Effect of Surfactant Chemistry on Deinkability

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Abstract

A detailed discussion of synthetic nonionic and anionic surfactant combination based near-neutral deinking is presented. It is shown that by choosing a nonionic surfactant with a desired hydrophile- lipophile balance during pulping and using a small amount of anionic surfactant during flotation, excellent deinking of LEP as well as dye-based inkjet and various other prints are obtained. All the results are obtained without adding any bleaching stage, which can further enhance the results. High flotation yield in the range of 80-85% with minimal fiber loss, as shown by thermogravimetric analysis, is also obtained.

Introduction

Recycling of paper and paper products are of paramount importance for various ecological and financial reasons. In the US, Europe, Japan and other countries, recovery and reuse of paper fiber has substantially increased over the last few decades. In the US, for example, 45% of all paper and paperboard was recycled in 1996. In 2009, in comparison, 63.4% of all paper consumed in the US was recovered [1] and over a third of all paper and paperboard recovered globally was done in the US. Also, in the last fifteen years use of virgin fibers in paper making has gone down from 53% to about 42% currently. Use of recycled fibers in the paper making has gone up by almost an equal amount in the same period [2].

Historically, deinking technologies at many recycling mills have been alkaline in nature. Such alkaline deinking methods use caustic chemicals which degrade the fiber strength and require elaborate and expensive waste water treatment methods. In addition, the cost of chemicals used for alkaline deinking can be high and also the fiber yield can be low. Neutral deinking, on the other hand, can increase the recovered fiber strength as well as reduce the total cost of chemicals substantially [3]. In addition, some research has shown that alkaline deinking can reduce the detached ink to sizes that are unsuitable for flotation deinking [4]. In a recent publication Ng and coworkers have demonstrated a highly efficient near-neutral deinking procedure for deinking of most digital print technologies [7]. In addition, the deinking methodology reported by Ng. and coworkers was shown to be efficient for most offset print technologies also. In this paper, the near-neutral deinking chemistry will be explored in greater depth. In particular, the choice of synthetic nonionic and anionic surfactants, their necessities in deinking of various print products, their effects on flotation yield, fiber loss and practical implementation issues will be discussed.

In the following sections, the flotation deinking steps, foam formation and dynamics, nonionic surfactant hydrophile-lipophile balance (HLB) [9], anionic surfactant choice, deinking optimization and deinking results for LEP, dye- and pigment-based TIJ prints, DEP (aka laser) prints and non-digital prints will be presented.

Flotation Deinking with Synthetic Surfactants

In the simplified flotation deinking method presented in this paper, the paper products and water are mixed with chemical additives and then agitated in a pulper to dislodge and disperse the inks from the fibers. The resulting pulp is then further diluted with water to a desired consistency and put in a laboratory scale flotation cell (Delta 25 by Voith paper). More chemical additive is also added in the flotation cell. After few minutes of flotation, the ink floats out of the fiber and carried to the top of the cell by the froth. The froth is the skimmed out of flotation cell along with the collected ink. Hand sheets filter pads and membrane filter pads were made to evaluate the deinking efficacy. At the heart of flotation is, of course, formation of foam with enough yield stress to be able to carry a wide variety of ink contaminants to the top of flotation chamber. Foams are defined as a two-phase medium of gas and liquid with the gas pockets trapped in a network of thin liquid film [8]. Generally, foams trap gas fraction of 80% or more. For formation of foam, surfactants are required and also gas flow at a rate higher than the quenching rate of foams is essential. In the formation of foam, the surfactant reduces the surface energy of the liquid (water in this case) so that it can wrap around the gas (air in this case) bubble. If the HLB of the surfactant is too low, then the foam size is too small to carry ink particles and if the HLB is too high then the foam size is too large to provide the desired foam stability. Large HLB may also alter the hydrophobicity of ink particles for effective removal by foam. Even though the discussion so far has focused on nonionic surfactants and it may be possible to deink many types of paper with these surfactants alone, some printing inks (e.g. water soluble ink jet dyes) are hydrophilic in nature and may not be possible to be completely removed by nonionic surfactants alone. For many of the samples analyzed and presented in this paper, some amount of anionic inks or components were found to be present and addition of small amount of an anionic surfactant like sodium dodecyl sulfate (SDS) or sodium laureth sulfate (SLES) were found effective. For these cases, it is understood that the anionic surfactant may be dissolving the anionic molecules (for example, anionic acid red 289 dye) and becoming part of the top froth during flotation.

