Fatty Acid Based Alkaline Deinking of Digital and Non-Digital Prints

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Abstract

A fatty acid based alkaline deinking chemistry is presented and is shown to be suitable for various digital and non-digital printed materials. In particular, the effect of different fatty acids is investigated in detail and also specificities involved with larger LEP ink particles and foam requirements are analyzed. The influence of chemicals used in paper manufacturing on sustainable froth foaming is presented and a possible solution is also discussed. Finally TGA analysis of flotation reject is presented and actual fiber loss is determined.

Introduction

Recycling and deinking of print products make economic sense. Traditional deinking technologies are tailored towards analog print products. With the advent of digital printing technologies, liquid electrophotography (LEP), dye-based thermal inkjet (TIJ) and some pigment-based TIJ inks are perceived to present deinking challenges [1]. It is highly desirable to innovate a generic deinking solution which caters to a wide range of ink-media combinations. Our prior work, based on a near-neutral HPES deinking chemistry, has shown good deinking results with digital and offset prints [2-4]. Since numerous recycling facilities around the world do employ alkaline deinking, it is equally desirable to develop effective alkaline-based chemistry. In this paper, we discuss an alternate fatty acid-based alkaline deinking chemistry which is shown to be suitable for successful ink removal in digital and non-digital printed materials. In particular, we will focus on three digital printing technologies, namely LEP, dye TIJ and pigment TIJ. Key results for other digital and offset prints with our alkaline chemistry will also be presented.

Deinking Methodology and Apparatus

Laboratory scale deinking apparatus, as shown in Figure 1, and the evaluation method are similar to that presented elsewhere [1,2]. The amount of sodium hydroxide (NaOH) was varied and was dependent on the print products' alkalinity. Both define the final pH of the pulped product. Sodium silicate acts as a pH buffering agent. It can also reduces alkaline yellowing of pulp and may have some detergency effect as well. The action of hydrogen peroxide, although mainly bleaching, has also been linked to further preventing darkening of the deinked pulp. The main detergency effect is provided by the fatty-acid soap, which is formed by saponification of NaOH and fatty acid.

For the froth-flotation deinking to succeed, there needs to be a continuous generation of a stable gas-liquid two-phase system called foam. In addition, the foam level and the size of foam bubbles should meet certain requirements for successful deinking of various printed materials. More specifically, the foam must have sufficient yield strength to carry a large distribution of ink particles to the top of the flotation cell where the ink-attached foam can be skimmed off. A comprehensive review of the chemistry of deinking was written by Beneventi, Carre and Gandini [5].

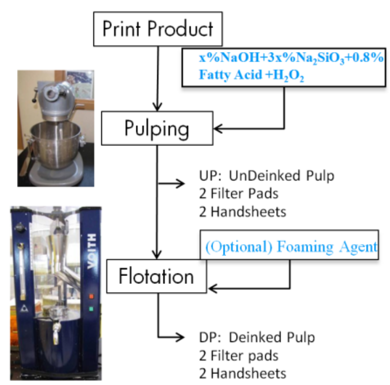
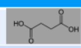
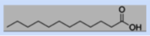
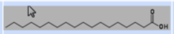
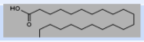
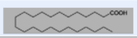


Figure 1. Procedural steps of lab-scale deinking evaluation.

Results and Discussion

In this work, saturated fatty acids, mono-unsaturated fatty acids and a poly-unsaturated fatty acid were tested in detail. Table 1 lists the effect of saturated and mono-unsaturated fatty acids in deinking LEP prints. The printed samples used in this study were prepared with a HP-Indigo 5500 digital press using a coated commercial paper. It is seen from Table 1 that, as the length of alkyl chain of saturated fatty acid increases, the speck count of deinked pulp (DP) decreases to a mininum (with corresponding 18 carbons) and then increases again. This optimality appears to be similar to the HLB effect observed in our near-neutral deinking chemistry [3] and seems to be related to the lowering of the surface energy of ink particles. However, none of the saturated fatty acids were found to be adequate in deinking LEP print samples.

Interestingly, mono-unsaturated fatty acids were found to be very effective. Oleic acid, which has been mentioned as a common fatty acid used in alkaline deinking chemistries [5] was seen to be better than all of the saturated fatty acids but still not good enough for LEP prints. Erucic acid (with 22 carbons), on the other hand, was seen to be particularly effective in removing larger LEP ink specks. When mono-unsaturated fatty acid carbon chain is increased beyond 22, as in nervonic acid (with 24 carbons), it was seen less effective than erucic acid. One poly-unsaturated fatty acid, namely linoleic acid, was tried and found ineffective in deinking LEP prints. It is to be mentioned that the finding reported in this work appears contradictory to some earlier publications where linoleic and stearic acid were both favorably mentioned for alkaline deinking [6,7], although it is not clear whether LEP was tried by the researchers mentioned in the liturature. Figure 2 shows a comparison of LEP deinking using oleic acid and erucic acid. Figure 2d clearly shows the efficacy of erucic acid in LEP deinking.

