Un-printing toner: Early results

Thomas A. M. Counsell[1], Julian M. Allwood[1]
[1]Sustainable Manufacturing Group, Department of Engineering, University of Camrbidge, United Kingdom.

Abstract

Office paper is made from a renewable material and therefore has a closed loop. Unfortunately the environmental impact of this loop is significant, as is that of the standard recycling process. Un-printing without significantly damaging the physical structure of paper might be environmentally preferable. This paper reports some early attempts to un-print conventional toner from conventional office paper. The first part discusses the many alternative approaches that might be pursued, the second part of the paper reports on some initial experiments in the use of laser ablation, solvents and wear. None are completely successful yet, and avenues for further research are proposed.

Keywords

Office Paper, Toner, Recycling, Repair.

1 INTRODUCTION

Office paper is a renewable material and therefore has a closed loop: from carbon dioxide and water, via a forest, through pulping, papermaking and printing processes to useful sheets and then via landfill or incineration back to carbon dioxide and water.

Unfortunately the environmental impact of this loop is significant: In the mid 1990's the IIED [1] estimated that the paper industry was the 3rd largest greenhouse gas emitter, and Muthukumara and Wheeler [2] of the World Bank estimated it might be the 4th largest water polluter and 5th largest air polluter. Industry data, at least for Europe [3], suggests that there has been significant progress since then in reducing water and air pollution, but no success in cutting absolute emissions of climate change gases.

The conventional alternative to this loop—replacing landfill, forestry and pulping with the sorting and cleaning of waste cellulose—reduces most air and water emissions, but has less effect on climate change emissions [4–5]. This is principally because waste wood is used to fuel the virgin paper process but not the recycled paper process, because recycling plants are often nearer to cities than forests. The print is removed from the cellulose after the paper has been dissolved into individual fibres. At this point, separating print from fibres is technically challenging, leading to process yields of 60% for office paper [6] and the reforming of the cleaned fibres into paper damages the fibres, limiting them to perhaps four cycles of reuse [7].

For office paper, an alternative could be to remove print while leaving the paper intact. This would allow the paper to be immediately re-used, avoiding the environmental impact of re-forming the paper. The only published work we have found on this topic is contained in patent filings, principally by Japanese photocopier and printer manufacturers. Our survey of these patents [8] reveals that the majority propose altering the print or the paper. Those that work on conventional toners and papers can be grouped according to whether they work by obscuring, adhesion, ablation, abrasion or solvents.

The patents do not detail which approaches work, nor the science behind their operation. Our current research project seeks to address these gaps in order to understand the research that is needed for the approach to be viable. This paper reports on some early work: the next section briefly discusses what generic approaches might be taken to remove toner, section three reports on some initial experiments using laser ablation, solvent washing and wear. A very provisional evaluation of their viability is made in section four, and section five concentrates on the significant gaps in research in this area.

2 APPROACHES TO REMOVING TONER

The patents we surveyed [8] proposed a variety of approaches to removing toner, but we were uncertain as to whether there were others. To explore this we used the work of Fritz Zwicky [9] to construct a 'morphological box' of all the ways that toner might be removed from paper. This involves exactly formulating the problem, breaking it down into a series of smaller decisions, enumerating all the options for each decision and then systematically combining all the options into a series of overall solutions, rejecting those that are physically impossible.

We formulated the problem as the need to eliminate the contrast between print and paper. The first method that we explored to do this is to remove the pigment from the paper. The pigment is embedded in globs of polymer, which are bonded to the surface fibres of the paper (see figure 1). We then broke the problem into a decision about which bond to break to remove the pigment, and how to break the bond. The options for the bond were pigment–polymer, polymer–polymer, polymer–cellulose or

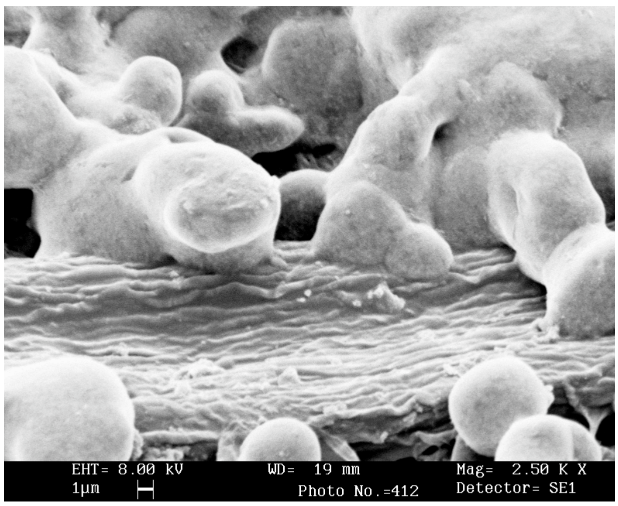

Figure 1: Electron microscope image of toner particles on cellulose fibre on surface of office paper (note that colour indicates electron transmission, not optical appearance).

