The Application of High Intensity Ultrasound to the De-inking of Recycled Papers.

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Abstract

This paper presents work done by the authors on the application of high intensity ultrasound to the de-inking of waste papers printed with digitally printed inks. These include fused toners, indigo inks and UV cured coatings. Generally, these are considered to be 'difficult to de-ink' systems when present in conventional recycling de-inking plants because they are difficult both to detach from the paper fibres and to break down to particle sizes that can be removed by conventional flotation techniques.

For all the systems investigated it was possible to both detach and reduce the size of particles down to flotatable size range of 20 to 120 microns. Temperature was found to play a role in heat fusible toner printed materials. De-inking of the tough films produced by UV curing inks showed no temperature dependence. Indigo inks which have been feared top present problems to the recycling industry found to be relatively easy to de-ink. The general conclusions are that the application of ultrasound can be used to aid the de-inking of waste paper and reduce the number of chemicals used.

Introduction.

Much of the paper we print on today contains recycled cellulose fibre, a trend that is growing with economic and environmental pressures. Concern has been expressed generally about the problems of de-inking papers printed using the new digital technologies. It is suggested that even small quantities of digitally printed products can seriously jeopardise the paper recycling process [1]. Dry toner systems such as Xeikon and Xerox are thought to be less problematic because detached ink particles can be broken down relatively easily by commercial dispergers. Since current world consumption of paper for digital printing is about 7.5 million tons per annum, which represents about 7.5% of the worldwide printing consumption, the de-inkability of digital prints has become an issue for recyclers.

The print quality achievable with recycled papers depends not only on the quality of the recycled fibres but also on the extent to which 'old ink' has been removed from the waste paper used. Flecks of ink which are visible seriously detract from the visual quality of the paper whilst particles present but invisible to the naked eye reduce the dynamic range of densities and hence the colour gamut producible. A task of major importance to the recycling process is therefore the ability to detach ink from the paper fibres and then remove it from the slurry. Some of the newer inks in use, notably those used in the digital printing processes are in the unfortunate category of 'difficult to de-ink' inks.

Digital printing uses various types of ink formulations. Water-based ink-jet inks present great problems for the paper recycling process where dye-based inks are employed because these colorants break down to molecular sizes when dispersed in water. The colorant then sticks to the paper fibres and can only be removed by extensive and wasteful washing. Inks may be 'set' by incorporating an acid/salt resin binder such as those employed in the water-based inks used in flexographic newspaper printing. These inks are printed in a slightly alkaline phase in which the salt is water-soluble. On contact with the lower pH paper, the acid form is produced which precipitates out to give a stable ink film. Unfortunately, the paper recycling process is performed under alkaline conditions which resolubilises the ink film again. Water-based ink-jet dye ink systems remain a problem for the paper recycling process and are not further discussed in this paper.

However, UV cured ink films and electrostatic toner systems including the Indigo process are in widespread use and it is these with which this paper deals. These inks are in themselves considered to be difficult to recycle by conventional means because they tend to form large flat platelets when they detach from the paper fibres and are sufficiently flexible to slide through the sieves and screens used in conventional fibre reclamation technologies. Furthermore, these particles are far too large to be removed by the flotation process which is the most significant means of removing ink particles from the paper slurry; the optimum size range for flotation is 20 to 150 microns.

Conventional de-inking processes rely heavily on a wide range of chemicals to de-ink and flotate the ink from the waste paper [2]. These in themselves damage the paper fibres which restricts the number of economic recycles and necessitates the neutralisation and disposal of thirteen or more noxious chemicals including sodium hydroxide. This paper describes the application and results of high intensity ultrasound irradiation both to detach ink films from digitally printed papers and, importantly, to break the detached films down into controlled particle size ranges amenable to separation in flotation chambers used in the paper recycling mill. The technique enables a reduction in the chemical processes used for conventional de-inking with their consequent disposal problems.