Fatty Acid	Formula	UP		DP	
		A_{50} (mm^2/m^2)	A_{250} (mm^2/m^2)	A_{50} (mm^2/m^2)	A_{250} (mm^2/m^2)
Succinic Acid ($C_4H_6O_4$)		$2x10^4$	$1.8x10^4$	$2.2x10^4$	$2.1x10^4$
Lauric Acid ($C_{12}H_{24}O_2$)		$1.75x10^4$	$1.5x10^4$	$3.22x10^4$	$2.7x10^4$
Palmitic acid ($C_{16}H_{32}O_2$)		$2.3x10^4$	$2.2x10^4$	$5.4x10^3$	$4.9x10^3$
Stearic Acid ($C_{18}H_{36}O_2$)		$2.1x10^4$	$2x10^4$	$3.9x10^3$	$3.4x10^3$
Arachidic Acid ($C_{20}H_{40}O_2$)		$2x10^4$	$1.9x10^4$	$4.35x10^3$	$3.95x10^3$
Behenic Acid ($C_{22}H_{44}O_2$)		$2.1x10^4$	$1.9x10^4$	$4.4x10^3$	$4.2x10^3$
Lignoceric Acid ($C_{24}H_{48}O_2$)		$2.16x10^4$	$2.0x10^4$	$5.5x10^3$	$4.9x10^3$

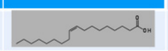
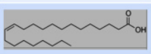
Fatty Acid	Formula	UP		DP	
		A_{50} (mm^2/m^2)	A_{250} (mm^2/m^2)	A_{50} (mm^2/m^2)	A_{250} (mm^2/m^2)
Oleic Acid ($C_{18}H_{34}O_2$)		$8.7x10^3$	$6.6x10^3$	$4.4x10^3$	$3.2x10^3$
Erucic Acid ($C_{22}H_{42}O_2$)		$3.8x10^3$	$2.2x10^3$	186	84
Nervonic acid ($C_{24}H_{46}O_2$)		$9.4x10^4$	$8.5x10^4$	$2.69x10^3$	$2.4x10^3$

Table 1. Effect of saturated fatty acid (top) and mono-unsaturated fatty acid (bottom) in deinking LEP print samples.

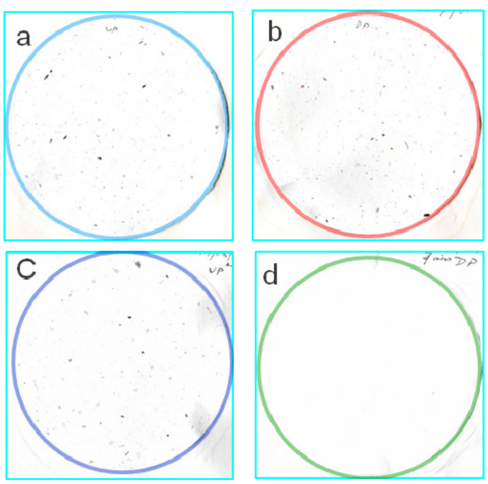


Figure 2. (a) Handsheet made from LEP undeinked pulp (UP) using oleic acid; (b) LEP deinked pulp (DP) using oleic acid; (c) LEP UP using erucic acid and (d) LEP DP using erucic acid.

Through repetitive tests with the erucic acid based alkaline chemistry, we found that the media and pH (particularly in the presence of fatty acids) play a noticeable role in the deinkability of digital prints. To elucidate these effects further, we studied the effects of pH on deinkability and foam sustainability.

Figure 3 shows that there exists a considerable range of pH where LEP coated commercial paper can be deinked satisfactorily, but in the case of LEP uncoated commercial paper, the lowest possible ink speck count was obtained at pH 10. DP speck count A_{250} was beyond the threshold level and the main problem was due to the presence of large ink particles (average diameter of ink specks over 0.8 mm) after 12 minutes of flotation.

