

Liquid phase plasma treatment for improved detachment of pigmented inkjet printed paper

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ABSTRACT: A new method of improving deinking of flexographic and inkjet printed paper has been investigated. It was found that the liquid plasma treatment method was able to improve the ink elimination and luminosity without negatively impacting the color a^* or ink elimination of the recycled paper. However, it was found that the filtrate darkening was increased by the liquid plasma treatment because the treatment was not able to increase the amount of ink removed through flotation. Because of this, the liquid plasma treatment is likely improving the deinkability parameters by improving the ink detachment of flexographic and inkjet inks.

Application: Liquid plasma treatment can mitigate the effects of hydrophilic inks on recycled paper quality. Mills will benefit from this and future research and development efforts on deinking of hydrophilic inks, such as flexographic and inkjet inks.

Inkjet digital nonimpact printing has been gaining popularity in recent years for newsprint and other publication applications due to its fast turnaround, on-demand printing capabilities, and exceptional print quality [1]. The percentage of flexographic printing also has increased in recent decades due to environmental and health concerns about traditional offset inks [2,3]. However, although these inks have been around for decades, the deinkability of these digital printing technologies is still unacceptably low for many paper recycling operations [4]. The poor deinkability of inkjet and flexographic inks is due to difficulties in separating the digital inks from paper fibers during traditional flotation deinking because of several important parameters [5,6]. First, these inks have been found to have submicron pigment particles (around 0.2 μm) after pulping in alkaline conditions compared to 10–250 μm for traditional offset pigments [5]. The small particle size of the pigments used in digital printing results in irreversible deposition in the lumen of pulp fibers [6]. Second, both inkjet and flexographic pigments are dispersed in water to reduce the use of volatile organic compounds (VOCs), which increases the hydrophilicity of the pigments [5]. The hydrophilic nature of the pigments prevents the flotation bubbles from effectively removing the ink particles and causes a buildup of ink in the filtrate [6]. Finally, pulp fibers interfere with the agglomeration of the ink particles to an optimal size for flotation, [7,8]. As a result, a limited percentage of flexographic and inkjet printed paper is used in deinking mills[1].

Because of these issues, there has been a large amount of research to mitigate them to increase the amount of paper

printed with pigmented ink that can be recycled. Some of the more successful efforts have been optimizing pulping conditions [9,10]; using enzymes such as laccase, cellulase, xylanase, and amylase [11]; and using coagulants, flocculants, or an electric-field technology to increase the size of the inkjet ink particles [12,13]. However, these technologies have not been able to fully reduce the negative impact of pigmented inks on deinking of recycled paper. Optimization of the pulping conditions by reducing pulping time and decreasing agitation was able to decrease redeposition of ink in the fiber lumen; however, the optimal conditions would only apply to 100% pigmented ink stocks because the optimal conditions for inkjet are inadequate for traditional inks[10]. To incorporate this with traditional inks, the operating conditions would have to be a compromise between the two, which would greatly reduce effectiveness of the technique on improving pigmented ink removal during paper recycling. There have also been many efforts to use enzymes for inkjet deinking. There has been some success, but the enzymes are very selective for the type of ink that they treat. Therefore, although very high ink removal efficiencies can be achieved in laboratory conditions, the ink composition is unknown in industrial applications and would be difficult to treat with this method [1]. Finally, there are several techniques that have been tested to increase particle size. Coagulants and flocculants have been shown to have little effect on the deinking efficiency of inkjet inks and they also cause large increases in yield losses [13]. Electric-field technology, on the other hand, was able to increase the brightness of recycled inkjet printed paper by 2 points and did not cause additional yield losses[12].

Because of the insufficient removal of inkjet and flexo-

graphic inks with these methods, a new method of assisting in the deinking of pigmented inkjet ink has been developed and investigated. This method is called liquid plasma polymerization; it uses an applied voltage across two submerged electrodes to generate a plasma region within the pulp slurry. Liquid plasma polymerization has been shown to drastically increase the particle size of pigmented inks in solution [14]. When used to treat recycled pulp before flotation, it is hypothesized that the increase in particle size will allow for reduced redeposition of ink and improved ink removal through flotation. The active species from the plasma region initiate polymerization of the inkjet ink particles, which greatly increases the size of the ink particles. Previously, liquid phase plasma treatment has been used for water decontamination and decoloration, polymerization, breakdown of organic molecules (such as phenol to carbon dioxide and water), and agglomeration of polymer suspensions [14,17].