This paper summarises the work done by the authors on the application of high intensity ultrasound to the de-inking and particle size engineering of thermoplastic toners, UV cured and Indigo ink films. The latter category was included as fears had been expressed that Indigo ink films would be problematic for recycling [1].

Experimental

Ultrasound de-inking exploits the cavitation energies created by the high frequency oscillations of an ultrasound horn. Movement of the horn tip at certain ultrasonic frequencies creates cavitation bubbles which implode to release energy, creating temperatures as high as 5500K and 200 atmospheres [3]. This results in high velocity jet streams with velocities between 128 and

$170ms^{-1}$ which impinge on the pulp and transfer energy which detaches the ink particles and breaks them down.

An ultrasound horn consuming up to 1.8 kW of electrical energy and transforming it into high intensity ultrasound having a frequency of 20kHz was used to transfer energy into a reaction chamber containing the pulp samples. Wastepaper samples were broken down into aqueous pulp slurries using a laboratory disintegrator. These slurries were then subjected to ultrasound irradiation for selected stepped periods of time and at different controlled temperatures, without the addition of de-inking chemicals.

The treated pulp samples were reformed into hand sheets and the filtrates collected. The ink particle size distributions in the hand sheets were established using image analysis and gave a measure of the frequency of particles occurring in the size ranges 8-25, 25-100, 100-250, 250-450 and >450µm. The particle size distributions in the filtrates were measured using a laser scattering technique which enabled the frequency of particles from 0.1 to 1000µm to be established. Inspection of the hand sheets enabled the changes in particle size distributions to be monitored with time and temperature.

Dry Toners

Dry powder toners used in digital printers and office copiers are thermoplastic and have a softening point at around 70 to 80°C. A heated drum is used to melt the toner particles and fuse the image to the substrate. Because they are fused into continuous films, they tend to form continuous films when detached from their substrate. The purpose of this investigation was to explore the effects of temperature and short-term exposure to high intensity ultrasound in detaching toner from paper under neutral pH conditions and breaking it down to flotatable sizes.

Experimental

The waste paper used in this investigation was collected from a number of office local sources in a single collection. The sample contained approximately equal volumes of laser printed and photocopier waste. The laser waste came from several HP Laser Jet 4M P Plus printers, the photocopier waste from two Sharp photocopiers (models 2022 and 2035).

Batches of pulp were produced by first soaking the torn pieces in distilled water for 3 hours then treating them in a British Standard Disintegrator for 2000 counts (consistency 3%). The resultant pulp was made up to 10 litres at a consistency of 1.5% with distilled water. Two litre aliquots were sonicated for various times with ultrasound at a frequency of 20kHz and an electrical power input to the horn of 1KW ± 20W. The sonication times chosen were 0, 1, 2, 5 and 10 minutes. The pulps were thoroughly stirred throughout the period of sonication.

The degree of detachment was estimated by dividing the treated samples into two. One half was washed thoroughly through a 100 mesh sieve having an aperture of 150x150mm. The size of the mesh allowed smaller detached particles to escape whilst the larger particles and those still attached to fibre were retained. The unwashed portion retained all particles attached or not. Hand sheets were made using the laboratory hand sheet former. The hand sheets were subsequently analysed by image analysis using the Ink Measurement Program (IMP) developed at PIRA International. By comparison of washed and unwashed samples, a measure of particle detachment was obtained. The de-inked particles were classified in terms of their diameters. The smallest diameter recorded by the IMP was 8µm.

In summary, it was found that for disintegration only with no sonication treatment, 30% of the particle population was above 100µm and 70% was less than 100µm in diameter. After 5 minutes sonication only 3.9% of the population was above 100µm, falling to 1.6% after 10 minutes when 98.4% of the population lay in the particle size ranges less than 100µm. After 5 minutes sonication, no particles greater than 450µm were detected and after a further 5 minutes of treatment no particles remained that were larger than 250µm.