surface cellulose–bulk cellulose bonds. The options for how to break it were: doing work, introducing heat or changing the local electron structure (by, for instance, adding a solvent). We then continued to break each of these options into further decisions, before assembling the options into the complete morphological box displayed in figure 2.

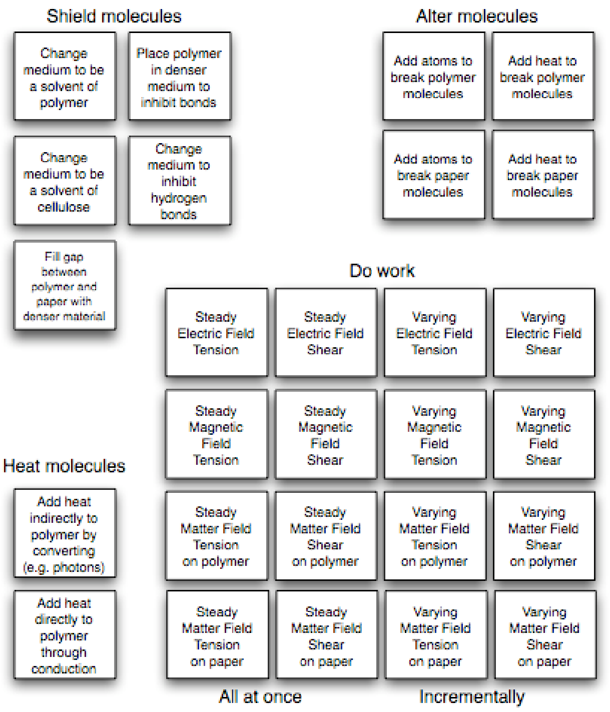

Figure 2: Morphological box of how toner might be un-printed from paper

The morphological box was helpful in categorising existing approaches, but not in deciding what further research to carry out. The proposed solutions were to generic to be tested and, unlike the periodic table of the elements, the arrangement gave no indication of the properties or performance of each solution and therefore couldn't be used as a guide to focus further research.

The process of trying to prioritise the approaches from the morphological box inspired an alternative perspective on the problem, illustrated in figure 3, that in order to eliminate the contrast between print and paper, we need to exploit a difference between print and paper (for example hardness, location or solubility) that would make the print more susceptible to damage than the paper under a particular set of conditions.

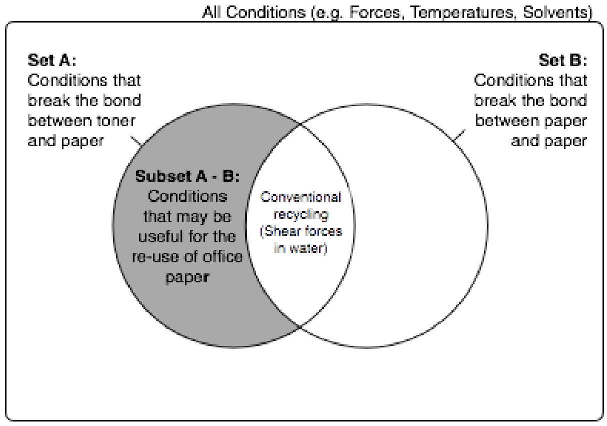

Figure 3: A definition of the problem

There is a great deal of variation in the properties of paper and of toner. Paper may vary in what type of wood it is made from, the size of the wood fibres used and the amount and type of additives. Toner may vary in the polymer used, the pigment and other additives used, size and regularity of shape. To be likely to work, an approach concept would need to rely only upon a difference between toner and paper that is essential to their readability and printability or on a corollary difference that must be true for these essential differences to exist. These essential differences (summarised in table 1) are probably location, colour, melting point and bond energies. This led us to perform our initial experiment with laser ablation (to exploit differences in colour), solvent washing (to exploit differences in bond energies), and selective wear (to exploit location and melting point). Some early results of these experiments are reported next.

