

Is deinkability of inkjet prints an issue?

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ABSTRACT: In the fast-growing digital printing market, a noteworthy development is the introduction of commercial inkjet web presses for on-demand newspapers and various publications and business forms. Despite the enthusiasm brought about by these new inkjet technologies, a number of deinking studies carried out in Europe have raised serious issues about the deinkability of inkjet prints. Some representatives of the digital printing industry question the validity of these conclusions. We carried out deinkability tests with different ratios of inkjet-printed newsprint at alkaline and near-neutral deinking chemistries, with fresh and aged papers. A representative pigmented inkjet formulation was used for the deinking tests and well-proven protocols were used to follow the fate of ink in pulping, flotation, and thickening. Under these conditions, our results were similar to those obtained by European researchers. Pigmented inkjet inks do not have the physicochemical attributes to be effectively collected by air bubbles during flotation. Causes for this poor deinkability of inkjet inks are discussed, as well as the potential means to enhance their deinkability.

Application: Ten percent is a reasonable estimate for the percentage of inkjet-printed paper that a mill can tolerate.

At the Drupa Print Media Fair 2008, a number of printer manufacturers introduced inkjet solutions for on-demand newspapers and various publications and business forms. Fast turnaround, on-demand printing (less waste), exceptional print quality, flexibility, and ability to personalize documents are major drivers for the dissemination of inkjet printing in higher-volume markets. Despite the enthusiasm, paper recyclers are starting to express serious concerns about the spread of inkjet printing technology. Indeed, recent studies carried out at the Centre Technique du Papier (CTP) in France and at the Paper Technology Specialists Institute (PTS) in Germany indicated that inkjet inks are generally not deinkable and are, therefore, incompatible with paper recovery and recycling [1–5]. These findings prompted INGEDE, the International Association of the Deinking Industry, to initiate a dialogue with printer manufacturers to find a solution to what could be a major threat to the paper industry. The initiatives to date have had limited success [6].

Deinking issues brought about by inkjet printing are very similar to those of any water-based inks, such as those used in flexography. Whether dye-based or pigment-based, inkjet inks will dictate the type of problem experienced in a deinking operation. For dye-based inkjet inks, the usual bleaching chemicals, hydrogen peroxide and sodium hydrosulfite, display limited color stripping capabilities for dyes [2]. This is already known to be an issue, especially in mills with limited washing capabilities, but the volume of dye-printed paper is not high enough to cause serious harm to a deinking operation. Pigmented inkjet inks that appear to be the dominant formulation in novel commercial presses contain a significant amount of hydrophilic and very finely divided pigments along with aggressive

dispersants, whose composition and properties are similar to those used in water-based flexography and gravure inks. In the early 1990s, water-based inks were considered to be the worst threat to the recycling industry [7,8]. For nearly 20 years, researchers in recovered paper recycling have tried to solve the flexographic ink deinking problems and though there has been some improvement, this issue has not been solved. The causes for the poor deinkability of water-based inks, and hence of brightness loss, can be summarized as follows [7]:

- Very small and hydrophilic ink pigments are generally easily dislodged from the fiber surface during pulping. The mechanical action imparted to the pulp in a pulper, however, causes the small ink pigments to enter into the lumen via pit apertures where they deposit irreversibly on the surface of fiber lumen.
- To be captured by air bubbles during flotation, free ink particles in the pulp suspension need to be a minimum size (about 5 μm). However, fibers present in the inky suspension interfere with the process of ink agglomeration during flotation, thus preventing the effective collection of water-based ink pigments by air bubbles.
- Pigmented water-based inks are not hydrophobic enough to be efficiently captured by hydrophobic air bubbles during flotation.
- During thickening, unfloated ink particles deposit reversibly on the external surface of fibers making up a mat.
- Very finely dispersed ink pigments ending up in the filtrate tend to build up in the water phase. Clarification of the dark filtrate is difficult; it requires an excessive amount of coagulants/flocculants and produces large losses (20%–25%) of valuable fiber from the deinking process.

These observations and conclusions are likely to hold today. Because the phenomena apply to the family of water-based inks, including the majority of pigment-based inkjet inks that would be incorporated in the fiber furnish of deinking plants, the very poor deinkability of inkjet prints reported recently by European researchers is not unexpected.

Klass and Romano [9], however, recently indicated that deinking of inkjet prints is and will continue to be a nonissue right now. They claim that INGEDE Method 11 ("Assessment of print product recyclability—Deinkability test"), used by PTS researchers in their extensive evaluation of deinkability of inkjet prints, is irrelevant to current commercial deinking processes in North America for the following reasons:

- The laboratory conditions used for artificial paper aging are not representative of natural paper aging.
- A Hobart pulper does not provide the type of mechanical action found in a properly designed industrial pulper.
- The method only includes one step of flotation, whereas many deinking systems currently use two or more stages of flotation.
- The deinking chemistry in the method does not include a flotation collector.