Microscopic evidence (Figures 1 and 2) suggests that whereas the larger toner particles (>400µm) appear to remain attached to fibre, smaller particles are detached. This is an important consideration in fibre reclamation because it is particularly useful if detached particles lie in the flotatable size range.

There is clear evidence of detachment for the smaller particle size ranges. A combination of increased temperature and sonication time considerably enhanced the extent of detachment. After 10 minutes sonication the percentage detachments of particles in the 8 - 25µm range were: 70% for temperature maximum 35°C (TR1), 83% for temperature maximum 45°C (TR2) and 92% for temperature maximum 80°C (TR3). The same sonication time and temperatures resulted in detachment of larger particles sized 25 - 100µm of 59%, 79%; and 78% respectively.

Tables 1, 2 and 3 summarise the effects of both temperature and sonication on the extent of toner detachment. There is no evidence of detachment of particles sized 250µm or greater. For particles sized between 100 - 250µm there is some evidence of detachment after longer periods (5 minutes) sonication. This effect is more pronounced as the temperature increases; after 10 minutes sonication TR1 gave 41% detachment, TR2 gave 31% and TR3 gave 78%.

Figure 1 *Toner particles attached to fibres after disintegration but prior to sonication.*

Sonication Time (min)	Percentage of particles removed (and average numbers per handsheet).				
	8 - 25 µm	25 - 100 µm	100 - 250 µm	250 - 450 µm	>450 µm
0	67.4 (71 - 23 = 48)	53.7 (59 - 27 = 95)	0 (37 - 37 = 0)	0 (12 - 12 = 0)	29.5 (7 - 5 = 2)
1	71.4 (81 - 23 = 58)	67.2 (142 - 47 = 95)	14.7 (34 - 29 = 5)	0 (4 - 6 = -2)	0 (2 - 4 = -2)
2	74.0 (101 - 26 = 75)	68.8 (187 - 58 = 129)	24.8 (27 - 20 = 7)	0 (2 - 2 = 0)	0 (1 - 1 = 0)
5	78.0 (119 - 26 = 93)	74.7 (253 - 64 =189)	39.4 (15 - 9 = 6)	0 (0 - 1 = -1)	0 (0 - 0 = 0)
10	83.5 (179 - 30 = 149)	79.1 (283 - 59 = 224)	30.7 (7 - 5 = 2)	0 (0 - 0 = 0)	0 (0 - 0 = 0)

Table 1. Percentages and average numbers of toner particles detached for every size range – TR1.
Percentages derived from the total numbers of particles for 12 hand sheets.
Average numbers (in parenthesis) are differences in average counts between unwashed and washed samples.

Sonication Time (min)	Percentage of particles removed (and average numbers per handsheet).				
	8 - 25 µm	25 - 100 µm	100 - 250 µm	250 - 450 µm	>450 µm
0	42.8 (50 - 29 = 21)	27.4 (66 - 48 = 18)	0 (28 - 35 = -7)	33.3 (8 - 5 = 3)	0 (5 - 5 = 0)
1	54.6 (84 - 38 = 46)	22.0 (106 - 83 = 23)	0 (24 - 27 = -3)	0 (4 - 4 = 0)	0 (2 - 2 = 0)
2	54.1 (93 - 43 = 50)	34.8 (141 - 92 = 49)	4.9 (19 - 18 = 1)	0 (2 - 2 = 0)	0 (0 - 0 = 0)
5	62.7 (129 - 48 = 81)	47.2 (176 - 93 = 83)	8.6 (8 - 7 = 1)	0 (0 - 0 = 0)	0 (0 - 0 = 0)
10	70.2 (154 - 46 = 108)	58.8 (184 - 76 = 108)	41.2 (3 - 2 = 1)	0 (0 - 0 = 0)	0 (0 - 0 = 0)

Table 2. Percentages and average numbers of toner particles detached for every size range – TR2.
Percentages derived from the total numbers of particles for 12 hand sheets.
Average numbers are differences in average counts between unwashed and washed samples.