3 INITIAL EXPERIMENTS

This section reports on the early results of three sets of experiments to investigate methods of un-printing toner by laser ablation, solvent washing and selective wear.

3.1 Laser Ablation

The idea of using a laser to remove print was briefly reported in 1965 by Schawlow [10], and later in Japanese [11], worldwide [12], and US [13] patents. These used a variety of wavelengths and operating conditions. There has also been relevant work on using lasers to clean surfaces as part of conservation work [14–15] and as part of a printing process [16].

The motivation for exploring laser ablation was to exploit the difference in colour between print and paper. Williams

Table 1: Essential differences between toner and paper cellulose

Difference		Origin	Potential Exploit
Colour	High contrast, usually black print on white paper	Required for reading	Lase at a wavelength absorbed by print over paper, to cause the print to ablate
Location	Print is on the surface of the paper	Required for reading	Cut or abrade the top of the paper surface
Melting temperature	Toner polymer melts and becomes fluid at a temperate below the decomposition temperature of paper	Required for printing	Use heat to melt the toner and apply a force to separate
Bond type	The toner polymer is likely to have a different bond energy, and different bond types from the cellulose fibres	Required for a different melting temperature	Use a solvent that dissolves the toner polymer in preference to the paper cellulose.

[17] provides a table of absorpancy against wavelength for toner and paper (reproduced in figure 4). This suggests that the largest difference in adsorption occurs at shorter wavelengths, in this case 750 nm.

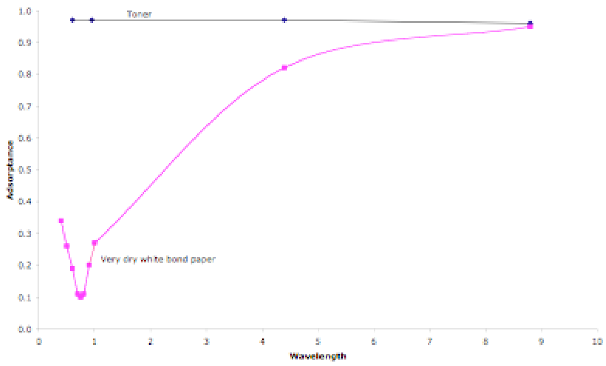

Figure 4: Absorptace of paper and toner adapted from Williams (1984) with wavelength measured in µm.

For our initial experiment we therefore used a Ti:Saphire laser operating at a wavelength of 780 nm. We printed a standard white 80gm un-coated office paper with a black square using a standard office laser printer. The laser was set to deliver 120 fs duration pulses at a rate of 1000 Hz. The samples were tested by focusing the laser on sample using a spot size of 16µm and then rastering across the printed area a rate of 0.02 m/s. As the raster progressed, the average power of the laser was reduced from 350 mW to 45 mW.

An optical inspection of the samples suggests that the toner was completely removed from within the track of the laser at the lowest tested average power (45mW). This can be seen in figure 5. As the power increased the area around the toner track was also ablated up to a width of c. 50µm. At higher powers (178 mW and above) some damage to the paper surface became visible.

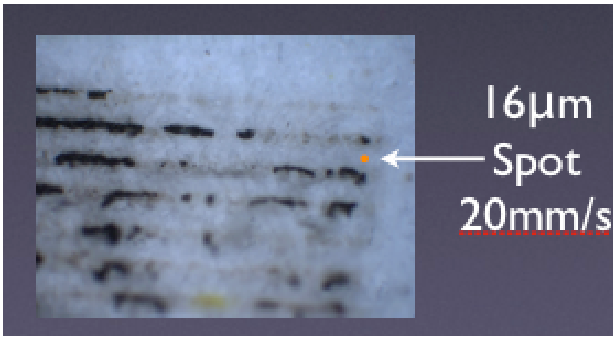

Figure 5: Close up of results of initial laser removal experiment

Our next steps are to evaluate the impact of varying the wavelength of the laser, using lower powers, altering the pulse sizes and frequencies and establishing whether the spot size and scan speed can be increased so as to rapidly erase the surface of an entire A4 sheet.

3.2 Washing in a solvent

The idea of using a solvent to remove toner print has been reported in five patents [18-22] which catalogue a large number of possible solvents.

