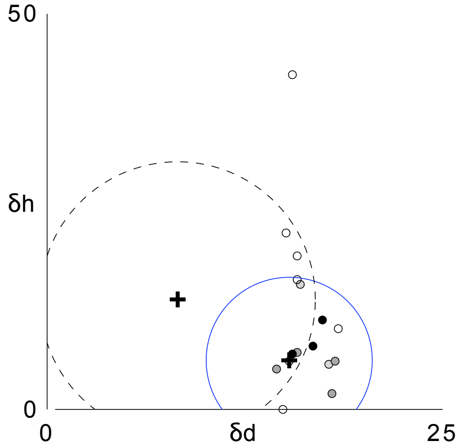


Figure 6.4 Teas chart plot solubility parameters of the toner and paper

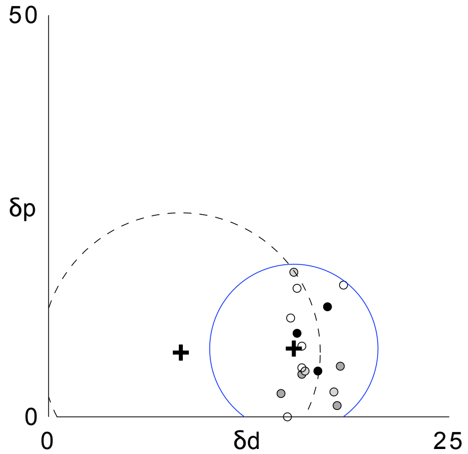
Toner and paper have distinct but overlapping solubilities. The distinctiveness can be seen in the Teas plot of figure 6.4. This



(a) $\delta_h \delta_p$



(b) $\delta_d \delta_h$



(c) $\delta_d \delta_p$

Figure 6.5 Plots of Hansen solubility parameters of the toner and paper shows the relative size of the three Hansen parameters for toner, paper and the solvents tested. Each dot is a known solvent. Each circle is a solvent that has been tested. Filled circles are those that have been found to dissolve the toner. As can be seen, it is likely that forces between toner molecules are created by more dispersive- and less hydrogen-bonds than those between cellulose molecules. This leads to an estimated Ra solubility difference between the paper and toner of $16.0 - 20.4$.

The overlap is visible in the three projections of the 3D Hansen solubility space shown in figure 6.5. The large dotted circle is the radius of solubility (Ro) of the cellulose, the large solid circle is that of the toner. The small circles are tested solvents. Those that have been filled were found to dissolve the toner. The sum of the estimated radii of solubility of the paper (17.4) and the toner (10.5) is greater than the distance between their Hansen parameters ($16.0 - 20.4$).

Taken together, this means that toner can be dissolved without also dissolving the paper. Table 6.9 classifies 896 solvents according to whether they should dissolve the toner, the paper, both or neither. Approximately half of the solvents should dissolve the toner but not the paper. Based on the estimated solubility parameters, 2-ethyl-croton-aldehyde should be one of the best solvents for toner, with a RED of 0.2 with toner and 1.0 with paper. However, this RED value is not a significant improvement on the values achievable by mixing more common solvents such as acetone and chloroform.

Table 6.9 Classification of the 896 solvents according to what they should dissolve

		Dissolves Toner	
		No	Yes
Dissolves Paper	No	139	471
	Yes	21	265

There are sources of doubt in this result: only one toner and paper combination has been tested; there is quite a wide range in the estimates for toner solubility parameters; the analysis does not examine in detail the effect of the solvents on the non-cellulose components of paper and the non-polymer components of the toner.

These experiments have found solvents that can remove one type of toner from one type of paper. It is not known how applicable the result is to other toners and papers. The test should be repeated to estimate the solubility parameters of other toners and papers. The volume of intersection between different toners could then be established. If there is a volume of intersection, and that is distinct from any of the paper Hansen parameters, then it is likely a solvent could be found to operate on a broad set of toners.

The range of estimates for the solubility parameters of the toner has arisen because of the range in volumes of detached pigment when using solvents to remove toner in the test, and the small number of solvents used in testing. The range might be narrowed by testing with further solvents and potentially by carrying out solubility tests under a microscope so that any swelling or dissolution of the toner or paper might be seen directly without relying on the indirect measure of pigment movement.

The solubility parameter for the toner has been based on the solubility of whatever must be dissolved in the toner for the pigment to become detached and then separate from the paper surface. It is presumed that this is the toner polymer, but the nature of the pigment may also be a factor. It has also been presumed in these estimates that cellulose is the only soluble component of the paper. There may be other components of the paper which have been altered or removed by the solvent.

Paper appears to be less soluble than predicted by its solubility parameters. Of the 16 solvents tested, 7 should have have dissolved the paper, based on the estimated solubility parameters of cellulose from Hansen [156]. They did not appear to do so. This suggests that either: the reported parameters are incorrect; the dissolution was not visible; the dissolution was operating slower than for the toner; the Hansen method is invalid in this situation. However, the lack of paper solubility is beneficial to the goal of using solvents to remove toner and therefore reuse paper.

Useful, but not perfect, removal can be achieved. Image h in figure 6.2 shows the best level of removal achieved. This placed the sample in a mixture of 4 ml of chloroform and 6 ml of dimethlysulfoxide for 240 s while applying ultrasound. The removal was not complete and it is still possible to read the original text. However, the original text does not interfere with the reprinted text (image h in 6.3) meaning the paper is re-usable. However, the cleaned sample has a slightly off-white colour, a slightly rougher surface and some ripples when compared to a new sheet of paper. This implies damage to some components of the paper, but this damage does not seem to affect reprinting.

6.5.2 *Optimising the operating parameters significantly improves removal*

Varying the operating parameters significantly improves removal:

1. Agitation is more important than the detailed choice of solvent.
2. Ultrasonic agitation is more effective than mechanical rubbing.
3. Mixing solvents can improve removal.
4. A minimum of $100 - 150$ ml of solvent is needed for effective removal.

Each of these is discussed in turn.

Table 6.6 shows that the variation in toner removal is much smaller between solvents than between levels of ultrasound. Water is the only one of the four solvents whose Hansen solubility parameters (listed in table 6.10) imply no solubility with the toner and therefore the only solvent where ultrasonic agitation appears to make little difference to removal levels. The other solvents have parameters that imply varying degrees of solubility, and once any level of solubility is possible it appears that agitation is critical. This may suggest that the toner polymer has some cross-linking that prevents complete dissolution.

Comparing the results of ultrasonic agitation (table 6.6) and mechanical rubbing (table 6.7) suggests that ultrasound is more effective than this particular approach to agitation. Rubbing visibly damaged the surface of the paper and tended to embed some of the toner's pigment deep into the paper structure. No similar effect is seen in ultrasound.

Alternative approaches to mechanical rubbing may be more effective. In particular, a few trials were made using a brush to flick the toner from the paper surface once it had been soaked in solvent. This tended to result in less damage to the paper and less pigment embedded into the paper but overall was less effective than ultrasound in removing print.

Furthermore, the effect of varying ultrasound frequency, power and the way the ultrasound is coupled to the solvent and paper have not been investigated. Adjusting these parameters may further improve the process.

Table 6.10 Estimated values of RED for the 16 tested solvents in order of decreasing predicted solubility of toner. Starred solvents are predicted to dissolve toner but not paper.