Sonication Time (min)	Percentage of particles removed (and average numbers per handsheet).				
	8 - 25 µm	25 - 100 µm	100 - 250 µm	250 - 450 µm	>450 µm
0	63.7 (66 - 24 = 42)	61.3 (53 - 21 = 32)	0 (44 - 52 = -8)	0 (16 - 17 = - 1)	0 (6 - 5 = 1)
1	75.7 (103 - 25 = 78)	62.8 (175 - 62 = 113)	4.5 (50 - 47 = 3)	38.7 (3 - 2 = 1)	0 (1 - 0 = 1)
2	82.1 (161 - 29 = 132)	72.7 (286 - 79 = 207)	47.3 (50 - 26 = 24)	0 (1 - 1 = 0)	0 (0 - 0 = 0)
5	88.2 (132 - 16 = 116)	77.8 (291 - 65 = 226)	60.5 (29 - 11 = 18)	0 (0 - 0 = 0)	0 (0 - 0 = 0)
10	92.3 (173 - 13 = 160)	78.7 (333 - 71 = 262)	77.8 (18 - 4 = 14)	0 (0 - 0 = 0)	0 (0 - 0 = 0)

Table 3. Percentages and average numbers of toner particles detached for every size range – TR3.
Percentages derived from the total numbers of particles for 12 hand sheets.
Average numbers are differences in average counts between unwashed and washed samples.

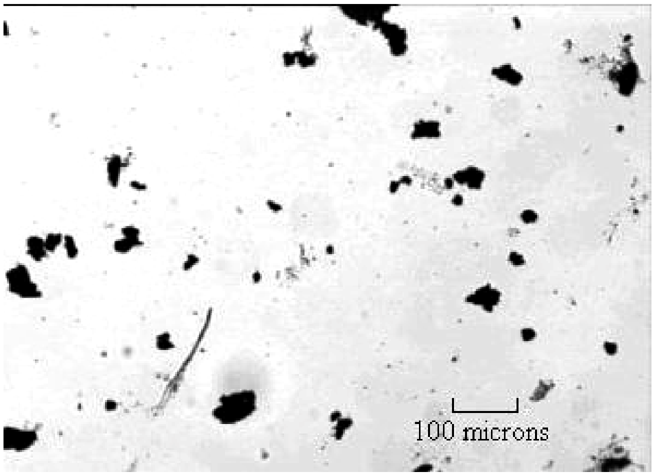

Figure 2 *Toner particles detached from fibres after 10 minutes sonication.*

UV cured ink films

UV cured inks and coatings produce tough cross-linked films which are particularly difficult to detach and break down in the recycling pulper. Unlike digital toners, they do not soften under the influence of heat. The ink vehicles may contain epoxy acrylates, polyol acrylates, urethane acrylates, polyester acrylates and hydroxyl polyesters that form impenetrable layers which resist alkaline recycling environments; these do not break up easily under normal recycling conditions.

Experimental

For the work on these inks, very thick films were deliberately chosen to present the greatest challenge to the ultrasound technique. These were produced using the screen printing process, rather than digital printing, using Sun Chemicals (formerly Coates Lorillieux) Violet NF Black 10-75 on a 90gsm machine-glazed paper. Prints were made of uniform solid, 20% and 50% halftone tints at 80 lines per inch. Minimal dot gain occurred for the 20% dot but the 50% printed up to 75%, giving dot diameters of 140 and 273 µm respectively. The latter two provided samples having small dot areas to start with and provided the opportunity to explore the efficiency of the technique for known smaller ink particles. Samples were prepared for ultrasound treatment and subsequently analysed using image analysis in the same way as for toners; sonication periods were up to 10 minutes.