In order to select which solvent is most effective we have started to follow the steps proposed by Burke [23] by which a conservator might pick a solvent for the removal of one substance from the surface of another. This is based on the work of Hansen [24–26] and Teas [27] who were interested in the development of paints.

This is based on the principal that the solubility of a polymer can be characterised by the contribution of hyrdrogen, dipole-dipole and London bond types to the overall strength of the intermolecular bond (known as solubility parameters). A solvent that has a similar set of three strengths is likely to be effective, as is a mixture of solvents that has a similar set of average strengths. The solubility parameters of a polymer can be gauged by measuring how effective a solvent with known solubility parameters is at dissolving it (the parameters for a large number of solvents are listed in [28]). Once the parameters are known, further solvents and mixtures of solvents can be proposed.

For our initial experiment we printed a block of text, an image and a grid of lines using a standard office laser printer onto samples of standard white 80gm uncoated office paper. Each sample was rolled and placed in a small test tube. Solvent was poured in until it covered the printed area. The test tube was placed in an ultrasound bath at room temperature for one minute. The solvent was then poured out of the test tube and the paper removed, unrolled and left to air dry at room temperature. The solvents used were the standard range available in a chemistry lab: Diethylether, Acetone, Ethylacetate, DMSO (Dimethyl Sulfoxide), Ethanol, Methanol, Isopropanol, Dichloromethane, THF (Tetrahydrofurane) and Toluene.

Of the solvents tested, THF was the only to remove significant quantities of toner, to the extent that the solvent appeared black. Visual examination of the samples placed in dichloromethane, DMSO, Toluene, Acetone and Ethylacetate showed some blurring of printed areas but no significant removal. The other solvents had no visible effect. These initial results have been approximately displayed on the Teas chart in figure 6 which illustrates the relative importance of each of the three bond types in the overall molecular bond strength. This indicates that the toner has mainly dispersive inter-molecular bonds. This indicates that it is likely to be possible to find a solvent that selectively removes toner, as the bonds between cellulose fibres are mainly hydrogen.

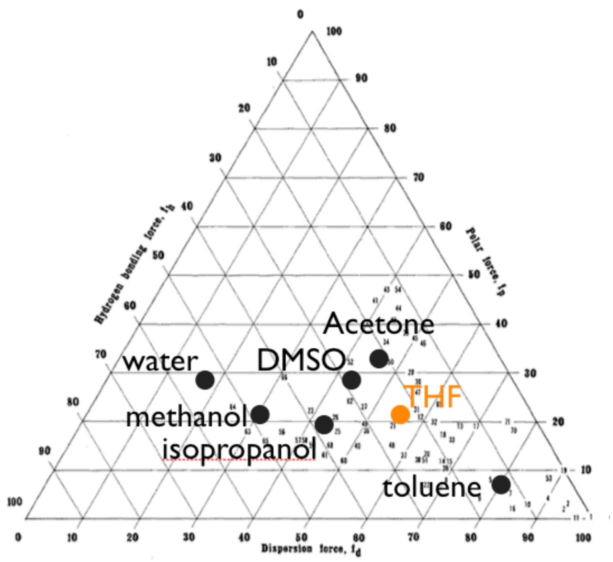

Figure 6: A Teas chart of the initial experiment results

The next step will be to try further solvents, and then mixtures of solvent, in order to derive a more accurate set of solubility parameters. This knowledge will then be used to identify and test other, more benign, solvents or mixtures of solvents that might remove the toner.

3.3 Selective wear

A US [29] patent application and a Japanese [30] patent report using selective wear to remove standard toner from standard paper. The former uses a hot roller to heat the paper to 40-80C and then passes it under a diamond abrasive grinding wheel that removes the top 10µm of the 70µm paper thickness. The Japanese patent heats a sheet of toner printed paper, and then rubs the surface with a counter-rotating felt roller. Standard literature on wear [31] suggests that polymers wear through three mechanisms: abrasive, adhesive and fatigue, with abrasive dominant for rough surfaces and stiff polymers. It also suggests that the wear rate depends on the speed of the wear surface. Bushan [32] highlights that at high speeds and pressures, wear can occur in polymers by localised melting.

Our initial experiment was to rub standard abrasive papers against samples printed on a standard office printer, at room temperature. The samples were wrapped around a rotating drum. A strip of abrasive was then hung over the rotating drum, fixed at one end and attached to a mass at the other. The abrasive grit, speed of rotation and mass were varied. The level of print removal was measured by analysing the average whiteness of an area that was originally printed black.