The deinking methodology is similar to that mentioned in the paper by Ng et. al [7]. The deinking print evaluation method and deinking score is based on ERPC deinking score card. In addition, thermal analysis of the flotation rejects to determine the organic and inorganic contents is also presented. The thermal analysis is done in a TA instruments' Q500 thermogravimetric analyzer (TGA) in an oxidative atmosphere. In many separate reference experiments, it was determined that almost all the organic components were decomposed by 400 ^{o}C and the remaining mass at 400 °C and beyond represents inorganic content (fillers and pigments such as precipitated calcium carbonate (PCC), ground calcium carbonate (GCC), clay and TiO_2). In the TGA, a heating rate of 3 °C/min was used and isothermal hold was employed when detectable mass change was observed.

Results for LEP

Most of the optimization of deinking chemistry is presented using LEP printed papers. These papers were printed on an HP-Indigo 5500 digital offset press using HP Indigo ElectroInk and Newpage Sterling Ultra digital coated paper. Table I shows the nonionic surfactants used in optimizing the chemistry. The chemicals are readily available commercially.

Non-Ionic Surfactant	Surfactant Formula	HLB (from literature)
Brij 52	$C_{16}H_{33}(OCH_2CH_2)_2OH$	5
Brij 30	$C_{12}H_{25}(OCH_2CH_2)_4OH$	9
Myrj 45	$H(OCH_2CH_2)_8CH2(CH_2)_{16}CH_3$	11.1
Brij 97	$C_{18}H_{35}(OCH_2CH_2)_{10}OH$	12
Brij 98	$C_{18}H_{35}(OCH_2CH_2)_{20}OH$	15.3
Brij 700	$C_{18}H_{37}(OCH_2CH_2)_{100}OH$	18
Methoxy PEG 350	$H_3C(OCH_2CH_2)_{12}OH$	19.3

***Table 1**. Nonionic surfactants, their formulae and HLB values.*

First question that will be answered is the optimum flotation time. For this experiment, 0.6 wt% MYRJ 45 was used for pulping. In addition 0.05 wt% (all weights are given relative to dry paper weight) pre-dissolved SDS was added in the Voith flotation tank with 5 % consistency pulp and was well mixed (for about 30 seconds). The Voith cell was then filled up with 45 °C hardness controlled water and flotation started. Samples of flotation reject and flotation accept were collected at regular intervals. Hand sheets were made with the flotation accepts and TGA analyses of the rejects were done according to the method mentioned earlier.

LEP ink is, generally, hydrophobic in nature and also breaks down in somewhat larger specks during pulping. If the removal of the ink specks is not good, visible ink specks may be observed in deinked fiber. The effect of flotation time has a direct influence on speck contamination for LEP prints. Figure 1 shows that within 10 minutes of flotation, speck contamination has significantly reduced to less than the target values of residual ink speck contamination stipulated by ERPC. The corresponding flotation yield is found to be around 80%. As flotation time increases, more fibers are lost. There are various factors that can cause fiber loss. For example Wu, Deng and Zhu have found that physical entrapment of fibers in the air bubble network and adhesion of hydrophobic parts of fiber surfaces on the air bubble surface contribute to fiber loss [9]. It may be anticipated that allowing extra time in flotation increases the probability of both of these

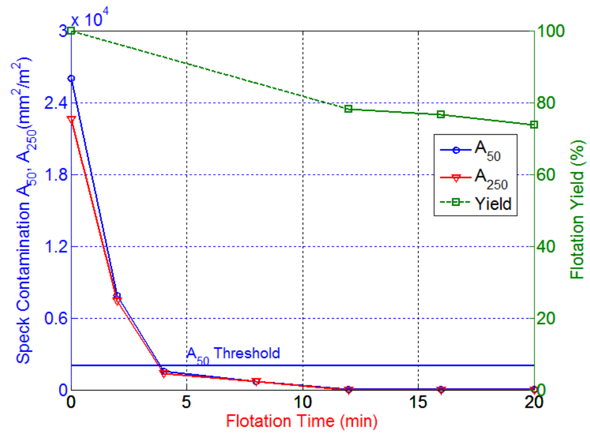

***Figure 1**. Speck contamination in the deinked pulp and flotation yield versus flotation time. 0.6% MYRJ45 and 0.05% SDS were used.*

factors and thus increasing fiber loss. Table 2 shows TGA analyses of rejects at different flotation times and with increasing time cellulose becomes a larger part of the reject. When compared with unprinted paper, the inorganic content of rejects is higher, suggesting that residual flotation accepts have lesser proportion of filler material, this may be a desirable attribute for some application, say hygienic tissue, where minimal amount of fillers are used.