				RED_e	
Solvent	δ_d	δ_p	δ_h	toner	paper
acetone	15.5	10.4	7.0	0.2	0.9
ethyl-acetate	15.8	5.3	7.2	0.3	1.0
tetrahydrofuran*	16.8	5.7	8.0	0.4	1.0
diethyl-ether	14.5	2.9	5.1	0.6	0.9
dichloromethane*	18.2	6.3	6.1	0.6	1.2
chloroform*	17.8	3.1	5.7	0.7	1.2
dimethyl.formamide*	17.4	13.7	11.3	0.8	1.1
acetonitrile*	15.3	18.0	6.1	0.9	1.1
toluene*	18.0	1.4	2.0	0.9	1.4
1-butanol	16.0	5.7	15.8	1.0	0.9
hexane	14.9	0.0	0.0	1.0	1.2
isopropanol	15.8	6.1	16.4	1.0	0.9
dimethyl-sulfoxide	18.4	16.4	10.2	1.0	1.3
ethanol	15.8	8.8	19.4	1.3	0.9
methanol	15.1	12.3	22.3	1.6	1.0
water	15.5	16.0	42.3	3.5	1.9

Tables 6.3 to 6.5 show that the removal of toner can be improved by mixing solvents so as to emulate a solvent with Hansen solubility parameters closer to that of toner. This is also shown by comparing figures c, d and h in figure 6.2. Dimethylsulfoxide alone is poor at removing print, chloroform is better but leaves readable text and a grey surface. Mixing the two results in a white surface with barely readable text.

However, the tables also show that individual mixture's performance does not match that predicted. This could be because the estimate of the solubility parameters of the toner are incorrect or because Hansen is incorrect in suggesting that the mixture performs approximately as the volumetric average of the component solvents.

Table 6.6 shows that removal of toner suffers when the volume of solvent drops below a particular level but does not improve substantially when above the level. This level appears to be dependent on the solvent used. The results imply that at least

$100 - 150$ ml of solvent would be required to clean a sheet of paper that had been covered with the standard 5% coverage of print that is quoted by printer-manufacturers. When phrased as 10 sheets of paper cleaned per litre of solvent this raises questions over the viability of the approach unless the solvent can be reused – a point discussed below.

In summary, these experiments suggest that solvents could be used to remove toner-print in a way that leaves office-paper in an immediately reusable state. The next section discusses the limits of this claim and scope for further research.

6.6 Discussion

This chapter is the first report of a systematic investigation of the use of solvents to remove toner from office paper. For the print-paper combination tested it is possible to remove sufficient print for paper to be reused using a mixture of dimethylsulfoxide, chloroform and ultrasound. However, this result has not been fully validated on other print-paper combinations, the parameters that could be studied have not been exhausted and more data is required to operationalise the process. This section will discuss how to surmount these limitations.

6.6.1 The results must be validated on other toner-paper combinations

The chapter has shown that the Hansen solubility parameters of the toner that has been tested are sufficiently distinct from those of the paper to allow a solvent to be found that dissolves the toner but not the paper. The variation in solubility parameters for other toners and papers requires further exploration. If all toners have solubility parameters distinct from all papers, then it will need to be established whether the solubility parameters of all toners are sufficiently close to each other for a single universal solvent to be found, or whether in practice the paper would need to be immersed in a series of solvents in order to remove all types of toner.

Furthermore, the solubility parameters of the minor ingredients of toner and paper may need to be investigated in detail. In particular it is not known if the solvents remove any paper additives that are critical to the reliability of subsequent reprinting or to the life-span of the paper. This could be done by estimating the Hansen solubility parameters for each common ingredient of paper, using these to estimate which are likely to be removed by the solvent and then discussing the implication of the loss of that component with paper and printer manufacturers.

6.6.2 *The influence of temperature and surfactants has not be explored*

Removing the toner pigment from the paper is a two stage process: first the bond between pigment and paper must be destroyed (in this case by dissolving the toner polymer that attaches it) and second pigment and paper must be separated in location. According to the models discussed in section §6.1 of this chapter, temperature is likely to influence solubility. This has not been explored in this chapter.

Nor has this chapter explored the use of surfactants. Most of the patents that have been filed in this area suggest that a surfactant is mixed with the solvent, presumably to help with the second stage of separating the pigment from the paper once the polymer is dissolved. Improving this separation has not been explored in this chapter. It seems likely that surfactants, solvent circulation and the introduction of electrostatic or magnetic attractors might lead to better separation, and hence a whiter appearance for the cleaned paper.

6.6.3 *There are practical challenges*

Even though a solvent mixture has been found that is effective at removing a toner without damage to the paper, there are two practical challenges to using this method outside of the laboratory: solvent safety and solvent recycling.

The most effective removal was found to be an chloroform-dimethylsulfoxide combination. If the process is carried out industrially at a central plant then use of these solvents is probably acceptable. If the aim is for a process that could be used at an office level, perhaps by integrating a removal process into an office photocopier, printer or recycling bin then chloroform is unlikely to be considered sufficiently safe for use. A safer alternative would need to be found. This may be possible by analysing the solubility parameters of benign solvents to find those which fall within the *Ro* of the toner estimated in this chapter.

The results of experiment 4 above imply that a litre of solvent will be required to remove print from about 10 pages, a volume that is likely to make the process uneconomic and potentially damaging to the environment. Solutions could be to alter the process to use less solvent or to reuse the solvent. An alteration to the process that might be researched would be to replace the solvent bath with a jet or spray of solvent (combined with other forms of agitation). To reuse the solvent, two barriers would need to be overcome: The first barrier to reuse will be to remove the pigment from the solvent. This is probably easily done on the basis of size or density. The second barrier will be to remove the polymer from the solvent once the solvent has become saturated. This will presumably require the solvent to be evaporated and re-condensed, leaving the polymer behind. This evaporation and condensation may cause further safety challenges and may require too much energy for reuse to be a viable alternative to conventional paper recycling. Such challenges could be reduced by selecting a solvent with an evaporation temperature as close as possible to room temperature.

In summary, there are both practical challenges and scope for further improvement in removing toner-print from paper with solvents, but the essential principle appears plausible: print can be dissolved without damaging the paper and, so long as ultrasonic agitation is used, the resulting paper can be readily re-printed and reused.

7 Feasibility

This chapter draws together the three experimental chapters by comparing their feasibility. The feasibility is split into operational, environmental and cost performance and scope for further improvement. The analysis in this chapter is approximate. The calculations are intended to give a sense of the feasibility of the processes studied in this thesis and therefore how worthwhile further research in this area might be.

7.1 Operational performance

This section will compare the ability of the three approaches to remove print and the level of damage to the paper that results. The speed and safety of the processes will then be considered.

7.1.1 Removal of print

Figure 7.1 shows samples of text that have been un-printed by each of the three approaches. All three approaches have removed the majority of the print. The text that is visible in the laser approach is not print but yellowed paper. The text and marks that are visible in the abrasive approach are, however, print that has not been entirely removed. All three approaches can be reused.

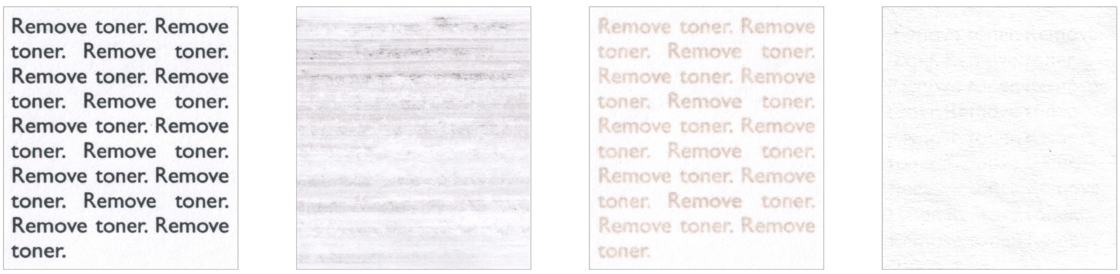
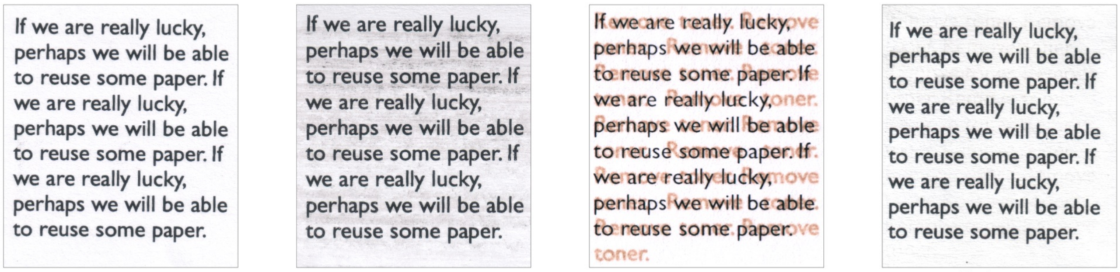


Figure 7.1 Toner removal performance of the three approaches.