Although a laboratory protocol never mimics industrial practices exactly, researchers in deinking who have used the INGEDE method recognize that it is a sound and well-thought-out method, especially when it is used for comparison purposes. Moreover, some of the arguments of Klass are inaccurate. For example, two-loop flotation processes are not the norm in North America, especially for newsprint manufacturing. Indeed, the majority of Canadian recycling plants were designed for a simple alkaline flotation loop (e.g., Thorold mills). Some recycling mills that had a second loop (e.g., formerly Newstech) have removed it because the yield penalty and energy consumption were too large compared to the benefits. Furthermore, the INGEDE Method 11 uses 0.8% oleic acid, which is a widely used flotation collector for laboratory deinking studies. Oleic acid is not an industrial collector but it is convenient to use in laboratory flotation tests because it is pure and easy to handle, and its performance approaches that of the best anionic collectors such as tallow fatty acids [10].

Klass also stated that current deinking systems would likely deink inkjet-printed old newspapers (ONP) because they can successfully deink ONP containing varying content of flexo-printed papers. Some deinking systems in Europe have indeed been designed to tolerate a significant percentage of flexo-printed papers, but that it is certainly not the case in Canada and in many U.S. mills. Moreover, the deinking plant adaptation in Europe to handle a few percentage of flexo is extremely expensive in terms of yield and bleaching chemicals. The water-based ink issue cannot be considered as solved because most recyclers still view flexo prints as

nondeinkable. On the other hand, inkjet printing is not yet an issue because it represents a very small fraction of the prints making their way to a recycling plant. It seems, therefore, that the current deinking systems would cope with low volumes of inkjet prints, depending on the brightness target and raw materials. The introduction of inkjet newspapers and direct mail by printer manufacturers may significantly increase the inkjet print content in recovered papers, which may eventually cause a problem.

Recognizing that inkjet inks may cause deinking problems, some inkjet ink and press manufacturers are presently assessing the deinkability of their inkjet prints. Ng et al. [11] showed that Hewlett-Packard (HP) inkjet inks were deinkable under neutral deinking conditions, two-stage pulping, and very long flotation times. Although the approach of testing the deinkability of HP inks is sound, the testing methods require some improvement. The dosage of the nonionic surfactant (0.6%) used in their deinking chemistry is 10–30 times higher than the normal usage. All recycling plants are very sensitive to the accumulation of surfactant in the water loop; build up causes overfoaming in flotation cells, pumping problems, loss of collection, and excessive yield loss. Their reported yield loss of about 30% indicated that the surfactant dosages were unrealistically high. Moreover, the high deinking score achieved with their method is partly caused by a flotation time of 12–20 min, which is two to three times longer than mill practice.

Miller [12] discussed deinkability of inkjet prints in his presentation at PaperCon 2009. It appeared that low shear during pulping, neutral pH, and ColorLok paper media all helped to improve the deinkability of inkjet prints; however, the improvements obtained to date are too modest to represent a breakthrough. Indeed, the low shear and neutral pH during pulping and short pulping time were the best operation conditions identified more than 10 years ago for the ONP/OMG (old magazine paper) deinking process [13–17]. These approaches may help to minimize the negative impact of introducing water-based inks in recovered paper, but none either alone or in combination is likely to eliminate the problem in mills processing blends of printed papers with more than 5%–10% water-based ink content.

To help clarify the issue of inkjet deinking, we have tested the deinkability of pigmented inkjet ink using best North America deinking practices. Faced with the hurdle of obtaining well-characterized commercial prints, with or without a bonding agent [18], we produced our own samples by printing a commercial inkjet ink (without bonding agent) on unprinted newsprint. This approach allowed very good control of paper furnishes for the deinkability tests. To simplify the preparation of inkjet-printed newspapers, we used a black and white image because results obtained with black and colored water-gravure inks showed that the floatability of the black and colored pigments was quite similar [19].

EXPERIMENTAL

Paper preparations

To reflect contemporary recovered paper compositions, deinkability tests were carried out with a blend of heat-set offset-printed papers (lightweight coated [LWC], supercalendered grade SCA, and supercalendered grade SCB), cold-set offset-printed ONP, and inkjet-printed ONP. Whereas the proportion of LWC (15%), SCA (15%), and SCB (10%) in the paper furnishes was fixed, the offset-printed ONP was progressively replaced by inkjet-printed ONP, with ratios of 0%, 6%, 12%, and 18% of inkjet-printed ONP in paper furnishes. A paper company supplied what it considered to be representative samples of LWC, SCA, SCB, and offset-printed ONP. Inkjet-printed ONP was prepared at FPInnovations using an Epson Stylus C88+ desktop inkjet printer (Seiko Epson; Nagano, Japan). A commercial inkjet ink, whose composition is shown in **Table I**, was used to print a standard black and white image on a single side of virgin newsprint. Because the prints of offset-printed ONP were double sided, the weight of inkjet-printed newsprint added to the blend was adjusted to reach the black area coverage of the offset-printed newsprint (i.e., about 15% per

	Amount (%)
Black pigment	5
Water and alcohol	83
Proprietary additives	12

I. Characteristics of inkjet ink.

side). The average pigment diameter determined by scanning electron microscopy (SEM) was found to be smaller than 0.1 μm .