Hand sheets prepared from pulped but unsonicated solid samples showed a wide range of particle sizes ranging from 60 to greater than 3600µm and above. Particle sizes were found to decrease regularly with increasing exposure time intervals 1,2,5 and 10 minutes. Typically, particles in the hand sheets in the range 2000 to 3600mm diameter decreased from an average of 6 particles per hand sheet for no exposure to zero per sheet after five minutes exposure. Clearly, the ink particles are broken down by the influence of ultrasound.

The efficacy of the technique for particles with a smaller starting size was explored using the half-tone samples. Figure 3 shows the progressive reduction in particle size for the 75% (nominally 50%) dots. The smaller size categories increase in number at the expense of the larger sizes. Figures 4 (unsonicated) and 5 (sonicated for 10 minutes) show visual evidence of the break up. Figure 6 shows the particle size distribution obtained for the 20% dot. In summary, ultrasound treatment of UV-cured inks detaches a significant proportion from the main body of the slurry and engineers the particle sizes down into the flotatable range.

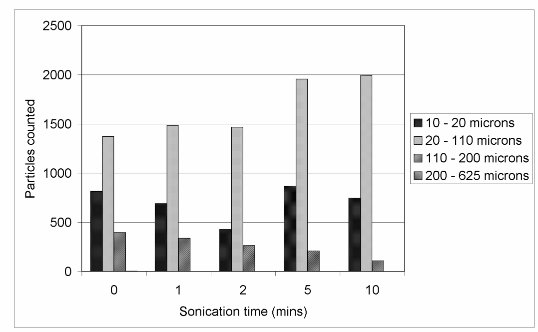

Figure 3. *Particle size distributions found on hand sheets from 20% unwashed samples.*

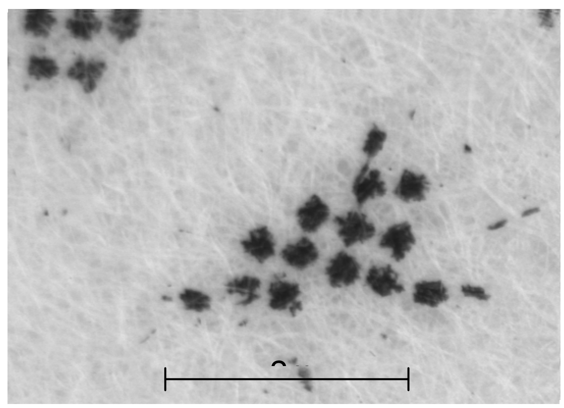

Figure 4 *75% half-tone dots, unsonicated, unwashed. The bar represents 2mm*

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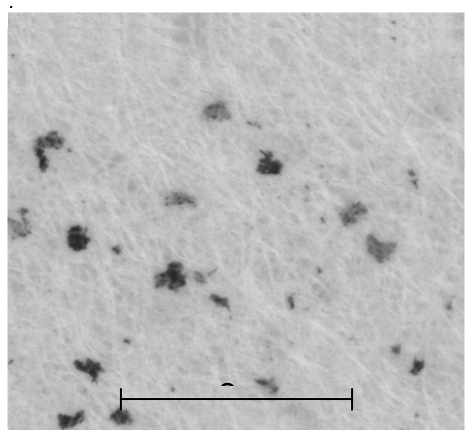

Figure 5. *75% half-tone dots, 10 minutes sonication, unwashed. The bar represents 2mm.*

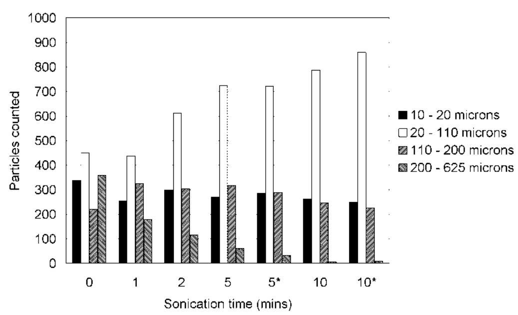

Figure 6. *Particle size distributions found on hand sheets from 75% unwashed samples.*