Even though MYRJ 45 was used for deinking in figure 1, it is worth investigating the optimum range of HLB of nonionic surfactants. Figure 2 shows the effects of nonionic surfactant variation on ink speck removal, flotation yield and actual fiber loss in reject. The fiber loss is found by multiplying flotation yield with the percent of cellulose in reject (TGA analyses is not shown for this particular case).Surfactant HLB range of 10-12 is found best. It is worth mentioning, as a comparison that oleic acid, a common fatty acid used in some deinking has a HLB of 2.

Time of Flotation (min)	**Cellulose In Reject (%)**	**Inorganic in Reject (%)**
2	**29.9**	**70.1**
4	**28.7**	**71.3**
8	**29.5**	**69.5**
12	**31**	**67.7**
16	**31.1**	**68.**
20	**36**	**64**
Whole Paper	**Cellulose=65.5**	**Inorganic=34.5**

***Table 2**. TGA analyses of reject with 0.6% MYRJ45 and 0.05% SDS.*

The concentration effect of nonionic surfactant on the various key parameters was studied. Here the amount of anionic surfactant in flotation was kept constant at 0.05 % while the amount of nonionic surfactant (MYRJ 45) was varied. At 0.6 % of the nonionic surfactant content, both measures of ink speck contamination became better than the target values. A higher amount seems to affect flotation yield, but the dependence was seen as weak.

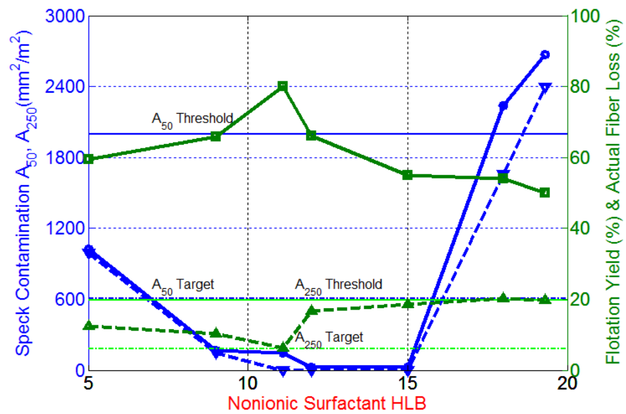

Figure 2*. Speck contamination in the deinked pulp and flotation yield versus HLB. Blue solid line represents A_{50}, blue dashed line represents A_{250}, green solid line represents flotation yield and green dashed line represents actual fiber loss. At the best point, just 6% fiber loss is seen.*

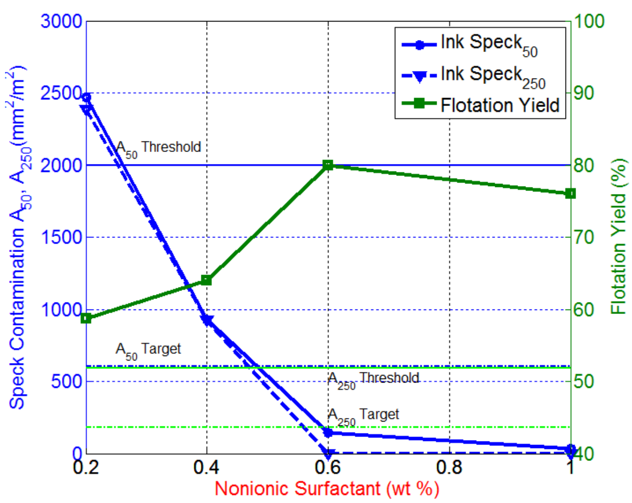

Figure 3*. Speck contamination in the deinked pulp and flotation yield versus MYRJ 45 content. 0.05% SDS was also used. The target and threshold values indicated are according to ERPC standard.*

Often it has been argued that there is a desirable range of ink speck size for effective flotation deinking and LEP ink sizes are, generally, totally outside this desirable range and thus not deinkable [5]. Following figure 4 and its inset show the particle sizes in undeinked pulp and deinked pulp in one of the deinking experiments (a 1.5 inch square sample of hand sheets are analyzed). While the undeinked pulp had huge number of small particles and even some as large as 1.8 mm in diameter, the deinked pulp had no ink speck larger than 150 µm in diameter. This result clearly demonstrates that with proper choice of deinking chemistry, large ink speck distribution present in LEP did not contribute to any loss of recyclability.