At FPInnovations, prepared or received papers were stored for one week at room temperature, after which they were placed in opaque plastic bags and stored at 4°C until they were used for deinking tests (labeled fresh papers) or submitted to artificial thermal aging (labeled aged papers).

Deinking protocol

Over the past 20 years, deinkability tests have been performed regularly at FPInnovations [20,21]. The validity of the conclusions derived from those test results frequently has been demonstrated in mill trials that eventually led to mill implementations (e.g., near-neutral deinking). The tests involved a series of deinking steps and a number of characterization tests for assessing the fate of ink particles during deinking. Because we have accumulated at FPInnovations a large bank of deinking data and have constantly improved our tests methods to mimic better mill operation, we have used our in-house methods instead of the INGEDE Method 11. Though the methods differ slightly, a side-by-side comparison of the two methods done recently at

FPInnovations has revealed very small differences in deinkability scores obtained following the two protocols.

Aging

Paper samples were aged artificially in an air oven kept at $60 \pm 3^\circ\text{C}$ for 72 h, according to the specifications of INGEDE Method 11. The relative humidity in the oven was typically in the 30% range. Aged papers were then placed in opaque plastic bags and stored at 4°C in a cold room until they were used. While these artificial conditions are harsher than those experienced by North American recovered papers under natural conditions, they have merit as a worst-case scenario.

Repulping

Papers were pulped for 5 min in a laboratory helical pulper operated at a temperature of 45°C and an agitator speed of 800 rpm. The suspension volume was 6.25 L at a pulp consistency of 10%. The following chemicals were used during repulping for the alkaline deinking chemistry: 0.5% sodium hydroxide (NaOH), 1.5% sodium silicate (Na_2SiO_3), 0.6% anionic surfactant (tallow), 0.05% nonionic surfactant (EO-PO type), 1% hydrogen peroxide (H_2O_2) (all on o.d. paper basis); the hardness of the pulp was adjusted with calcium chloride (CaCl_2) to attain 60 mg/L (as Ca^{++}). For near-neutral deinking, 1.5% sodium sulfite (Na_2SO_3), 1.5% Na_2SiO_3 , 0.6% anionic surfactant, and 0.05% of nonionic surfactant (all on o.d. paper basis) were added to the pulper along, with CaCl_2 to reach 60 mg/L of Ca^{++} .

Storage and homogenization

The pulp was diluted to 5% consistency and stored in a water bath at a temperature of 45°C for 60 min. Immediately after storage, the pulp was diluted to 1.2% consistency and homogenized with a British disintegrator at 3000 rpm for 5 min. The hardness of the pulp suspension was adjusted to 80 mg/L (as Ca^{++}) with CaCl_2 during storage and disintegration.

Flotation

After storage and homogenization, an aliquot of the pulp was diluted in a 6.5-L Leeds flotation cell to 1% fiber consistency. The hardness of the pulp suspension was kept to 80 mg/L (as Ca^{++}) and the pulp was mixed at 1200 rpm for 1 min. After this conditioning period, flotation was carried out for 5 and 10 min, respectively, at an impeller speed of 1200 rpm and an air flow rate of 3 L/min. At regular intervals, the froth was scraped from the surface.

Characterization

Optical properties

Pulp samples were taken after disintegration (for total ink) and after flotation. Total and bound ink concentrations were determined on filter pads, before and after a hyperwashing treatment, according to procedures previously described

elsewhere [22]. Brightness, luminosity and effective residual ink concentration (ERIC) were determined for these specimens using a Technibrite Micro TB-1C (Technidyne; New Albany, IN, USA).

Pulping with high ratios of inkjet-printed ONP produced a dark gray that masked the detection of dirt specks in the handsheet. After flotation, removal of ink caused more dirt specks to be detected; hence, the dirt count measured on handsheets produced after pulping and even after flotation underestimated the speckiness of the pulp. To remove this artifact, dirt specks and physical dirt counts were determined on handsheets prepared from hyperwashed pulp after pulping and flotation using FPIInnovations' microscanner QC Model (OpTest Instruments, Hawkesbury, ON, Canada), based on TAPPI T 563 ("Equivalent black area [EBA] and count of visible dirt in pulp, paper and paperboard by image analysis").