7.1.2 *Usability when re-printed*

Figure 7.2 shows each of the samples after they have been passed through the printer for a second print. Although all of them have slight defects (principally spots where the toner has not stuck) they are broadly similar and the text in each case is legible.



Re-printed text | Abrasive | Laser | Solvent

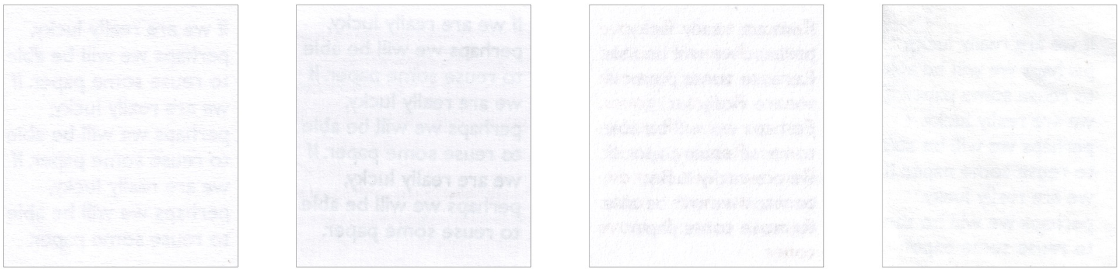
Figure 7.2 Re-print performance of the three approaches.

All three samples are recognisable as differing from virgin paper. However, on their first reuse cycle they all function effectively and could be considered, to a greater or lesser extent, as viable substitutes for fresh paper. The least viable is the lased paper because the original text is readable – which is likely to raise issues of security and privacy as well as legibility of subsequent prints.

7.1.3 *Damage and limits to reuse*

Looking again at figure 7.1, the most obvious damage is caused by the laser. Here the paper directly under the lettering has been yellowed, rendering the original meaning clear even without the print. The damage to the solvent treated sample is also visible – it has wrinkled slightly as it has dried. Although difficult to represent visually, the texture of the three samples has also changed. The abraded sample has a smoother surface, the lased surface is rougher where the paper has yellowed and the solvent sample is slightly stiffer and rougher. This might be expected to result in variation in the quality of re-printing.

Although the laser damage is the most visible, it causes less problems than that caused by the wear process. The abrasive process results in a visible thinning of the paper which can be seen as a slightly greater readability of text when viewed through the paper from the wrong side in figure 7.3. All the samples can be



Re-printed text Abrasive Laser Solvent

Figure 7.3 View from the reverse of the sheet showing change in opacity.

un-printed and re-printed a second time with the same techniques. The thinning of the abrasive paper means that it is likely to cause feeding difficulties after the second print and will be unusable on the third cycle. The yellowing of the lased paper is slightly visible from the other side of the sheet in figure 7.3 (for instance, the word 'toner' is visible on the bottom line). After five cycles of un-printing and re-printing this yellowing has become very visible. The solvent treated paper has been tested through two cycles of printing and print removal and there are no obvious limits to the number of times this could be repeated. The effect of the processes on the longevity of the paper has not been tested.

7.1.4 *Speed & Scalability*

The time taken for each experiment to remove the print from each of the larger 9 cm^2 samples was similar and lengthy. An important question is how these speeds would scale to A4 sheets of paper, and how the scaled speeds would compare to the capital cost of the process. The scaling is estimated in table 7.1 and will be discussed here, the capital costs are discussed in section §7.3.2 below.

Table 7.1 Estimates of the speed and scalability of the three approaches

Speed (minutes)	Abrasives	Lasers	Solvents
Experiments on a 9 cm^2 sample	5	8	4
Scaled up to an A4 sheet	347	520	277
Potential best for an A4 sheet	1	1	4

The abrasive experiments took five minutes, the laser experiments took eight minutes and the solvent experiments took four minutes to remove the print from the 9 cm^2 sample. Linearly scaling these rates to estimate the time to remove print from the 624 cm^2 of an A4 sheet gives times that range from 4 to 9 hours. Fortunately each of the processes can be made quicker than their current experimental form.

The rate of the abrasive process is limited by the contact area between the abrasive and the paper and the time spent rubbing each spot. The experimental apparatus has a 2 by 6 mm contact area, and each spot is rubbed in six passes for a total of 6 seconds. The contact area could be increased so that the abrasive drum rubs a 2 mm width over the length of an A4 sheet. This would reduce the total time to just under 7 minutes. If six rollers were used in parallel so that only one pass were made then the total time could be reduced to just over a minute.

The laser process scanned a spot across the sample eight times at 400 mm/s with a line spacing of 40 µm. On average only 5% of the area of a sheet is printed (this is the figure quoted by printer manufacturers and appears to be valid when checked anecdotally). If the laser could be targeted at the print, and be made to move instantly across blank areas, then it would take half an hour to clean an average sheet. If the spot size was doubled (with a corresponding doubling in power, line spacing and line speed) then this time could be halved. Given a maximum wall-plug power draw of 3 kW and a laser wall-plug efficiency of 5%, the laser power could be increased by perhaps two orders of magnitude. If this permitted the spot size to be similarly increased then the time to clean an A4 sheet would also drop to of the order of a minute.

The solvent process placed the sample in a solvent mixture in an ultrasound bath for four minutes. It is likely that this could be easily scaled to clean A4 sheets in the same time by using a bigger ultrasound bath and more solvent. It is also possible, given the significance of the ultrasound on the cleaning, that using a more powerful ultrasound could cut this time further. Furthermore, the bath could be expanded so it could clean several (perhaps hundreds) of sheets simultaneously.

For comparison, the average daily paper office paper use of 5 to 30 sheets per person estimated in the introduction of this thesis (§1.2.1) is equivalent to a maximum rate of one sheet every half hour. This means that an un-printing process that could remove toner from an A4 sheet every five minutes could be placed next to a small laser printer serving six people and if it could remove toner from one sheet every minute it could be placed next to a small photocopier serving thirty people. The processes could only be placed in an office environment next to the photocopier or printer if they were safe, this is discussed next.

7.1.5 *Safety*

The experiments were sufficiently safe to be carried out in standard engineering laboratories. The level of safety required for an office environment is likely to be much higher. This subsection considers the hazards and the ways they might be mitigated.

The wear process relies on high speed rotating parts. However these can be relatively small and therefore the kinetic energy could be contained easily. There are also likely to be hazards relating to trapped fingers, but these are probably no more significant than for an office paper shredder.

The lasing system relies on a high power laser operating outside the visible wavelength. As such it is a 'class 4' laser and subject to stringent health and safety requirements. However, the shielding for such lasers is well developed for use in industrial applications and so a version can probably be introduced safely into an office environment.

The solvents used in the dissolution approach are not safe for office use. The system would have to be completely sealed to prevent their escape. To reuse the solvents a distillation system would also need to be added – further adding to the safety implications. However, as mentioned in section §6.6, it may be possible to rapidly identify safer alternative solvents using the Hansen Solubiltiy parameters of the working mixtures.