EXPERIMENTAL

Paper preparation

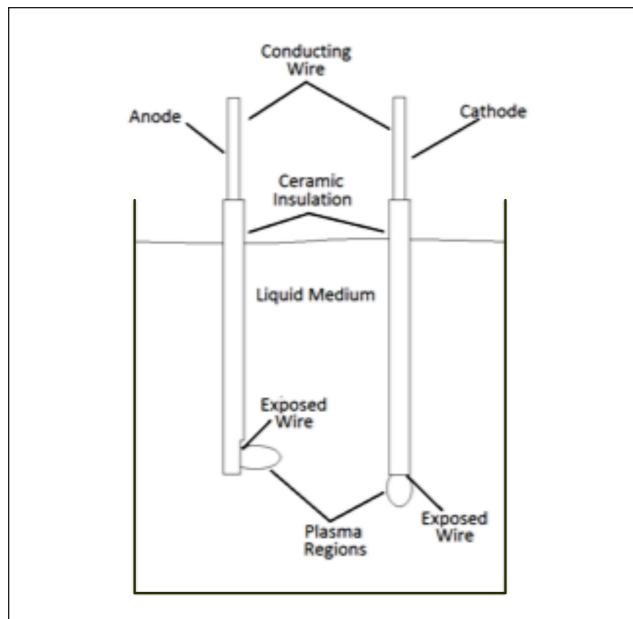
Inkjet and flexographic printed newsprint was used in these experiments. The inkjet newsprint was prepared at Georgia Institute of Technology, and the flexographic newsprint was a commercial print (*The Telegraph*; Macon, GA, USA). For the inkjet printing, a commercial pigment-based inkjet ink (HP 96, LD Products; Long Beach, CA, USA), was used to print a black and white image of the International Association of the Deinking Industry (INGEDE) gray deinking test page on one side of virgin newspaper (30-lb newsprint sheets, Uline; Pleasant Prairies, WI, USA) using an inkjet printer (Deskjet 1000, HP; Palo Alto, CA). The newsprint was then stored at room temperature in a dark cabinet for one year before being used in the deinking experiments. The flexographic newspaper was stored in the same manner for one year as well.

Apparatus used

Liquid phase plasma treatment was used to improve the deinkability of these hydrophilic inks. The apparatus shown in **Fig. 1** was used to generate the liquid phase plasma. The apparatus has a volume of 1 L, and the solution is stirred vigorously during the treatment process. To induce the plasma, two electrodes are submerged in the solution 4 cm apart. The electrodes are identical and were made by inserting a PVC-insulated 14-gauge copper wire into a ceramic tube with inner diameter of 0.156 in. (McMaster-Carr; Aurora, OH, USA). The copper wires were inserted into the ceramic tube so that 4 cm of the insulated wire was exposed in the solution. The copper wire was replaced after each use. A direct current voltage of 2.5 kV and amperage of 650 mA was applied across the electrodes to form the plasma in solution for a discharge time of 2 min.

Pulping and deinking method

Deinkability tests were carried out with either 100% inkjet printed newsprint or 100% flexographic printed newsprint



1. Diagram of apparatus for liquid plasma treatment.

depending on which ink was being evaluated. Deinking was performed by following INGEDE Method 11 "Assessment of print product recyclability—deinkability test," which was used as a reference method. INGEDE Method 11 is a standard laboratory deinking procedure that is widely used in the paper industry to approximate the industry deinkability of a printed paper. Modifications of the method were used to test the effect of liquid phase plasma treatment on the deinkability of flexographic and inkjet inks. For each of the pulping and deinking methods, a mixer (Professional HP Mixer, KitchenAid; St. Joseph, MI, USA) and a 5-L flotation apparatus (D12 Laboratory Flotation Machine, Metso Minerals; Danville, PA, USA) were used for the pulping and flotation steps, respectively.