Flotation efficiency

Basics of ink flotation have been described in detail [23,24]. It is customary to define ink removal by flotation using one of these two terms: flotation efficiency (FE) and flotation efficiency of free ink (FE^{free}). FE in Eq. (1) represents an overall flotation efficiency because it includes the population of ink particles attached to long fibers or too small to be captured by air bubbles (e.g. inkjet ink particles in pulp suspensions). These two categories of ink particles float so slowly that to a good approximation, they can be considered unfloatable (Eq. [1]).

$$FE = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

where C_0 is initial ink concentration and C represents the ink concentration at given flotation time.

Flotation efficiency of floatable (or free) particles is defined as in Eq. (2):

$$FE = \frac{C_0 - C}{C_0 - C_\infty} \times 100 \quad (2)$$

where C_∞ is the concentration of unfloatable ink; the numerator $C_0 - C$ is the amount of free particles floated, and the denominator is the initial concentration of free (or floatable) ink. In general, FE is significantly smaller than (FE^{free}), unless C_∞ in Eq. (2) is zero.

Though flotation efficiency is a useful parameter, it is highly dependent on the type of cell used and flotation time. The key parameter in flotation is the rate constant, k (in min^{-1}) in the collection zone. Although it is customary to call k a constant, it varies with a large number of factors such as degree of mixing, aeration rate, size of particles, and degree of hydrophobicity of particles. However, under constant operating conditions, k can be considered as a

constant. It can be determined from the integrated form of first-order kinetics (Eq. [3]):

$$\ln \frac{(C_0 - C_\infty)}{(C - C_\infty)} = kt \quad (3)$$

A convenient way to estimate k and C_∞ is to use an iterative technique on flotation data obtained at a minimum of two flotation times [23].

The rate constant can be related to cell operating parameters as follows in Eq. (4):

$$k = \frac{E_k S_b}{4} \quad (4)$$

where S_b is the so-called bubble surface area flux or bubble surface area generation rate per unit time per unit cross-sectional area of cell, and E_k is the collection efficiency factor that combines many physicochemical factors such as type, size, and degree of hydrophobicity of ink particles.

Irreversible ink redeposition

Hyperwashed fibers were examined by scanning electron microscopy (SEM) to find the location of irreversibly deposited ink particles. Carbon-coated samples were prepared for SEM examination by cutting very thin layers of different pulp samples to expose the surface of fiber lumens.

Filtrate darkening

Filtrate darkening (the difference in membrane luminosity before and after filtration) was determined on the basis of INGEDE Method 11, but with some minor modifications due to the equipment in our laboratory. To have a basis weight of 225 g/m², 1.89 g of o.d. deinked pulp was diluted with tap water to a volume of 472.5 mL. The pulp suspension was filtered on a Whatman No. 4 filter paper (Whatman; Maidstone, Kent, UK) in a 110-mm diameter Büchner funnel. A 100-mL aliquot of filtrate was then filtered on a cellulose nitrate membrane filter of 0.45- μm pore diameter. The membrane filter then was removed and dried in a dessicator. Reference membrane filters were made in the same way but using 100 mL of tap water (without pulp). The luminosity of the membrane filter and of the reference filter was determined under identical conditions.

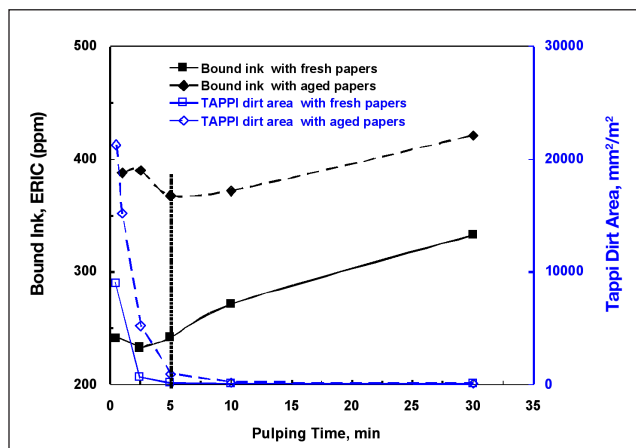
Flotation loss

Froth samples collected from the overflow of the Leeds cell were first weighed and then filtered on a Whatman No. 1 filter paper. After oven-drying at 105°C, the amount of rejected solids was determined. Flotation loss was calculated on the basis of the ratio of total dry solids in the froth over those in the cell prior to flotation.