Indigo inks

Little information has been released about the composition of Indigo inks but it has been suggested that they contain a mineral oil varnish and pigments similar to lithographic inks [4]. The toner system comprises pigmented thermoplastic polymer particles dispersed in a non-polar solvent. According to the US Patent [5], at temperatures below 40^{o}C the thermoplastic polymer is insoluble in the carrier oil. Above 50^{o}C, the polymer is able to solvate in the carrier liquid and above 70^{o}C the polymer particles melt and fuse.

During the printing process the liquid toner is transferred to an offsetting blanket which is heated to 100^{o}C. This causes the suspended toner particles to melt and fuse together, forming a 'hot adhesive liquid plastic'. When the ink contacts the relatively cool substrate it solidifies, sticks to it and is stripped off the blanket, leaving no residue behind.

Experimental

To explore the efficiency of ultrasound in the de-inking and size reduction on Indigo digital prints, two types of image and two types of substrate were selected for comparison. The first image comprised a combination of graphic images and text, since these are the most common types of printed matter. The second comprised solid areas of ink since these were considered to be potentially the most problematic to break down. In both cases, black ink was used to simplify ink particle counting.

The two papers chosen were 115gsm Mediaprint Silk and Indigo's Sapphire coated paper. All prints were made using an Indigo 3000 press. The preliminary investigations to establish the optimum sonication conditions were carried out on the Mediaprint Silk printings. As with dry toners, temperature may have an important effect on the de-inking of Indigo prints. Temperatures of 20^{o}C, 40^{o}C and 60^{o}C were maintained during sonication using a temperature controlled water bath. Samples were irradiated at two power densities; 140 kWm^{-2} and 188 kWm^{-2}.

The power density of the applied ultrasound is critical in achieving ink particle breakdown. At 140kWm^{-2}, even 20 minutes of treatment did not produce significant changes in particle size distribution, although it was marginally more effective at 20^{o}C. The reduction in effectiveness at higher temperatures is attributed to coalescence of softened Indigo ink particles under the influence of increasing ultrasound fields.

At a power density of 188kWm^{-2}, there is evidence of substantial breakdown of particles. This is noticeable after 10 minutes of treatment and is significantly more pronounced after 20 minutes. This is observed for all printings on both Mediaprint Silk and Sapphire coated papers although there is some evidence that de-inking of Sapphire coated papers is more readily achieved. The higher power density rating was found to be very effective in breaking down large particles to the flotatable size range.

Indigo inks do not appear to be as difficult to remove as has been generally feared and can be de-inked to about 90% simply with disintegration and washing under neutral conditions. Application of ultrasound, however, detaches almost 100% of the ink. Ultrasound can be used to engineer the break down of ink particles to flotatable sizes for the de-inking process.

Summary

For all the systems investigated it was possible to both detach and reduce the size of particles down to the flotatable size range of 20 to 120 microns. The general conclusions are that the application of ultrasound can be used to aid the removal of ink films from waste paper, engineer particle size distributions and reduce the use of chemicals from the de-inking stage of recycling.

References

[1] U. Schmitz.and A.Fischer, "Recycling killer in digital clothing: digital inks cause recycling problems", Druck Medien, pp34-35, (2004).
[2] R.C. Thompson, "The technology of paper recycling." Professional Printer 41 (3), pp12-21, (1997).
[3] R.C. Thompson and A. Manning, "A review of ultrasound and its applications in papermaking", Progress in Paper Recycling, 14, (2), pp26–42, (2005)
[4] Landa B., Ben-Auraham P., Hall J. and Gibson G. "US Patent No 4794651" (Dec 27th 1988).
[5] Cody H. "Innovative products emerge in response to expanding demand for digital papers". Pulp Pap 77 (3), pp30-32, (2003).