7.2 Environmental performance

The broad potential for un-printing to reduce climate change gases from office paper was assessed in chapter §2. That assessment was based on the existing 'e-blue' un-printing system that is available on the market. This section provides a brief assessment of the energy impact of the three approaches that are reported in this thesis. The section is split into two parts: energy use and pollution.

7.2.1 Energy use

Energy use can be divided into direct energy consumption and embodied energy in consumables. The former is relatively straightforward to estimate. The latter is not. Unlike the e-blue system, it is not certain that that the three experimental reuse approaches will offer significant energy savings over the conventional paper process.

Table 7.2 Comparison of the energy use of the three approaches

	Conventional paper		Reused paper		
Per A4 sheet	Virgin	Recycled	Abrasive	Laser	Solvent
Direct energy (kJ)	200	100	110	120	50
Embodied energy (kJ)	?	?	?	?	180

Based on data from the Paper Task Force [20] a sheet of A4 paper takes approximately 200 kJ of energy to manufacture, and approximately 100 kJ to recycle (excluding the solar energy used by the trees).

For the abrasive process, the critical energy assumption is the power required for the motor. The loads are low, so if we assume each roller requires a 100 W motor, then roughly 40 kJ of wall plug energy would be needed to rub a side of A4. When combined with an approximate UK grid energy efficiency of 38% [159] this implies perhaps 110 kJ of primary energy – equivalent to paper recycling. However, where paper recycling requires 100 kJ to clean a sheet of A4, the abrasive process would require this much energy per side.

For the laser process, the critical assumptions are the efficiency of the laser and the proportion of the page that is lased. The sample produced in §5.4 was done at an average power of 1.4 W, which implies 44 kJ of laser energy if an entire sheet of A4 is lased eight times or 2 kJ if the lasing could be restricted to the 5% printed area. Assuming the laser has a typical 5% wall plug efficiency [160] and the electricity grid has 38% efficiency lasing a side of A4 paper would need 2 300 kJ if the entire side and 120 kJ if only the typical 5% is lased. This is again of the same order of magnitude as an conventional recycling, but once again applies per side of A4 rather than per sheet.

For the solvent process the direct energy input is the ultrasound which is currently operating at unit80W for the 4 minutes of soaking. This is equivalent to a primary energy of approximately 50 kJ. This is half the energy required for conventional recycling.

However there is likely to be a significant embodied energy in the solvents.

There are no estimates of the embodied energy in the infrastructure required to create and recycle paper. Similarly, there are no estimates for the embodied energy in abrasives, lasers or solvents. The embodied energy is likely to be significant. For example, in order to clean the toner from the solvent in order to allow the solvent to be reused it would need to be distilled. In the current experimental system each A4 sheet would use a tenth of a litre of solvent. Distilling this much DMSO:Chloroform mixture would require at least 180 kJ of primary energy. Experiments have not been done on how much cleaning the solvents would actually require, but this emphasises the importance of establishing the potential.

The environmental reason for considering energy consumption is the tendency for energy production to be linked to emission of climate change gases. As discussed in section §2.4, estimating the climate change gas impacts of the approaches will depend on the direct energy, the type of fuel used to provide the direct energy and non-energy emissions (principally from the landfill of waste paper). For the discussion of feasibility here it is worth mentioning that half the energy for a typical virgin paper process comes from effectively CO_{2e} neutral wood and that some of the energy for a typical conventional paper recycling process will come from effectively CO_{2e} neutral waste paper. Since in most countries grid electricity is more than 50% generated from oil and gas it implies that to make a reduction in climate change gas emissions the energy from the reuse process would need to be less than the conventional recycling approach. It is not yet possible to be confident that this would be the case.

7.2.2 *Pollution*

It is also difficult to be confident about the relative performance of the approaches in terms of environmental impact from non-energy pollution.

Non-energy pollution from using abrasives is mainly in the waste abrasive. This may be slightly worse than the volume of landfill occupied, since the glues in the abrasive may have polluting products.

Non-energy pollution from using the laser is in the disposal of the laser. The laser may contain heavy metals that will require careful treatment in the waste stream and rare materials for which no recycling processes have been developed.

Solvents that escape to air or water are likely to be considered as pollution. Separate from the human health risk discussed above, smaller concentrations may be toxic to wildlife. This is most likely if waste solvent is not disposed of carefully and if no efficient solvent reuse process is developed.

This pollution from these three approaches should be compared to the pollution from conventional office paper production and recycling systems. The conventional office paper production system is not benign. Muthukumara & Wheeler [161] estimated that pulp and paper was the 3rd most significant industry in terms of water pollution per unit output out of 72 industries analysed in the 1990s, and 5th in terms of air pollution. Life cycle analyses, such as carried out by the Paper Task Force [20], sustainability assessments, such as carried out by Grieg-Gran [162 163], and best practice documents, such as produced by the EIPPCB [21], indicate that water pollution occurs from pulping chemicals and waste water from the paper-making process. Air pollution occurs mainly in the energy generation to power both processes and slightly from the recycling of the pulping chemicals. Recycling eliminates the pollution from the pulping stage but leaves the solid and liquid waste from the pulp cleaning processes. In the case of office paper recycling, about 40% of the incoming paper mass becomes waste.

The pollution considerations are also made more complex when the forests that are used in paper-making are considered. The forestry process is not entirely benign. But paper-making does support forests which are considered beneficial to the environment. The impact of using a reuse technology, or even of increasing recycling, on the forests is difficult to predict but may be critical in the overall effect on the environment.

7.3 Cost

A sheet of office paper typically costs one or two euro cents. Table 7.3 contains very approximate estimates of the cost of the three experimental processes. This section explains the estimates, which are divided into consumable, capital and energy costs.

Table 7.3 Estimate of approximate cost per sheet

	Abrasive	Laser	Solvent	
Consumable Cost	50	5000	50	euro
Consumable Life	1300	20000	1000	A4 sides
Capital Cost	1000	20000	2000	euro
Capital Life	100000	100000	100000	A4 sides
Cost per sheet				
Consumables	4	25	5	euro cent
Capital	1	20	2	euro cent
Energy	1	1	2	euro cent
Total	6	46	9	euro cent

7.3.1 Consumable cost

For the abrasive process, the key consumable cost assumption is how often the abrasive needs to be replaced. In the experiments the abrasive was replaced after rubbing the equivalent of 3 m of print and had a surface area of 2.5 cm^2. Using an equivalent replacement cycle, a hundred A4 sheets of abrasive could be used to rub clean 1300 sides of A4. Assuming a cost of 50 euros for a hundred sheets gives a cost per sheet of 7 euro cents.

For the laser process, the key consumable cost assumption is the life and cost of the laser lamp. A typical life for an industrial laser system might be 10 000 hours, during which time it could lase 20 000 sheets. The typical cost of a lamp is not known, but if we assume it is a quarter of the total laser cost (discussed below) then the cost per sheet would be 25 euro cents.

For the solvent process, the key consumable cost assumption is how often the solvents need replacing. If we assume that there is an effective solvent recycling process that loses only 1% of the solvent on each pass, then a litre of the solvent mixture would be required for every 1000 sheets. The solvent mixture currently costs 50 euro a litre which works out as 5 euro cents per sheet. If no solvent recycling process was in place then a litre would be required every 10 sheets, equivalent to 5 euros per sheet.

The consumables appear largest cost for each of the processes. The potential for lower consumable costs is discussed in section §7.4 below.

7.3.2 Capital cost

For the abrasive process, the capital costs are likely to be low. It will require a paper feed mechanism and a motor to drive the abrasive wheel. Its cost is therefore likely to be comparable to a mid-range printer (estimated here at 1000 euros).

For the laser process, the capital cost is likely to be much greater and has been estimated here at 20 000 euros based on the cost of a basic ND:YAG laser system.