RESULTS

Optimal pulping time

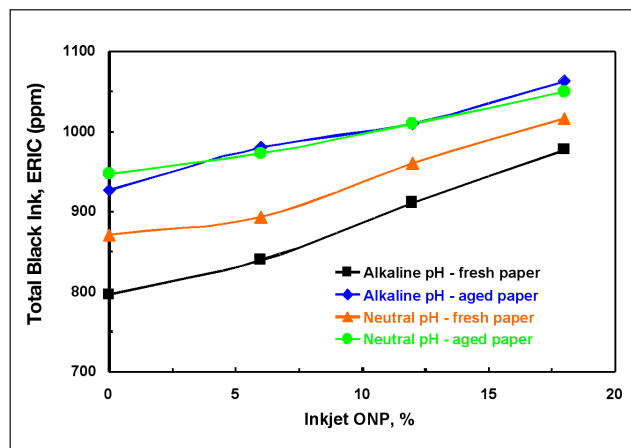
To establish the optimal pulping time for this blend of papers, fresh and aged papers containing 18% of inkjet-



1. Ink detachment, redeposition, and TAPPI dirt area with extended pulping time for the paper furnish containing 18% of inkjet-printed old newspapers (ONP).

printed ONP were each pulped up to 30 min using alkaline deinking chemistry. All pulp samples were removed from the pulper at regular intervals and then hyperwashed to determine the amount of bound ink (as ERIC) and dirt specks. **Figure 1** shows the bound ink and dirt area as a function of pulping time for both fresh and aged papers. With fresh paper samples, bound ink concentration increased after 2.5 min as detached ink particles, transferred to the water phase from the fiber surface, started to redeposit in fiber lumen, in agreement with our previous findings with water-based flexo inks [13,14]. When fresh paper samples were artificially aged, the amount of bound ink significantly increased at each pulping time. The minimum bound ink was observed at 5 min pulping time for aged samples and 2.5 min for fresh paper samples. The rate of ink redeposition in the lumen was analogous for fresh and aged papers, as revealed by the similar slope of the two curves past the minimum in bound ink.

On the other hand, the amount of visible dirt specks decreased with pulping time for fresh and aged paper samples. Longer mechanical action caused the dirt specks in general to be better detached from the fiber surface, broken down, or both so that they became undetectable as specks. After 5 min pulping time, dirt area was 250 ppm and 1125 ppm for fresh and aged papers, respectively. In both instances, the dirt level was below the upper threshold specified by INGEDE for an acceptable recyclability. With the INGEDE method, the parameters with a desired high value have a lower threshold, and the parameters with a desired low value have an upper threshold; falling below a lower threshold and exceeding an upper threshold results in a negative score. If one individual score is negative, then the assessment of the print product is not suitable for deinking. Very similar results were obtained with near-neutral deinking chemistry. With the incorporation of inkjet-printed newspapers in this paper blend, a 5-min pulping time was optimal and used thereafter in all tests.



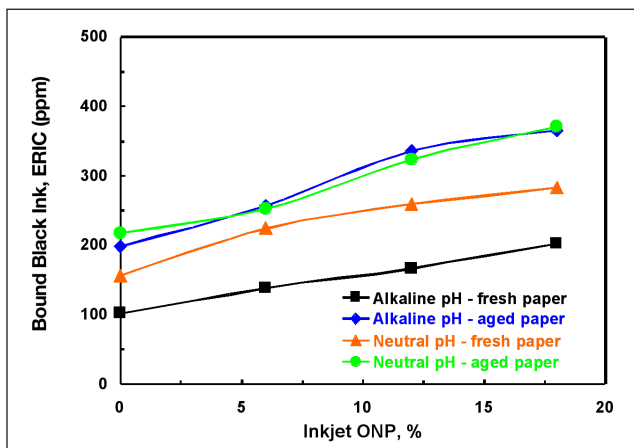
2. Effect of inkjet ONP on total black ink concentration with alkaline and near-neutral deinking chemistries.

Ink concentration and ink removal

To evaluate the deinkability of recovered paper containing different ratios of inkjet-printed ONP, increasing amounts of inkjet ONP were added in the paper furnishes to replace offset printed ONP. **Figure 2** shows that total black ink concentration after pulping increased markedly as the proportion of inkjet-printed ONP rose for both fresh and aged paper furnishes, under alkaline and near-neutral deinking conditions. Because the print coverage of inkjet- and cold-offset printed ONP was very similar, the rise of total ink concentration (as ERIC) with increasing proportion of inkjet-printed ONP indicated that ink pigments released during pulping were smaller in inkjet prints than in offset prints.

For fresh papers, total ink after pulping with near-neutral deinking chemistry was approximately 50–70 ppm higher than with alkaline chemistry, in agreement with previous results obtained in laboratory and mill trials [25–28]. Because pulping with alkaline and near-neutral deinking chemistries started with the same blend of papers and hence the same amount of ink, higher ERIC values during pulping at near-neutral pH indicated a greater degree of fragmentation of ink particles under a near-neutral condition. It was suggested that a drop of pH during pulping altered pulp rheology, which in turn contributed to a greater fragmentation of released ink particles (higher total ink) [29,30].