Modifications to pulping method for liquid phase plasma treatment

The efficacy of the liquid phase plasma treatment was evaluated using three independent modifications to INGEDE Method 11. These modifications will subsequently be referred to as direct treatment, indirect treatment, and filtrate treatment. Each of these modifications uses the plasma-generation method described previously but produces the plasma in different solutions throughout the deinking process. The solution used in the plasma generation apparatus was either pulp at 1% consistency, deionized water with calcium chloride, or pulp fines.

In the direct treatment method, pulp at 1% consistency was treated directly before flotation. In the indirect treatment method, dilution water was treated directly before diluting the pulp during pulping, storage, and flotation. Finally, in the filtrate treatment method, the 1% consistency pulp was dewatered to 5% consistency. The filtrate was next treated with the liquid plasma and then mixed with the 5% consistency dewatered

Parameter	Y (Points)	Color a*	A (mm ² /m ²)	Ink Elimination (%)	ΔY (Points)
Lower threshold	47	-3.0	--	40	--
Upper threshold	--	2.0	2,000	--	18

1. Deinkability thresholds for old newsprint (ONP) as defined by INGEDE Method 11.

tered pulp. In addition to testing each of these treatment methods individually, the direct and indirect treatment methods were also combined to see if the two methods used different mechanisms to improve the deinkability of the pulp; this is referred to as combined treatment

Measurement methods

Three runs of pulping and deinking were performed for each of the treatment methods, and pulp samples were taken after pulping as well as after flotation. An undeinked filter pad was made from the pulp taken after pulping, and a deinked filter pad, handsheet, and filtrate darkening filter pad were made from the pulp sample taken after flotation. The filter pads and handsheets were made according to INGEDE Method 1 “Test sheet preparation of pulps and filtrates from deinking processes.” Brightness, luminosity, color a*, ink elimination, and filtrate darkening were measured for each of these samples using a Technidyne Color Touch ISO (Technidyne; New Albany, IN, USA), and the total dirt particle area for the handsheets was measured using SpecScan 2002 (Apogee Technology; Verona, PA, USA) according to INGEDE Method 2 “Measurement of optical characteristics of pulps and filtrates from deinking processes.”

RESULTS AND DISCUSSION

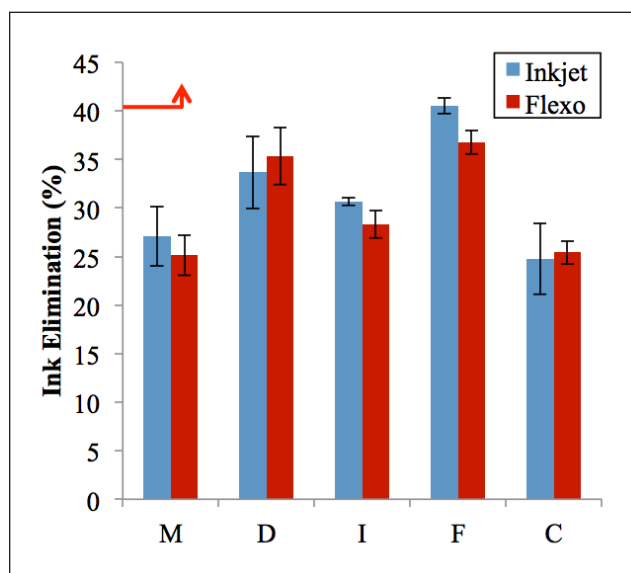
To test the deinkability of flexographic and inkjet printed newsprint with liquid plasma treatment, the ink area, ink elimination, luminosity, brightness, and filtrate darkening were compared to the deinkability standards (INGEDE Method 11) for old newsprint (ONP) as shown in **Table I**.

The treatment method was also varied to test the mechanism of the liquid plasma treatment, and four variations of the liquid plasma treatment were performed. The liquid plasma phase was used to treat the recycled pulp at three points in the deinking process: (1) the dilution water, (2) the recycled paper at 1 mass% before flotation, and the (3) filtrate of the recycled paper dewatered to 5 mass%. These were called indirect, direct, and filtrate methods, respectively. The indirect and direct treatment methods were performed together for the combined treatment method.