For the solvent system, the capital cost is likely to be higher than for the abrasive process, but less than the laser system. The basic solvent bath and ultrasound will not be expensive, but the distillation unit probably will be. A rough estimate of 2000 euros has been made.

In each case the life of the capital equipment is estimated to be 100 000 sheets – equivalent to three years of 10 people using 30 sheets a day. During this time all three processes are expected to require consumables as outlined in the section above (abrasives, laser flash lamps and solvents).

The capital cost is just under half of the cost per sheet of the laser process but less critical for the other two approaches.

7.3.3 Wall-plug energy

The cost of energy has been estimated from the primary energy estimates in section §7.2.1, adjusted to wallplug energy using the UK grid energy efficiency of 38% and then multiplied by an assumed cost of 0.3 euros per kWh. In the case of the abrasive and laser processes, the cost is approximately 1 euro cent per side of A4 cleaned. The energy required to distil and therefore reuse the solvents has been included in the solvent process, giving a larger energy cost of 2 euro cents per sheet.

7.3.4 Cost Comparison

The cost of the abrasive process is of the same order of magnitude as a sheet of new paper. The solvent process is a third more expensive and the laser process are an order of magnitude more expensive. Furthermore, as with the energy analysis, the costs are per side of A4 sheet whereas a new sheet of paper costs 2 euro cents for two clean sides.

The estimates help emphasise the importance of research to improve the cost effectiveness of each approach. In the case of abrasives attention should be focused on the life and cost of the abrasive material. In the case of the laser it is the cost and life of the laser itself (particularly the flash lamp). In the case of the solvents the emphasis should be on the efficiency of the solvent recycling process.

7.4 Scope for improvement

None of the processes are feasible replacements for paper in their current form. In particular the environmental benefit does not appear large and the quality of the un-printed paper is, at best, only just comparable to low quality office paper. This section contains speculation about the potential for improving the performance of each approach.

7.4.1 Abrasive process

Approaches to improving the performance of the wear process were discussed in section §4.5. It was suggested that better performance could be achieved by exploring the use of smoother non-abrasive rubbing surfaces, by varying the temperature and by introducing a control system. In particular, it seems probable that the whiteness of the surface of the paper can be improved although possibly not the number of times the underlying paper can be cleaned before it becomes to damaged to be reused.

The energy performance of the system depends on reducing the power required by the motors and reducing the time the motors spend running. It seems likely that the motor power could be halved by spinning the abrasive at 3 rather than 6 m/s – the difference in removal between those two speeds was not found to be significant in section §4.3.1. The time spent rubbing could be reduced by using a control system that incorporated feedback as to the level of remaining print. This could at least halve the area rubbed by avoiding entirely blank areas. Furthermore, in manual trials of varying the amount of time spent rubbing according to the amount of print remaining, the average rubbing duration was halved. Taken together this would offer the chance of a factor eight reduction in energy. This would offer energy savings of 80% compared to conventional recycling.

The cost performance of the system depends on reducing the frequency with which the abrasive needs to be changed. The limits of this have not been evaluated, but given the stability of the transfer layer in the abrasive life experiment reported in §4.3.1 it seems plausible that this could be doubled. This would make the abrasive process only twice as expensive as new paper and of the same order as the typical cost of printing. If, as mentioned in section §4.5, the abrasive were replaced with a metal surface then it might be possible to extend the life still further and possibly introduce a cleaning process to remove excess print. This might eventually allow the cost to become comparable with new paper.

7.4.2 *Laser process*

The performance of the laser process would be improved if the yellowing of the paper under the text could be avoided. Approaches to this were discussed in section §5.4. The most likely possibility (a shift to using shorter pulse lasers) would also be expected to increase the cost of the approach.

The energy performance of the system depends on increasing the efficiency of the laser. ND:YAG lasers currently have a typical maximum efficiency of 8% at which point the laser system would use 20% less energy to clean one side of A4 than the energy needed to recycle a sheet of paper. If the laser efficiency reached 12% then the process would be preferable to conventional recycling even for sheets that have been printed on both sides. Semiconductor lasers have been developed with efficiencies of 20, 30 and 40%. If an appropriate laser of 40% efficiency could be developed then the laser system would offer energy savings of 80% compared to conventional recycling.

The cost performance of the system depends on reducing the capital cost of the laser system and extending the life of the laser lamp. These would both need to change by an order of magnitude for the system to be competitive. Given the general development in the field this may be possible.

7.4.3 *Solvent process*

The performance of the solvent process appears to be acceptable. A slightly altered solvent formulation and adding a pressing process might eliminate all paper damage. Adding a circulating and filtering system might further increase the whiteness of the cleaned paper by preventing the pigment from redepositing on the paper after the toner polymer is dissolved. Using the Hansen solubility parameters it might also be possible to find a more benign combination of solvents that have similar performance.

The energy performance of the solvent approach depends on the volume of solvent used and the energy required to clean it. DMSO has a high boiling point and therefore is energy intensive to distil and recycle. Pure Chloroform rather than the DMSO:Chloroform mixture would require half the energy to distil, making the system less energy intensive than virgin paper manufacturing. Further improvements might be possible by choosing other solvent mixtures and careful design of the recycling apparatus to minimise the heating required. This might eventually make the energy intensity comparable to conventional recycling.

The cost performance of the solvent approach also depends on the volume of solvent used and the energy required to clean it, and therefore might have similar scope for improvement as above. The cost of the solvent mixture is driven by the high price of DMSO (about 90 euro per litre). Chloroform, by comparison, costs 5 euro per litre. It might be possible to combine a cost analysis into the Hansen solubility parameters to find the most cost effective solvent. If this mixture had a cost more like the cost of chloroform then the total cost of the solvent process might fall to 4 euro cents per sheet – only double the cost of a new sheet.

7.4.4 *Combining approaches*

There are three possible combinations of the three approaches.

The solvent chapter briefly reported on experiments that used abrasive rubbing with the solvent instead of ultrasound. These tended to result in greater paper damage and less print removal than the ultrasound alternative. Adding very small amounts of solvent to the rubbing process might result in improved rates of removal by swelling the toner and not the paper. Solvents might also be used to clean the abrasive in order to allow its reuse and therefore might reduce the overall cost of the wear approach.

It is possible that combining a small amount of solvent with a laser process might be effective. If the solvent swelled the toner it might increase the rate at which it is vaporised and reduce the thermal conduction into the paper, possibly reducing the yellowing of the paper and the laser power required.

Using abrasion to smear the print before removing it with a laser would not reduce the yellowing, but might mean the yellowed area was no longer a readable copy of the original text.

7.4.5 *Speculation of the future potential for toner removal*

Of the three approaches reported in this thesis, the solvent approach appears both closest to viability and to have the most straightforward agenda for further research: investigate benign (and cheap) solvents with similar Hansen solubility parameters to the mixture found; investigate the energy required and efficiency of recycling solvents.

The wear process also appears to have scope for straightforward research. It seems plausible that the process energy could be reduced and longer life abrasives found. The resulting paper is unlikely to be as white and thick as virgin paper but it might have the potential to be as cheap and to require less energy.

The long run feasibility of lasers is much less clear. The yellowing of the paper appears to be a difficult problem and the economics and environmental potential do not appear sufficiently compelling to prioritise research in the area.

8 Conclusions

This chapter concludes this thesis by summarising the original contributions of each chapter and proposing implications for research and practice.

8.1 Original Contributions

The following original contributions are documented in this thesis:

1. A comparison of the possible options for reducing the climate change impact of office paper. This is the first published comparison to include reuse and electronic paper as options.
2. The first review of existing work on un-printing.
3. An abrasive and allied rubbing conditions that remove toner-print from office paper, leaving it in a reusable state.
4. A laser and allied lasing conditions that remove toner-print with damage limited to the area under the removed text.
5. A mixture of solvents and ultrasonic agitation that removes toner-print from office paper, leaving it in a reusable state.
6. A comparison of the feasibility of the three approaches, containing initial estimates of their economic, environmental and operational potential.