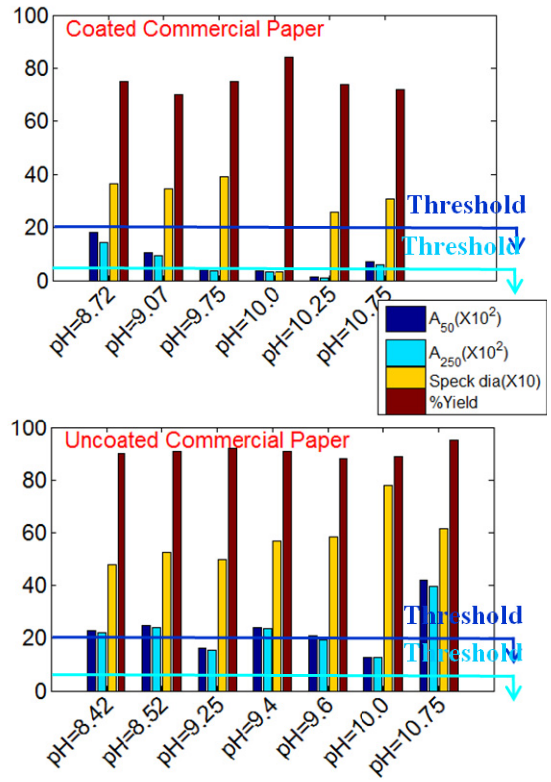


Figure 3. Effect of pH on a coated commercial paper (top) and an uncoated commercial paper (bottom). The speck counts (A_{50} and A_{250} according to ERPC deinking scorecard (from www. paperrecovery.org/uploads/Modules/ Publications/ERPC-005-09-115018A.pdf) (in mm^2/m^2), speck diameter (in μm) and yield (in %) are shown.

In INGEDE M11p deinking simulation method, a pH of 9-10 is specified. It is likely that paper manufacturers add defoaming agents, such as silicon oil or hydrophobic silica in paper making. The purpose of such defoaming agents is to "puncture" smaller air bubbles, in paper making process, and allows coalescence into larger bubbles. It is possible that such chemicals may interfere with the saponification and foam sustainability while such papers are used in deinking. Figure 4 examines typical LEP ink particles of an uncoated commercial paper at the beginning of a froth flotation (using the erucic acid-based alkaline chemistry) and suggests that for effective removal of larger ink particles (> 0.5mm), several air bubbles are needed to attach to them. As flotation progressed, the amount of foam was seen to quickly quench as shown in Figure 5. In the case of the coated commercial paper, in contrast, an appropriate level of foaming with small bubbles was observed. In Figures 5a and b, it is shown that at exactly midway between the 12 minutes of total froth flotation, only coalesced large foam bubbles remained in the case of uncoated commercial paper. Such foams are unstable and break down easily, therefore cannot carry larger ink particles to the top of the flotation cell. In Figures 5c and d, on the other hand, sustainable small foam bubbles are maintained for the entire duration of the flotation. It is therefore not surprising that the LEP coated commercial paper was seen to deink very well.

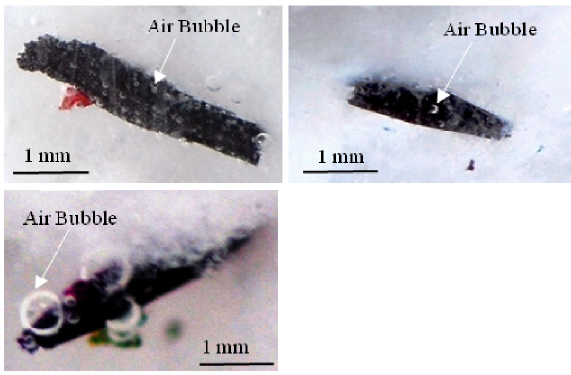


Figure 4. Froth flotation of LEP prints. Three different ink particles are shown with several small foam bubbles attached to each ink particle. These pictures are taken at the beginning of flotation.

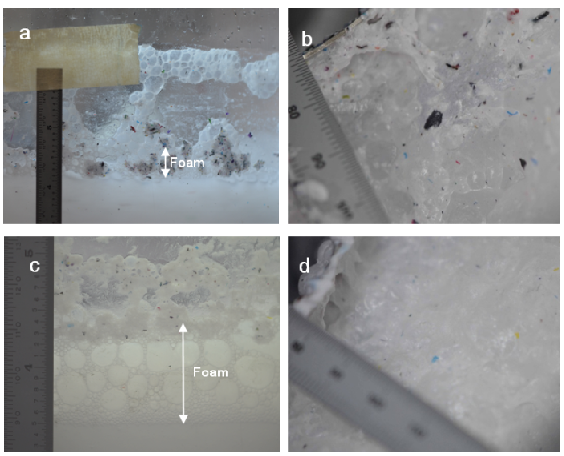


Figure 5. (a) Foam level as observed from the side at 6 min of flotation (LEP uncoated commercial paper); (b) A top view of the froth foam. (c) Foam level as observed from the side at 6 min of flotation (LEP coated commercial paper); (d) A top view of the froth foam.