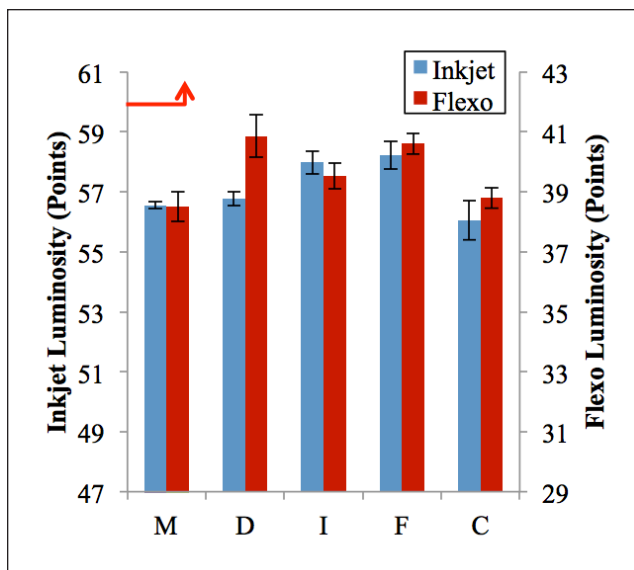
The major problem with deinking of hydrophilic inks is the reattachment of ink, much of which occurs during the breakdown of paper. Adding treated water at an early stage could allow for decreased reattachment by an increase in ink particle size, which was the goal of the indirect treatment method. However, to improve deinkability the ink must be

removed by flotation, which is assisted by an increase in the ink particle size. This is the goal of the direct and filtrate treatment methods, which are more likely to produce larger particles in a dilute solution. Finally, the combined treatment method was performed to determine if the methods could work together for improved deinking.

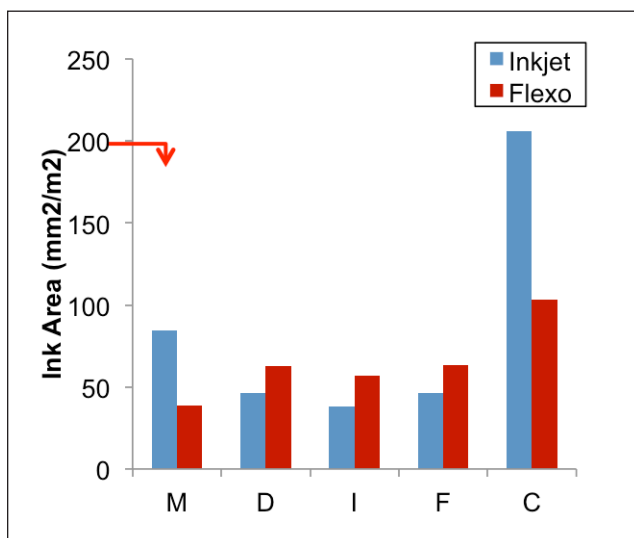
When comparing the liquid plasma treatment to the reference method, there are clear improvements in ink elimination and luminosity for both inkjet and flexographic printing (**Fig. 2**). The indirect and direct treatment methods were able to improve the ink elimination to some extent, but the filtrate treatment was able to increase the ink elimination above the threshold to 40.5% for inkjet and 36.8% for flexographic ink. Similar results were seen when looking at the luminosity, as can be seen in **Fig. 3**. In addition, each of the treatment methods except the combined method improved the total dirt particle area of the inkjet and flexographic printed papers. A reduction in all of these measurements indicates that a greater amount of ink is being removed from the paper fibers when treated with the liquid plasma except when the combined treatment is used. In addition, the color a* was in the optimal range for each treatment method, including the reference method. The negligible effect of the treatment pro-



2. The ink elimination was measured for each of the treatment methods (the reference method [M], direct [D], indirect [I], filtrate [F], and combined treatment [C]). The red arrow indicates the threshold ink elimination value.