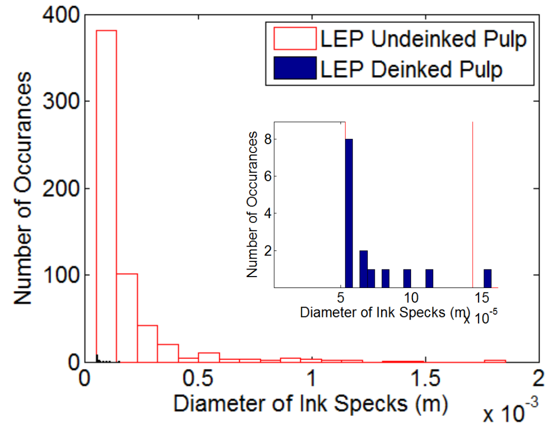

Figure 4*. Speck contamination in the undeinked pulp and deinked pulp. 0.6% MYRJ45 and 0.05% SDS were used. The histogram in the inset expands the deinked pulp's particles size seen only at the bottom left corner of the main figure.*

Other Digital Prints

While the near-neutral deinking chemistry was shown to work effectively in LEP, its effectiveness in TIJ (dye and pigment based inks) and DEP need to be examined. Dye based inkjet is somewhat different from LEP in that some or all of the inks may be hydrophilic [11] and hard to remove by flotation. Since only hydrophobic inks get attached to the foams, removal of water soluble ink is difficult. Of course in an industrial recycling process, post flotation washing and rigorous bleaching may help in removing these dyes, some laboratory scale deinking studies have not succeeded in deinking dye based inkjet prints [5]**.**

In the near-neutral deinking presented here, it was seen that addition of SDS was particularly effective in removing these anionic ink molecules. With right amount of SDS, dye based inkjet was to deink satisfactorily . It is likely, as was explained earlier, the likeness of the dye molecules and SDS molecules (both being anionic molecules with polar and nonpolar ends) helped SDS 'dissolves' anionic dyes. It was also found that slightly higher amount of SDS was needed in obtaining "good deinkability" as defined by ERPC deinking score card. Incomplete removal of water-soluble dyes from flotation cell manifests themselves as filtrate darkening [5]. In laboratory scale deinking of dye TIJ prints, filtrate darkening presents a challenge. Figure 5 shows the deinking results of dye TIJ, where this figure shows that a minimum of 0.1 % SDS is needed to bring the filtrate darkening parameter below the threshold level of 18%. Increasing SDS, of course, has the disadvantage of lowering flotation yield. At 0.1% SDS in flotation, yield was seen at ~ 76%, and deinking score was 74 and can be classified as "good deinkability" according to ERPC standard.

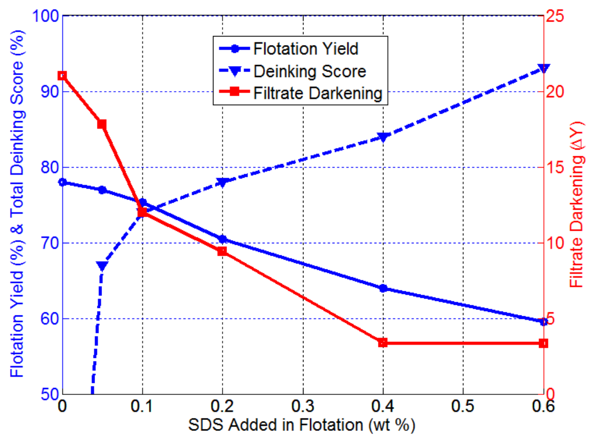

***Figure 5**. Flotation yield, total deinking scores (left scale) and filtrate darkening (right scale) vs. SDS for dye TIJ. MYRJ 45 was kept constant at 0.6%.*

Figure 6 summarizes all the digital prints, where the monitoring parameters have been normalized using a straight line transformation. In this normalization, target value has been assigned as 1 and threshold value has been assigned as 2. Thus a normalized value of 1.5 indicates actual parameter value halfway between target and threshold while a value of less than 1 will indicate actual parameter value of better than the target. The threshold for deinking score is taken as 71 (threshold for good deinkability) and a target of 100 is used. In general, lower the value of a normalized parameter better is its true performance measure. The flotation yield is, of course, not scaled as this is not part of the ERPC score. True % yield is shown in Figure 6.