Figure 2 also indicates that paper aging increased total ink concentration whether pulping was carried out under alkaline or near-neutral deinking chemistries, in agreement with previous findings [20,21]. Because the mass of ink applied on a given paper type was independent of pH conditions during pulping, higher total ERIC values in pulps obtained with aged prints revealed that oxidation of the prints promoted ink fragmentation during pulping. Though print aging and reduced pH during pulping both promoted ink breakup, paper aging was the predominant factor, because the total ink of aged prints was similar under alkaline or near-neutral deinking



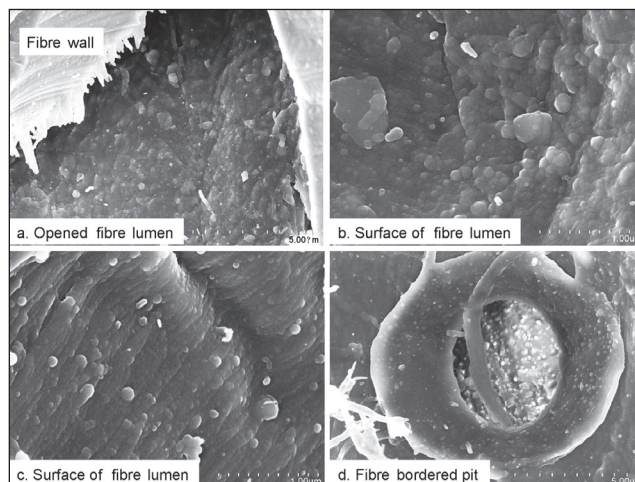
3. Effect of inkjet ONP on bound black ink concentration.

chemistries. For paper furnishes with 0% inkjet-printed ONP, aging increased total ERIC by about 120 ppm under an alkaline pulping condition and about 75 ppm under a near-neutral pulping condition. As offset-printed ONP was progressively replaced by inkjet-printed ONP, the effect of aging on the rise of ERIC became less important for both alkaline and near-neutral deinking chemistries. Thus, aged inkjet prints fragmented to a lesser extent than aged offset prints, because inkjet ink ingredients were less prone to the autoxidation phenomenon, which is responsible for aging [31–33].

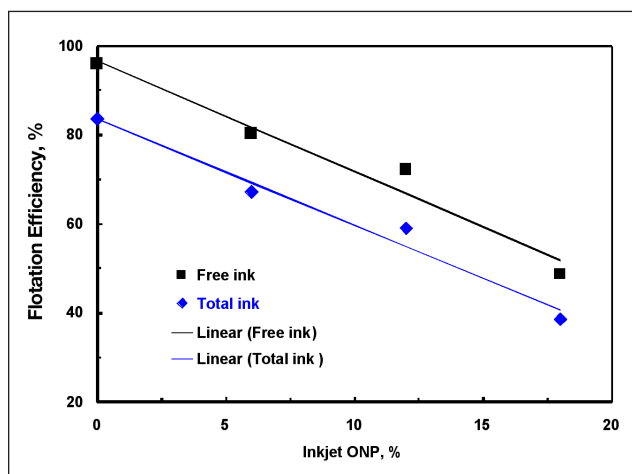
Figure 3 presents the amount of ink (as ERIC) attached to fibers after pulping and/or redeposited in the lumen (i.e., bound ink) as a function of inkjet-printed ONP ratio in fresh and aged paper furnishes treated under alkaline or neutral deinking conditions. Whether the pH was alkaline or neutral, the amount of bound ink in fresh and aged papers increased as the amount of inkjet ink increased in the paper blend.

Figure 4 presents a series of SEM photomicrographs of hyperwashed pulp with ERIC of 375 ppm after repulping a paper blend with 18% inkjet-printed newsprint for 5 min. Examination at low and high magnification shows that ink particles of 0.1–0.3 μm were irreversibly deposited on the surface of the fiber lumen. These small ink particles were also adsorbed on the walls of bordered pits. These observations are in line with those made previously with water-based flexo ink [13,14]. This phenomenon of ink re-entry in the fibers was largely a mechanical one that occurred when particles were much smaller than the pit openings. Once in the lumen, their darkening power, and hence their effect on brightness or luminosity, was similar to that of ink particles located on the external surface of fibers.