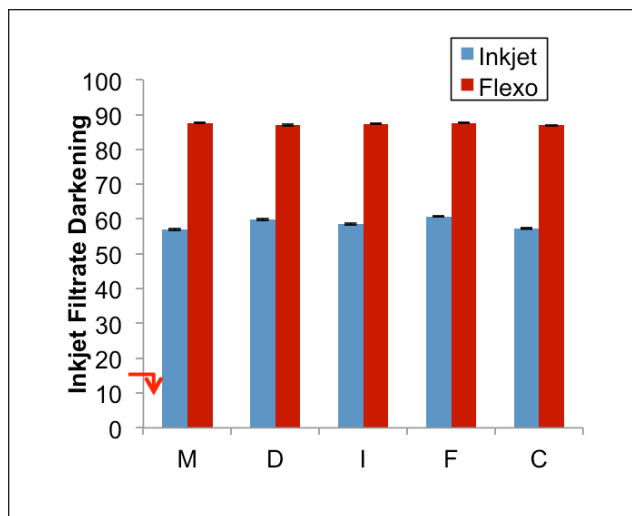
3. The luminosity was measured for each of the treatment methods (the reference method [M], direct [D], indirect [I], filtrate [F], and combined treatment [C]). The red arrow indicates the optimal luminosity value.



4. The ink area was measured for each of the treatment methods (the reference method [M], direct [D], indirect [I], filtrate [F], and combined treatment [C]). The red arrow indicates the optimal ink area value.

cess on the color a^* showed that the process is not discoloring the fibers in the red-green spectrum. Similarly, the total dirt particle area was in the optimal range as defined by INGEDE for each treatment method. However, it is clear that there is a significant increase in the total dirt particle area when using the combined treatment method, as can be seen in **Fig. 4**.

Although the deinkability of inkjet printed newsprint has been improved up to this point, the filtrate darkening of the system was not improved through treatment with the liquid plasma process. In fact, the filtrate darkening was increased by each of the treatment methods in this study, as can be seen

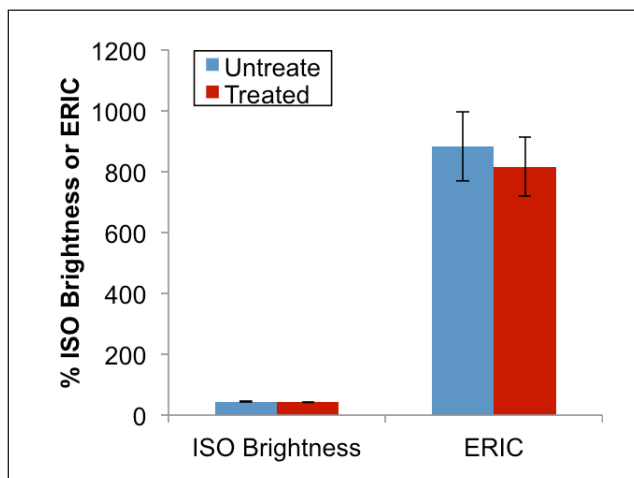


5. The filtrate darkening was measured for each of the treatment methods (the reference method [M], direct [D], indirect [I], filtrate [F], and combined treatment [C]). The red arrow indicates the threshold ink area value.

in **Fig. 5**. In previous research, it was found that the inclusion of 10% inkjet printed paper in the wastepaper stream was the upper limit for deinking mills due to an increase in filtrate darkening when deinking inkjet printed paper [1]. In addition, the deinkability is even worse for flexographic printed paper. Because of this, filtrate darkening is an important property for the deinkability of both flexographic and inkjet printed paper because increased filtrate darkening results in the recycling of higher concentrations of ink in the recycling plant. If the ink is not removed by flotation, it will build up in the system and reduce the optical properties of the pulp as run time increases.

The negative effect on filtrate darkening suggests that the treated inkjet and flexographic inks are not being removed by the flotation process because there is significant improvement in ink elimination and luminosity of the paper. To test this hypothesis, the ISO brightness and effective residual ink concentration (ERIC) of the rejects from flotation were evaluated for untreated and filtrate-treated pulps. As can be seen in **Fig. 6**, there is not a significant difference in either the brightness or ERIC value for the reject of untreated and filtrate treated samples.