The presence of large foam bubbles observed in Figure 5 can be overcome by adding an appropriate amount of foaming agent(s) during the flotation to re-generate smaller sized foam to facilitate the ink removal. In this work, 0.05 - 0.1% sodium dodecyl sulfate (SDS) was added in the last two minutes of flotation and the uncoated paper was deinked to a satisfactory level. There still remains room to optimize the nature, dosage and timing of the foaming agent addition. Figure 6 shows the effect of SDS addition where the otherwise ‘not suitable for deinking’ uncoated commercial paper was deinked successfully.

It is seen from Figure 3 that an average flotation yield of 75% is obtained for the coated commercial paper and 90% was obtained the uncoated commercial paper. Of particular interest is to determine what portions of actual fiber and filler were lost during the froth flotation. Figure 7 shows thermogravimetric (TGA) analysis, in an oxygen atmosphere, of the original

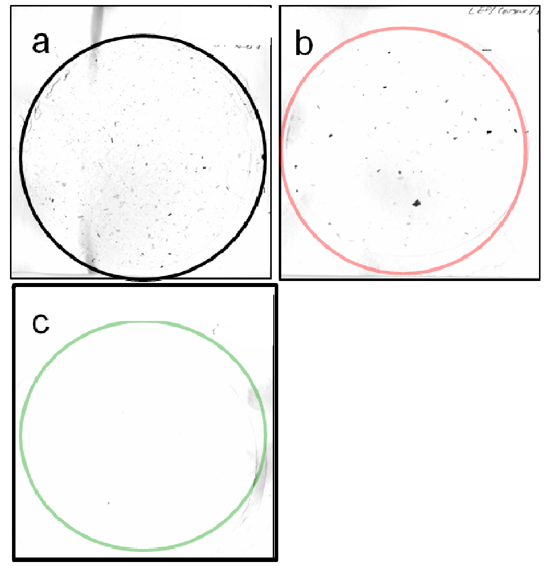


Figure 6. Deinking of a LEP uncoated commercial paper. (a) UP, (b) DP with erucic acid-based alkaline chemistry and 10 minutes flotation. A_{50} = 1.3x10^3 mm^2/m^2, A_{250} = 1.1x10^3 mm^2/m^2. (c) 0.05% SDS was added at the 10^{th} minute of flotation and continued for 2 more minutes, A_{50} = 101 mm^2/m^2., A_{250} =12 mm^2/m^2. Yield = 88%.

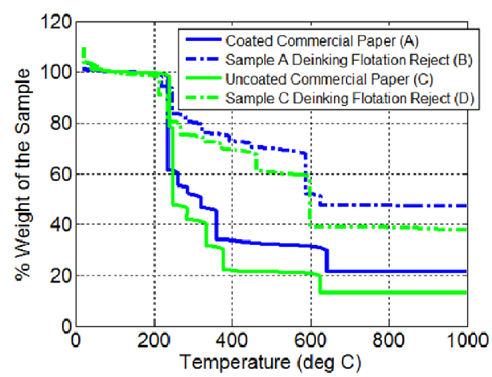


Figure 7. TGA analyses of commercial papers and flotation rejects.

commercial papers and the flotation rejects. It can be assumed that all the organic-based materials present in the samples were decomposed completely by 400°C, leaving behind the inorganic materials. The organic and inorganic contents are summarized in Table 2. It is important to note that the flotation selectively removes more fillers than cellulose fibers, a desirable attribute in deinking. From the flotation yield and organic/inorganic content aalysis, we determined the actual fiber and filler losses. In the case of the coated commercial paper, only 6.85% fiber is lost. This number is very close to that reported in our previous work [3] for the same commercial paper using our near-neutral HPES chemistry. In the case of uncoated commercial paper, the fiber loss was even lower and found to be only 3%.

Even though the focus so far has been on LEP, erucic acid was found to be effective in deinking other digital prints derived from various digital printing technologies. In Figure 8a, we compare the deinking results of oleic acid-based deinking and erucic acid-based deinking of various ink-media combinations. In these evaluations, dye-based TIJ prints were printed with an HP Deskjet printer and pigment-based TIJ prints were obtained from an Edgeline printer. In both cases, ColorLok ™ paper was used. It was presented above that LEP prints suffers from high ink speck count (A_{50} and A_{250}) with conventional oleic acid-based deinking. Both dye- and pigment-based TIJ prints fall short in filtrate darkening (ΔY) with the oleic acid-based chemistry; the former suffers in low ink elimination (IE) as well. Athough not reported here, DEP (aka laser) prints are deinkable using the conventional oleic acid-based chemistry. Offset prints also work well with the same chemistry.