As expected, the amount of print removed as the speed and mass increased. Less expected was that the amount of print removed increased as the abrasive became finer (see figure 7) and that with fine abrasives there was very little damage to the paper surface. Examining the sample under an electron microscope revealed that a thin layer of the toner polymer had been spread over the paper surface. It is possible that this was partially protecting the paper surface.

The next steps will be to explore the effects of further increases in mass and speed, and further reductions in grit size and to seek to understand the mechanism by

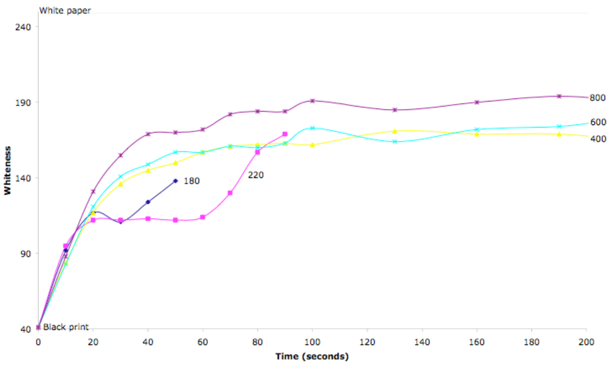

Figure 7: Print removed related to abrasive grit size (higher is finer), with 400g mass and at 200 rpm.

which the print seems to be selectively removed. The impact of temperature will then be explored, as will the type of abrasive surface.

4 INITIAL EVALUATION

The experiments surrounding each approach are not yet complete, but we can make some tentative comparisons between the three methods.

Operationally the laser ablation approach appears the most effective, removing most print, but under our current experimental conditions is very slow–it would take 3 hours to clean a sheet that had 5% print cover. The solvent is almost as effective, but some of the pigment in the toner is redeposited on the paper surface once the polymer is dissolved, and a method of recycling the solvent is likely to be required. The wear process produces sheets that are visibly less clean than virgin paper, but could be usable. The operational challenge will be to clean the abrasive surface to allow it to be repeatedly used.

We can tentatively suggest that the wear process may be the most environmentally benign, since it uses very little power. The laser, based on 5% print coverage, 45mW power and 9% primary energy efficiency, would also use less energy than consumed in current paper recycling. The environmental impact of the solvent is hard to gauge at this stage. It is likely that recycling the solvent would be energy intensive, and the most effective solvent tested (THF) can potentially form explosive compounds when exposed to air, long term exposure can cause dermatitis, kidney and liver damage and it is narcotic.

The economic performance of the wear process is likely to depend on the ability to clean and re-use the abrasives, and that of solvents on the ability to clean and re-use the solvent. The laser used in our experiment has a cost of GBP 180,000, making it highly uneconomic.

5 DISCUSSION

Our experiments in un-printing toner have not yet resulted in a method that is as good as conventional recycling. However, the initial results reported here suggest there is potential in un-printing and plenty of research to be done: in developing a low cost laser that can ablate print, in pinpointing the solubility of toners and in understanding the mechanisms of selectively wearing a polymer from a paper surface.

ACKNOWLEDGMENTS

This work is supported through the EPSRC Doctoral Training Account at the Department of Engineering and the University of Cambridge. The experimental assistance of Dr Huck, Professor Hutchings and Dr Tunna is gratefully acknowledged.

REFERENCES

[1] IIED, 1996, Towards a sustainable paper cycle. International Institute for Environment and Development.

[2] Muthukumara, M. & Wheeler, D., 1997, In search of pollution havens: Dirty industries in the world economy, 1960-1995. World Bank Poverty Environment Growth Working Papers.

[3] CEPI, 2005, CEPI Sustainability Report 2005. Confederation of European Paper Industries.

[4] The Paper Task Force, 1995, Paper Task Force Recommendations for Purchasing and Using Environmentally Preferable Paper. Environmental Defense Fund.

[5] The Paper Task Force, 2002, Update and Corrections to the Paper Task Force Report. U.S. Environmental Defense Fund.

[6] EIPPCB, 2001, Reference Document on Best Available Techniques in the Pulp and Paper Industry. European Integrated Pollution Prevention and Control Bureau.

[7] Smook, G.A., 2002, Handbook for Pulp and Paper Technologists. Angus Wilde, 3rd edn.