However, it was determined that the amount of ink on the fiber surface is being reduced by the liquid plasma treatment. This suggests that the liquid plasma treatment is able to increase the detachment of ink from the fiber surface or prevent redeposition of ink onto the fiber surface, both of which are very important in the deinking process. There are several plausible explanations for this observation. First, it is expected that the liquid plasma treatment will cause polymerization of the ink particles resulting in increased particle size, as has been seen in other polymerization applications [19]. All of the measurements are optical measurements, so with no increase in removal of ink by flotation, the optical mea-



6. The ISO brightness and ERIC of the reject from flotation are shown for untreated and direct treatment of 100% inkjet printed paper.

measurements would detect less area of ink. However, the results showed an increased concentration of ink in the filtrate after paper formation, which indicates that ink removal is improved with this treatment method. The treatment method also results in dissolved copper, which has been shown in previous studies to compress the stabilizing polymer layer on the pigment surfaces [20]. This polymer layer is responsible for the hydrophilic nature of the ink, and it has been shown that the ink will reattach to the fiber surface during dewatering [7,21]. A compressed polymer layer would minimize reat-

tachment of the ink by making the ink particle less hydrophilic [20]. Copper dissolution could also be responsible for the poor performance of the combined treatment method. The amount of dissolved copper in this treatment is expected to be 3 to 5 times greater, which could lead to precipitation of copper. Because the brightness and ink elimination are dependent on light absorption, copper could cause an increase in the measurements.

CONCLUSION

The liquid phase plasma treatment process has been shown to improve luminosity and ink elimination of recycled 100% flexographic and inkjet newsprint while having a negligible effect on the color a^* , which was in the optimal range for ONP as defined by INGEDE. In addition, the liquid plasma treatment improved the ink area for inkjet printed paper and had an insignificant effect on the ink area of flexographic printed paper. The filtrate treatment method was the most effective at improving these properties. However, the filtrate darkening for the pulp was increased by all of the liquid plasma treatment methods, and the brightness and ERIC of the reject from flotation was insignificantly different for untreated and filtrate treated inkjet pulps. Because of this result, it is unlikely that the increase in brightness, luminosity, ink elimination, and total dirt particle area is due to increased removal of ink by flotation after treatment. Instead, the ink detachment from the fiber surface was assisted by the plasma treatment, which would end up in the filtrate of the papermaking process. This may be due to the increase in ink particle size

ABOUT THE AUTHORS

Digital printing is becoming more and more prevalent in the printing industry. Currently, there is no good method of deinking the hydrophilic inks that are generally used in these printing processes. Because of this, it is necessary to find a workable solution to the problem before the increased use of hydrophilic inks makes many paper grades undeinkable.

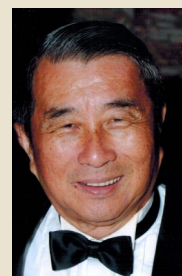
There has been extensive research on the stability and destabilization of hydrophilic inks. However, these destabilization methods were shown to result in redeposition of the ink onto the pulp when paper fibers were present. The current research relates to destabilization of the ink without causing redeposition of the ink onto the pulp.

Separation of hydrophilic inks is a difficult problem to overcome. This research shows a possible method of improving deinking of hydrophilic inks, but we have not yet been able to completely mitigate the problem. The most surprising result from this research was the lack of removal of the hydrophilic inks even after destabilization occurs. Instead, we found that the ink was being removed in the filtrate, which was very interesting.

It would be difficult for mills to directly use the results from this paper, but the results will be useful for future research and development efforts on deinking of hydrophilic inks,



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such as flexographic and inkjet inks. The next step of this research is to apply the concepts discovered in this paper to improve flotation deinking of hydrophilic inks. It was determined that the ink could not be removed through flotation even after destabilization, so it would be necessary to look into flotation next.

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from the treatment or the increase in hydrophobicity of the ink particle from the addition of copper ions from the treatment. **TJ**

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