Sample	Organic Content (%)	Inorganic Content (%)	Deinking Fiber/ Filler Loss (%)*
A	66.3	33.7	
B	27.4	72.6	6.85/18.15
C	78.1	21.9	
D	30.5	69.5	3.0/7

*% loss is calculated wrt dry paper wt. Fiber and Filler loss combined make up the flotation loss.

Table 2. Summary of TGA analyses of coated and uncoated commercial papers, and flotation rejects.

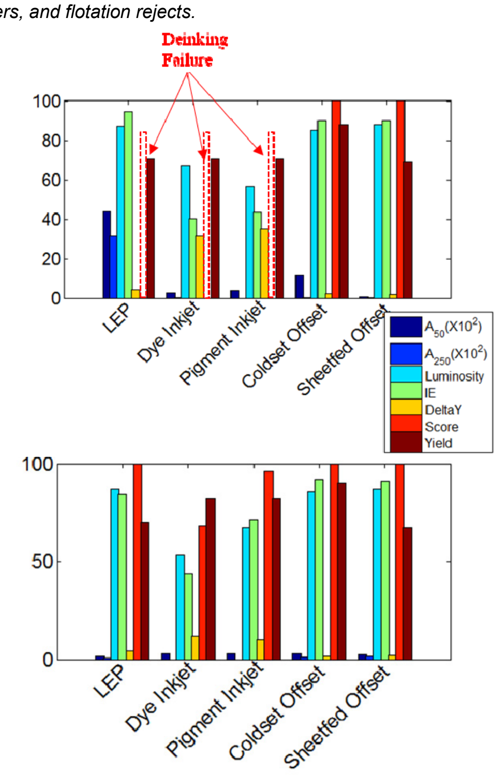


Figure 8. Summary of conventional oleic acid-based deinking of digital and non-digital prints (top) and erucic acid-based deinking of similar prints (bottom).

Erucic acid-based chemistry, as shown in Figure 8b, is observed to deink LEP prints very well. In addition, it is also able to obtain good deinkability with both dye- and pigment-based TIJ prints. DEP prints are found to deink very well. It is interesting to point out that offsets prints were observed to deink satisfactorily with both chemistries.

Conclusion

A fatty acid-based alkaline deinking chemistry is presented that can efficiently deink LEP, dye based inkjet, pigment based inkjet and various offset prints. This alkaline deinking chemistry is shown to be an attractive alternative deinking chemistry which, in addition to the earlier reported near-neutral HPES chemistry, can serve as a generic chemistry for a wider range of ink-media combinations.

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Author Biographies

Manoj K. Bhattacharyya received his PhD from Carnegie-Mellon University in Electrical and Computer Engineering. Dr. Bhattacharyya has been working in Hewlett Packard Laboratories for over twenty five years and has worked on many different research areas related to printing technologies.

Hou T. Ng has a PhD in Chemistry and is a project manager/ principal scientist at HP Labs. Dr. Ng has worked in a variety of research areas including nanotechnology, MEMs, printed electronics, semiconductor technologies, LEP and inkjet technologies.

Laurie Mittelstadt has MS degrees in Material Science and in Physics and Astronomy. Ms. Mittelstadt is a project scientist at HP Labs. She has a broad range of expertise in printing technology as well as fuel cells and laser ablation.

References

[1] B. Carre, L. Magnin, C. Ayala, International Conference on Digital Production Printing and Applications, May 2005, Amsterdam, the Netherlands.

[2] Hou T. Ng, Manoj K. Bhattacharyya, Laurie Mittelstadt, and Eric G. Hanson, NIP 25, Sept 2010, 173.

[3] M.K. Bhattacharyya, H.T. Ng, L. Mittelstadt and E.G. Hanson, NIP 26, Sept 2010, pp 112-115.

[4] Hou T. Ng, Manoj Bhattacharyya, Laurie Mittelstadt, and Eric G. Hanson, NIP 26, Sept 2011, 88.

[5] D. Beneventi, B. Carre and A. Gandini, "Phsyco-Chemical Aspects of Deinking", COST E46-A Deinking Primer.

[6] Y. Zhao, Y. Deng and J.Y. Zhu, Progress in Paper Recycling, Vol. 14, No. 1, November 2004.

[7] Ferguson, L. D., Deinking Chemistry; Part 2, Tappi J., 75(8) J 49-58, 1992.