8.2 Implications

Together with the limitations of the research outlined in chapter §1.2, each of the contributions has implications for further research. These implications are discussed here according to the group that they might interest.

Toshiba have developed and launched the first commercially available system that allows toner print to be neutralised and office paper reused. The implication of the analysis in chapter §2 is that their product has a greater potential than any other approach to reducing climate change gas impact of office paper. They should continue.

The conventional approach to life cycle analysis treats presents results in the form of a linear flow from 'cradle' to 'grave'. Chapter §2 presented the result as a loop. This made it easier to identify missing processes that might offer environmental benefit. Environmental analysts might find it worthwhile creating similar loops for other products.

One way of considering missing processes that is highlighted by the loops is to match each process with one that reverses its effects. Printer manufacturers might consider how their printing processes might be undone. The review of un-printing in chapter §3 suggests a structure for exploring different approaches to this task and the later experimental chapters give some sense of the potential obstacles. A three-way collaboration between printer manufacturers, paper conservators and fraud prevention agencies might be a fruitful way to pursue these processes.

The experiments reported in this research have tested the feasibility of removing toner and the potential for paper reuse. The experiments showed feasibility but were limited in only using a single toner-paper combination. If the feasibility is more widely proved, then the way would be open for more detailed research to understand the principles behind the removal processes and to develop predictive models of their operation. This would allow for further optimisation of the un-printing processes.

The obstacles highlighted in the final chapter might offer a guide for interesting research in the fields of lasers, abrasive and solvents: laser research on how to remove material at a low enough temperature to avoid thermal conduction; abrasive research into selective transfer and fatigue wear of polymers and into how abrasive life can be prolonged in these regimes; solvent research to find benign equivalents to particular Hansen Solubility estimates and to understand the significance and optimisation of ultrasound on selective removal.

The results of the experiments reported in this thesis suggest that un-printing might be feasible. If this is true, then there may also be interest in adapting and automating the techniques that paper conservators use to repair paper. Paper manufacturers might also expand their attention from a concern about the stability and archival quality of their papers to consider their paper's resistance to damage from use (e.g. tears and folds).

Once a working system was in place, there would be important questions about the acceptability of a process that doesn't remove standard pen, pencil or highlighter, about the impact reusing paper on its final recyclability and about the social changes that might result from the availability of the technology. In particular, it would be unfortunate if an ability to reuse paper resulted in a greater number of sheets printed, offsetting any environmental benefit.

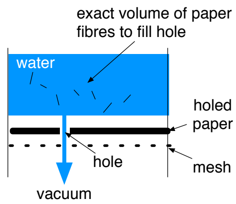
To return to the question that opened this dissertation: You've finished reading this thesis. What do you do with it next? This research suggests that it might be possible that one day you would answer "I'll un-print it and reuse the paper."

A Paper repair

This appendix briefly reviews the techniques used by paper conservators to repair damaged documents, grouped according to the type of damage the technique repairs. The techniques are drawn from standard text-books and journals. They show that repair is possible but that it is manual and that it takes place under different constraints than would apply to repair for paper reuse.

Creases. A leaflet by Alper [164] describes a standard procedure to flatten creases: First place the creased paper in a room temperature but very humid (65-100%) environment for four to six hours. Then place it between blotting paper and press it between sheets of glass.

Holes. Holes can be repaired by leafcasting or by gluing patches. Leafcasting is used for small or irregular holes and is described in a UNESCO report by Wachter [165]: The holed paper is placed on a sieve connected to a vacuum pump. The amount of missing paper is calculated (Mowery [166] developed an automated system to do this based on a video camera linked to a computer) and that quantity of paper fibres (and mineral fillers if required [167]) is placed in a large quantity of water. The water/fibre suspension is poured over the holed paper. The vacuum pump sucks the water through the sieve and the new fibres collect in the holes. Upon drying the new fibres bond with the surrounding paper, filling the hole. Two articles [165;168] report that Per Laursen and Lars Gronegard of Copenhagen have automated this process to allow holed sheets of paper to be continuously repaired, but no further detail on their machine has been found.



A side-view schematic of the leafcasting process for filling holes in paper

A leaflet by Ogden [169] suggests that larger holes are repaired by gluing new sections of paper in place over the hole. He recommends that the patches are made from mulberry fibres (rather than the wood fibres used in most office papers) and that the glue is a rice or wheat starch paste.

Tears. Lener [170] devotes a chapter of his book on paper preservation to four methods of repairing tears and holes. For tears where the torn edges align he recommends re-joining the edges with a PVA glue or with a wheat starch paste. For more difficult tears he recommends gluing tissue over the tear, or using a specialist 'document repair tape'.

Other damage. Waste paper may also be stained or stuck with adhesive tapes. Standard texts[171;172] contain recipes for dealing with such damage, although all are manual and all carry caveats about the potential to harm the underlying paper.

It is difficult to gauge the potential for automating the techniques of paper conservation. Existing manual techniques are intricate and contingent on the exact type of paper and damage to be repaired. But two constraints placed on paper conservation techniques do not apply to paper reuse: the original text does not need to be preserved and the impact of accidentally ruining a sheet of waste paper is not significant.

B Tables of related patents

This appendix lists US, Japanese and European patents that are connected to the field of un-printing. They are organised into tables according to the mechanism that they propose. Some tables are divided by a horizontal line. Patents listed below these lines are believed to be extensions, divisions or duplicates of earlier patents listed above the line.

Table B.1 Patents on the removal of toner by adhesion

1981	US4276118[173]	Deinking Waste Electrophotography Copy Paper *Extends conventional recycling by trailing polymer beads in water to attract and separate the toner particles from the paper pulp.*
1996	JP8262937[75]	Method and Device for Removing Image Forming Substrate from Image Holding Body *Presses adhesive belt against paper. Cool. Then peel apart, lifting print away.*
1996	US5540815[174]	Method of Recycling an Image Carrying Medium and an Image Separating Member Therefor *Paper bathed in water, solvent and surfactant at 180C, polymer roller peels toner off.*
1996	US5547793[175]	Method for Using Image Support Regeneratively and Tool for Forming Image on Image Support *Mentions a toner pen. Bathes in a water-soluble polymer.*
1997	US5593937[176]	Image-Bearing Member and Method for Recycling the Same *Uses a bleach as well as water, surfactant and an adhesive roller.*
1997	US5619765[177]	Device for Removing a Film-like Image Forming Substance *Metal, rather than polymer, adhesive roller.*
1998	US5735009[178]	Device for Removing a Substance Deposited on a Sheet *The paper is pressed between the adhesive belt and a bumpy surface.*
1998	US5759278[179]	Liquid Applying Apparatus and an Image Forming Substance Removing Apparatus *Uses water and surfactant, but not a water soluble polymer.*
1998	US5839143[180]	Apparatus for Regenerating Image Support from Used Image-Bearing Support *Uses a series of rollers with different adhesive properties.*
2000	US6115579[181]	Apparatus for Removing Print from a Recording Medium

Continued. . .