In **Fig. 5**, the overall flotation efficiency (FE in Eq. [1]) and the flotation efficiency of free black ink (FE^{free} in Eq. [2]) in fresh paper blends pulped under alkaline chemistry and floated for 5 min are presented as a function of the ratio of inkjet-printed ONP. Overall flotation efficiency and free ink removal deteriorated markedly as the amount of inkjet ink increased. To understand whether the causes leading to the



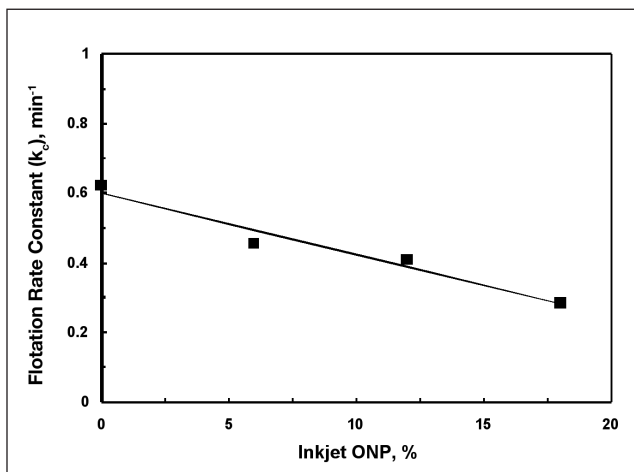
4. Scanning electron microscopy photomicrographs of post-hyperwashed pulp: (a) fiber lumen surface at low magnification; (b) and (c) fiber lumen surface at high magnification; and (d) fiber bordered pit.



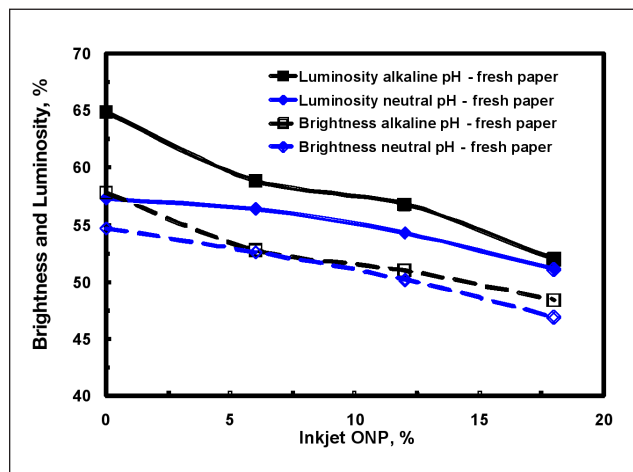
5. Effect of inkjet ONP on flotation efficiency of total ink and free ink for fresh paper.

poor flotation of pigmented inkjet inks were similar to those identified for water-based flexo and gravure inks [19,34], flotation of pure suspension of inkjet ink (100 mg/L of pigment) but free of fibers was carried out. With a conventional alkaline collection chemistry, flotation efficiency of more than 90% was obtained after 5-min flotation. These results were consistent with those obtained with water-based flexo ink; the presence of fibers during flotation interfered with inkjet ink agglomeration and with the collection of ink pigments by air bubbles [7].

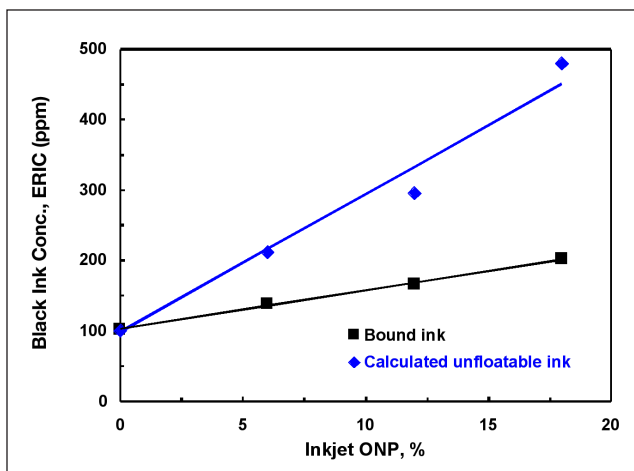
Instead of flotation efficiency, the rate constant (k in Eq. [3]) was used to compare the effect on flotation of the ratios of inkjet-printed ONP under alkaline condition for fresh paper blends. **Figure 6** shows that flotation rate constant decreased linearly with an increase of inkjet-printed ONP content. At a given inkjet-printed ONP content, paper aging and deinking chemistry both had an effect on flotation, but



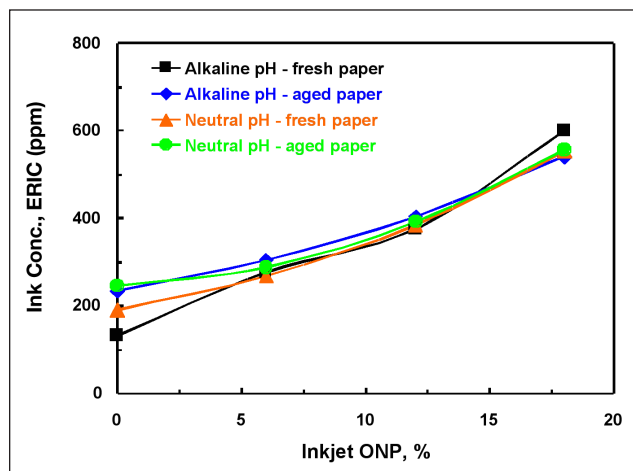
6. Effect of inkjet ONP on flotation rate constant for fresh paper under alkaline deinking chemistry.