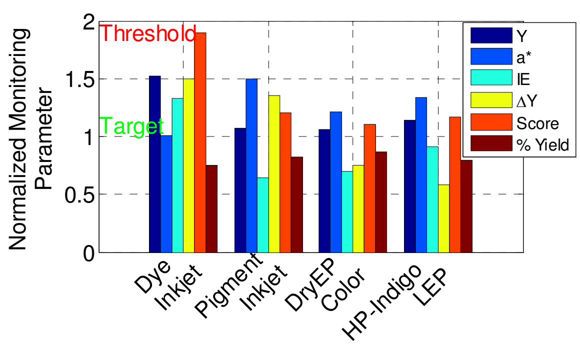

***Figure 6**. All the digital prints' normalized deinking parameters are plotted. DryEP (aka the laser printer is the easiest to deink and pigment TIJ and HP-Indigo LEP have also excellent deinkability.*

Finally Figure 7 shows TGA analyses of all the digital samples done in this paper. For all the cases, except dye TIJ, 0.6% MYRJ 45 and 0.05% SDS were used. In the case of dye TIJ 0.1% SDS and 0.6 % MYRJ 45 were used. It is interesting to observe that LEP paper seem to have a different grade of calcium carbonate compared to the paper used in non-LEP papers. It is possible the former has PCC vs. GCC for the later. All of the deinking rejects have more inorganic material than the original paper, probably a desirable point for some end application. The organic material in reject (i.e. fiber, polymeric binders of paper and ink) was seen to be lowest in LEP, while it was largest in dye TIJ.

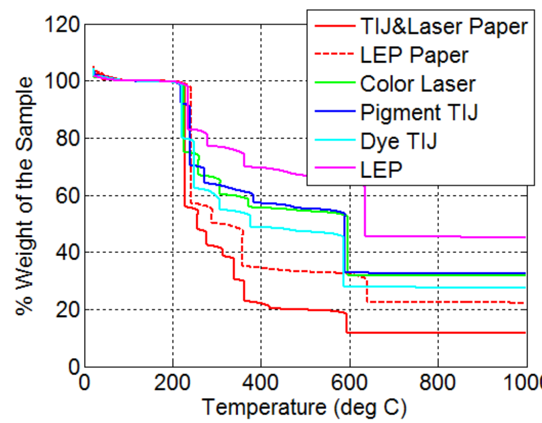

***Figure 7**. TGA thermal analyses in oxygen atmosphere of flotation rejects for all the samples.*

Non-Digital Prints

The deinking chemistry presented here was also used to deink a variety of non-digital prints. Figure 8 summarizes three such cases. MOW (mixed office waste) includes printed paper from variety of sources and was actually collected from a recycling mill, whereas sheetfed and coldest web samples were printed with the standard pattern mentioned by Ng et. al [7] in commercial printing facilities. All of the papers were deinked satisfactorily to meet ERPC "good deinkability" standard.

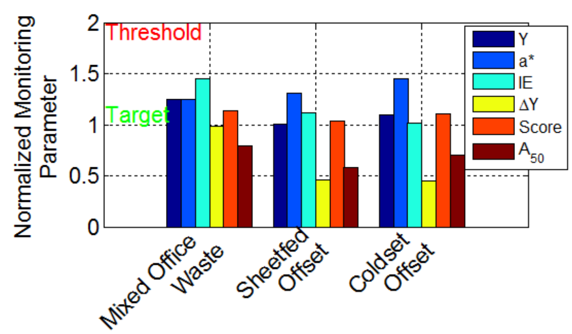

***Figure 8.** All the non-digital prints' normalized deinking parameters are plotted. For all the cases 0.6% MYRJ45 and 0.05% SDS were used.*

Conclusion

A near-neutral deinking method has been presented. The highly efficient method was shown to deink all types of digital and non-digital prints.

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