Table B.1 The removal of toner by adhesion (continued)

		The adhesive roller is angled so that toner is lifted diagonally from the paper.
2004	US6696149[182]	Image Stripping Member and Image Stripping Apparatus and Image Stripping Method Using the Image Stripping Member *Uses an adhesive roller with varying adhesiveness, and an unspecified 'releasing agent'.*
1996	US5574538[183]	Method and Apparatus for Removing Image Forming Substance from Image Holding Member Forming Processing Situation Mark *Very similar to US5547793[175]*
2002	USRE37645E[184]	Method and Apparatus for Removing Image Forming Substance from Image Holding Member Forming Processing Situation Mark *Re-issue of US5574538[183]*
1997	WO9705323[185]	Device to Promote Reuse of Office Laser-Print Paper *Very similar to JP8262937[75]*
1997	US5605777[186]	Method and Apparatus for Regenerating Image Holding Member *Very similar to US5547793[175]*
2000	USRE36963E[187]	Method and Apparatus for Regenerating Image Holding Member *Re-issue of US5605777[186]*
1997	US5607534[188]	Method of Recycling Support Material for Image-Bearing Member *Very similar to US5547793[175]*
1997	US5642550[189]	Apparatus for Removing Image Forming Substance from Image Holding Member *Very similar to US5547793[175]*
1999	US5896612[190]	Method and Apparatus for Removing Image Forming Substance from Image Holding Member *Division of US5642550[189]*
2000	US6156127[191]	Method and Apparatus for Removing Image Forming Substance from Image Holding Member *Division of US6156127[191]*

Continued. . .

Table B.1 The removal of toner by adhesion (continued)

1997	US5652989[192]	Apparatus for Removing an Image Forming Substance from an Image Deposited Recording Medium *Very similar to US5547793[175]*
1997	US5689754[193]	Regenerating Apparatus for Recording Medium *Very similar to US5547793[175]*
1999	US5855734[194]	Device for Removing a Substance Deposited on a Sheet *Division of US5735009[178]*
2001	US6189173[195]	Device for Removing a Substance Deposited on a Sheet *Division of US5855734[194]*
1999	US5968272[196]	Liquid Applying Apparatus and an Image Forming Substance Removing Apparatus *This is a division of US5759278[179]*
2000	US6117240[197]	Liquid Applying Apparatus and an Image Forming Substance Removing Apparatus *This is a division of US5759278[179]*
1999	US5897726[198]	Method of and an Apparatus for Removing Image Forming Substance from an Image Supporting Body *Very similar to US5547793[175]*
2000	US6080255[199]	Method of and an Apparatus for Removing Image Forming Substance from an Image Supporting Body *Continuation of US5897726[198].*

Table B.2 Patents on the removal of toner by abrasion

1993	JP5232737[73]	Method and Device for Reproducing Copying Paper *The paper is heated, then passed under a counter-rotating felt roller which scapes the toner from the surface.*
1997	US5694657[94]	Regenerating Apparatus of Recording Medium *Baths paper in water, surfactant and a fatty acid ester (to swell toner) before brushing.*
2002	US20020003549[72]	Printing Paper Regeneration Apparatus *Uses a diamond abrasive roller.*
1997	US5678157[95]	Regenerating Apparatus of Recording Medium *Very similar to US5694657[94].*

Table B.3 Patents on the removal of toner by ablation

1992	JP4281096[45]	Apparatus for Whitening Paper Surface *Laser scans the paper, varying its intensity in inverse proportion to the reflected light.*
1995	WO9500343[200]	Paper Recycling Apparatus Using a Laser Beam *Scan of paper taken, and used to guide laser onto printed area of paper.*
1997	US5614339[46]	Object Recycling by Laser of Coating Material *Laser is fired through the paper at the underside of the toner.*

Table B.4 Patents on the removal of toner by a solvent

1989	JP1101576[51]	Method and Device for Reproducing Copying Paper *Bathed in a solvent with ultrasound.*
1992	JP4091298[52]	Method for Recycling Copying Paper *Adds a surfactant to the solvent and ultrasound.*
1996	US5542985[93]	Method of Recycling a Waste Recording Member *Bathed in mixture of water, organic solvent and surfactant then rubbed.*
1997	DE19646421[55]	Toner Image Removal Without Damaging Recording Medium *Bathed in organic solvent, then rubbed to remove toner.*
1999	WO9947743[96]	Method and Apparatus for Deinking Paper *Bathed in water, surfactant, 2 named water soluble solvents and then rubbed to remove toner.*

Table B.5 Patents on the removal of other print types

2001	US6236831[106]	Method and Apparatus of Recycling Office Paper *One of the methods in this patent is to apply a bleaching agent to printed areas of a sheet*
1986	GB2161752[201]	Process for Producing Individualised Copies of a Printed Sheet or Web *Although not aimed at reuse, this patent mentions the removal of print by laser ablation or 'ultrasonic energy'.*
1999	GB2336428[202]	Method and Apparatus for Thermography *Specific to magnetic thermographic inks, this suggests can heat and suck them from the surface.*

Table B.6 Patents on obscuring print

1941	GB535755 [105]	Improvements in and Relating to the Preparation of Discarded Printed Sheets for Reuse *Proposes spraying or silk screening a white titanium paste onto the whole surface of used paper.*
1992	US5113221 [203]	Image Forming Apparatus Having a Plurality of Toner Developers Including White Toner *Adds a white toner to a colour laser printer. This is applied only where the new sheet needs to be white.*
1992	JP4327299 [204]	Production of Recycle Paper *Original patent not available.*
2001	US6236831 [106]	Method and Apparatus of Recycling Office Paper *Scans the used sheet and deposits obscuring material on the printed areas.*

Table B.7 De-colourable print patents

1993	EP0542286[205]	Decolorizable Toner. *Toner that becomes colourless when heated.*
1994	US5290346[206]	Ink for Printer *Ink jet ink that becomes colourless when heated.*
1995	JP7181713[207]	Method for Repeated Use of Image Holding Body *Combination of using a de-colourable toner and adhesive removal.*
1995	WO9504955[208]	Mutable Composition and Methods of Use Thereof *Pigment that becomes colourless when exposed to UV radiation.*
1996	WO9622335[209]	Novel Colorants and Colorant Modifiers *Another pigment that becomes colourless when exposed to UV radiation.*
1997	US5643356[210]	Ink for Ink Jet Printers *WO9622335[209] applied to ink jet ink.*
2001	US6203603[119]	Erasable Image Forming Material *Suggests can use IR radiation, heat or a chemical to remove colour.*

1995	US5400123[211]	Image Forming Apparatus Capable of Erasing an Image Recorded in a Sheet *Similar to EP0542286[205]*
1995	US5405726[212]	Method and apparatus for decolorization, and image forming apparatus *Similar to EP0542286[205]*
1998	US5777639[213]	Ink-Jet Recording Method and Apparatus Using a Light-Tonable Recording Liquid *Similar to US5290346[206]*
1998	US5721287[214]	Method of Mutating a Colorant by Irradiation *Development of WO9622335[209]*
1999	US5908495[215]	Ink for Ink Jet Printers *Duplicate of US5643356[210]*
2001	US6235095[216]	Ink for Inkjet Printers *Continuation of US5908495[215]*

Continued...

Table B.7 De-colourable print (continued)

2000	US6071352[217]	Erasing Method and Erasing Apparatus for Performing That Erasing Method *Similar to US5290346[206]*
2001	US6296713[218]	Erasing Method *Division of US6071352[217]*
2001	US6211383[219]	Nohr-Mcdonald Elimination Reaction *Improvement on WO9622335[209]*