[8] Counsell, T.A.M. & Allwood, J.M. 2006, Desktop paper recycling: A survey of novel technologies that might recycle office paper within the office. In Press. Journal of Materials Processing Technology.

[9] Zwicky, F., 1967, The morphological approach to discovery, invention, research and construction. In F. Zwicky & A. Wilson, eds., New Methods of Thought and Procedure: Contributions to the Symposium on Methodologies, 273–297, Springer, Berlin.

[10] Schawlow, A.L., 1965, Lasers. Science, 149, 13–22.

[11] Massaro, D.J. & Woolston, M., 1995, Paper recycling apparatus using a laser beam. Worldwide Patent WO9500343, Assigned to Inversion Dev Corp.

[12] Niikura, J., Hado, K., Taniguchi, N. & Gamo, K., 1992, Apparatus for whitening paper surface. Japanese Patent JP4281096, Assigned to Matsushita Electric Ind Co Ltd.

[13] Tankovich, N., 1997, Object recycling by laser of coating material. U.S. Patent US5614339, Assigned to Lumedics Ltd.

[14] Steen, W.M., 2003, Laser material processing. Springer, London, 3rd edn.

[15] Szczepanowska, H.M. & Moomaw, W.R., 1994, Laser stain removal of fungus-induced stains from paper. Journal of the American Institute for Conservation, 33, 25–32.

[16] Stewart, R., Li, L. & Thomas, D., 2001, Multipass laser ablation of three coloured ink from a paper substrate. Journal of Materials Processing Technology, 114, 161–167.

[17] Williams, E.M., 1984, The physics and technology of xerographic processes. Wiley, Chichester, UK.

[18] Orita, K. & Chikui, Y., 1989, Method and device for reproducing copying paper. Japanese Patent JP1101576, Assigned to Tohoku Kako Kk.

[19] Higuchi, I. & Takahashi, M., 1992, Method for recycling copying paper. Japanese Patent JP4091298, Assigned to Niigata Eng Co Ltd.

[20] Yamamoto, T., Yamomoto, K., Nishiguchi, K., Yoshida, M. & Atarashi, H., 1996, Processing device for sheet-like media. US Patent US5528788, Assigned to Minolta Co Ltd (Jp).

[21] Machida, J., Tanaka, S. & Yoshida, M., 1996, Method of recycling a waste recording member. U.S. Patent US5542985, Assigned to Minolta Camera.

[22] Bhatia, S., Pichel, M. & Ashu, J.T., 1999, Method and apparatus for deinking paper. Worldwide Patent WO9947743, Assigned to Decopier Technologies.

[23] Burke, J., 1984, Solubility parameters: Theory and application. In The Book and Paper Group Annual, vol. 3, chap. 4, The American Institue for Conservation.

[24] Hansen, C.M., 1967, The three dimensional solubility parameter - key to paint component affinities: I. solvents plasticizers, polymers, and resins. Journal of Paint Technology, 39.

[25] Hansen, C.M., 1967, The three dimensional solubility parameter - key to paint component affinities: Ii. dyes, emulsifiers, mutual solubility and compatibility, and pigments. Journal of Paint Technology, 39.

[26] Hansen, C.M., 1967, The three dimensional solubility parameter - key to paint component affinities: Iii. independent calculations of the parameter components. Journal of Paint Technology, 39.

[27] Teas, J.P., 1968, Graphic analysis of resin solubilities. Journal of Paint Technology, 40.

[28] Barton, A.F.M., 1991, CRC handbook of solubility parameters and other cohesion parameters. CRC Press, Boca Raton, 2nd edn.

[29] Mitsuhashi, M., 2002, Printing paper regeneration apparatus. U.S. Patent US20020003549, Assigned to Nippon Electric Co (Jp).

[30] Yamazaki, T., 1993, Method and device for reproducing copying paper. Japanese Patent JP5232737, Assigned to Tanezo Yamazaki.

[31] Hutchings, I.M., 1992, Tribology: Friction and wear of engineering materials. Edward Arnold.

[32] Bhushan, B., 1999, Principles and Applications of Tribology. John Wiley and Sons Inc.

CONTACT

Julian Allwood

Department of Engineering, Mill Lane, Cambridge, CB2 1RX, United Kingdom.

Jma42@cam.ac.uk

Thomas Counsell

Department of Engineering, Mill Lane, Cambridge, CB2 1RX, United Kingdom.

tamc2@cam.ac.uk