Table B.8 De-colourable paper patents

1992	DE4132288 [220]	Paper and Ink for Repeated Printing and Erasing - Uses Arrangement Which Can Be Changed from Visible to Invisible State Such as a Layer of Photochromic Material *Describes a paper that is made of a material whose colour can be reversibly changed by heat, magnetism or particular wavelengths of light.*
1992	JP4153079 [221]	Erasable and Rewritable Paper Printing Ink and Printing Apparatus and Erasing Apparatus Using Them *Paper whose colour can be reversibly changed using two different wavelenghts of laser light.*
1994	EP0583483 [222]	Rewritable Recording Device. *Colour reverses at different temperatures.*
1998	US5738910 [223]	Printing Process for Enabling Repeated Use of Printing Paper *Coat the paper with starch, use an iodine based ink, and decolour the ink later with a dilute sodium thiosulfate*
2002	US6342305 [224]	Colorants and Colorant Modifiers *Sheet becomes colourless under UV radiation.*
1992	FR2668735 [225]	Paper and Ink for Repeated Printing and Erasing - Uses Arrangement Which Can Be Changed from Visible to Invisible State Such as a Layer of Photochromic Material *Duplicate of DE4132288* [220]
1997	US5614461 [226]	Image Formation Method Using a Reversible Thermosensitive Recording Material *Similar to EP0583483* [222]
1998	US5801743 [227]	Image Formation Method Using a Reversible Thermosensitive Recording Material *Similar to EP0583483* [222]
2001	DE29522284U [228]	Method of Making a Substrate Comprising a Colored Composition by Using an Improved Mutable Composition and so Produced Substrate *Similar to US6342305* [224]

Table B.9 Low adhesion paper patents

1969	GB1143114[229]	Improvements in and Relating to Printing *Soak the paper in parafin before printing. Re-soaking in parafin after printing causes print to be removed.*
1994	JP6019181[138]	Reusable Copying Sheet *Add a clay layer to the surface of the paper. When immersed in water this swells, causing toner to be loosened.*
1994	US5353108[230]	Apparatus for Cleaning Printed Paper *Uses an unspecified 'relasing paper'.*
1994	EP0601502[139]	Deposit Easy Removable Coating Fixed to Material Surface. *Add a resin layer to the surface of the paper that swells on immersion in water.*
1995	US5474617[231]	Image Holding-Supporting Member and Regenerating Method Thereof *Paper coated with a water soluble polymer before print. Causes toner bond to weaken on immersion in water.*
1996	GB2293612[232]	Reusable Recording Paper *Paper coated with a waterproofing agent (and optionally a water soluble polymer)*
1998	US5782254[233]	Recyclable Image Recording Support Material Method of Producing the Same and Method of Recycling the Recyclable Image Recording Material *Paper pre-treated with a surfactant.*
1997	US5643380[234]	Method of Recycling Image-Deposited Recording Material and Apparatus for Recycling the Same *Use a 'commercial releasing paper'. Seems to be a polymer backing, cellulose layer, then an unspecified swelling layer.*
1997	US5672223[235]	Method of Recycling Image-Deposited Recording Material and Recording Material for Use with the Recycling Method *Alter the sizing of the paper to reduce adhesion*
1998	US5736286[236]	Method for Recycling Image-Deposited Recording Material and Liquid Composition for Use with the Recycling Method *Paper with a surface layer that swells in water.*

Continued. . .

Table B.9 Low adhesion paper (continued)

1998	EP0832946[237]	Coating Facilitating Removal of Adherent Matter and Method of Using the Same *Swelling surface layer and water soluble polymer treatment.*
1998	US5729349[238]	Method and Device for Determining Fiber Orientation of Paper and Apparatus for Removing Image Forming Substance from Paper *Polymer base layer plus water swelling resin surface layer, held together with adhesive layer*
1999	US5872076[239]	Method for Reusing Image Recording Materials and Apparatus Therefor *Add chemicals to reduce adhesiveness of toner. E.g. silicone oils or compounds.*
1999	US5968301[240]	Method of Recycling Image Supporting Material and Apparatus Thereof *Added a polymer swelling layer to a polymer base.*
2000	US6128464[241]	Apparatus for Removing Printing Material from a Recording Member on Which an Image Is Recorded by the Printing Material *Polymer sheet.*
2000	EP0985543[242]	Recyclable Recording Material Containing Microparticles *Swelling layer with 'micro-particles' of low adhesion material embedded.*
2001	EP1099988[243]	Imaging Material Regenerating Apparatus and Liquid Processing Method *3 or 5 layer structure: Polymer base, adhesive, swelling resin surface.*
2003	US2003050190[244]	Image Forming Material Method and Device for Removing Images and Image Forming Process and Apparatus *Coats surface of paper with a low melting point polymer.*
1999	EP0926562[245]	Apparatus and Method for Regenerating an Image Holding-Supporting Member *Division of US5474617*[231]

Continued...

Table B.9 Low adhesion paper (continued)

1998	US5769957[246]	Regenerating Method and Apparatus of Image Holding Supporting Member *Similar to US5736286[236]*
1999	US5970272[247]	Apparatus for Reusing Image Recording Materials *Duplicate or extension of US5872076[239]*
1999	DE19856808[248]	Re-Usable Image Recording Medium with Strong Surface Preventing Damage by Rubbing or Brushing *Similar to EP0601502[139].*
2000	EP1020771[249]	Recyclable Image-Recording Material *Similar to EP0601502[139].*
2000	EP1020772[250]	Recyclable Image-Recording Medium *Similar to EP0601502[139].*
2000	DE19940310[251]	Device for Removing Print from Printed Recording Medium for Recycling Applies Aqueous Solution after Drying Recording Medium *Similar to EP0601502[139].*
2001	US6296034[252]	Image-Forming Material Removing Apparatus *Similar to US5872076[239]*
2002	EP1168106[253]	Apparatus and Method for Removing a Print Material on a Recording Medium *Similar to EP1099988[243].*
2002	US2002022103[254]	Recyclable Image-Recording Medium *Similar to EP0601502[139].*
2002	US6489039[255]	Recyclable Image-Recording Medium Method for Manufacturing the Same and Method for Removing Printed Material from the Image-Recording Medium *Similar to EP1099988[243].*
2003	US6531213[256]	Recyclable Image-Recording Medium Surface of Which Has Specified Saturated Swelling Amount *Very similar to US6489039[255]*

Table B.10 Other patents that change the print

1980	US4188139[47]	Method and Apparatus for Correctably Printing Characters with Sublimable Ink *Use an ink that sublimes at a low temperature and heat to erase.*
1998	US5753400[79]	Method for Repeatedly Using Image Holding Member *Alter the toner to reduce its viscosity, and therefore penetration into the paper. Remove by liquid to sell paper, and then adhesive roller.*
1998	US5813216[257]	Solid Writing Tool and Method of Erasing Lines Drawn Therewith *Describes a novel sort of pen that deposits an easy to remove polymer.*
2001	US5545381[54]	Device for Regenerating Printed Sheet-like Recording Medium *Biodegradable toner that can be removed by enzymes*
1994	WO9406634[48]	Ink Applicator *Similar to US4188139*[47]
2000	US6047758[258]	Method for Repeatedly Using Image Holding Member *Continues US5753400*[79]

Table B.11 Other patents that change the paper

1941	GB541435[259]	An Improved Process for the Treatment and/or Salvage of Drawing Paper *Coat the paper with a dark gum. Print by scratching to expose light paper. Re-coat to reuse.*
1995	JP7072649[56]	Reusable Copying Paper *Add a surface coating that is solvent resistant, and then use solvent to remove toner.*
1997	US5678158[90]	Apparatus for Repetitively Using a Toner Image Carrier *Polymer sheet and toner with a weaker bonding force, so can be rubbed off.*
1999	DE19837232[59]	Writing Surface Giving Permanent Record but Easily Erasable *Add a water reppellent coating, write with crayon, wipe clean.*
2003	WO03078172[60]	Print Protection Embedded Print Protected Page Embedded Text Page Embedded Text Kit and Methods Relating Thereto *Write on a PVC sheet and use a solvent to remove print.*
1997	US5634405[58]	Methods for Removing Ink from Polymeric Substrates *Similar to JP7072649[56].*
2000	US6150066[91]	Method and Apparatus for Repetitively Using a Toner Image Carrier Sheet *Division of US5678158[90]*
2002	US2002172809[61]	Print Protection Embedded Print Protected Page Embedded Text Page Embedded Text Kit and Methods Relating Thereto *Duplicate of WO03078172[60]*

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List of Figures

List of Tables