8. Effect of inkjet ONP on pulp luminosity and pulp brightness after 5-min flotation.



7. Bound ink and unfloatable ink.



9. Residual ink concentration after 5-min flotation.

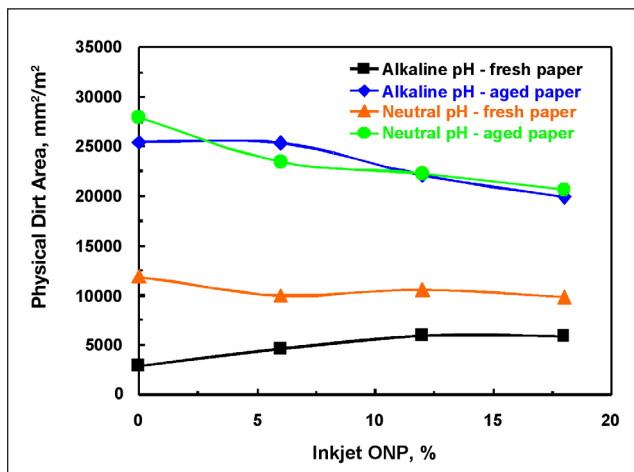
it was much smaller than raising the proportion of inkjet print in the blend. To complete the flotation picture, the population of unfloatable ink particles in the pulps produced under alkaline chemistry for fresh blends of papers with various inkjet-printed contents was estimated from Eq. (3). **Figure 7** shows that when the paper mix was free of inkjet print, the amount of unfloatable ink was equal to 100 ppm ERIC, which corresponds to the amount of offset ink attached to long fibers (bound ink). As the content of inkjet-printed ONP increased, however, the number of bound and unfloatable ink particles increased. Not only did the rate constant of the floatable fraction of ink particles decrease (see Fig. 6) with increasing levels of inkjet ink particles, but a greater proportion of the ink mixture became unfloatable.

The two sets of flotation results presented in Figs. 5 and 6 can be explained in two different ways. One explanation is that the overall rate of the entire population of ink (offset and inkjet) was negatively impaired with increasing inkjet ink

concentration because the surface active agents present in the inkjet ink reduced the size of offset ink particles or reduced their hydrophobicity, or both, and hence their capture by air bubbles. An alternative explanation is that the size distribution of the inkjet ink population was floatable though at a low rate because it had a minimum size to be collected by air bubbles, whereas the second part of the population contained inkjet ink particles that were too small to be captured by air bubbles. With either explanation, the end result was that inkjet inks had an unacceptably low floatability.

Pulp brightness and luminosity after flotation

Figure 8 shows that pulp brightness and luminosity after 5-min flotation decreased significantly when the proportion of inkjet-printed ONP increased. With 18% of inkjet ONP, pulp brightness was only 46%–48%, which was about 10 percentage points lower than the current deinked pulp brightness from offset printed ONP (56%–58%). Because low



10. Effect of inkjet ONP on physical dirt specks after 5-min flotation.

brightness is caused by a higher concentration of unfloatable ink particles (**Fig. 9**), there is no bleaching chemical that can recover the brightness loss.

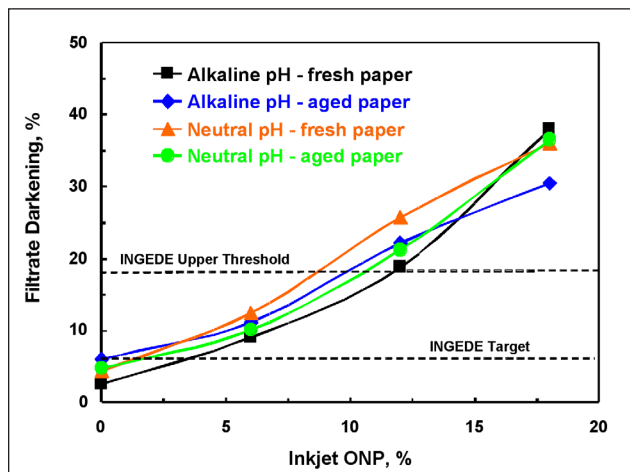
It is already known that the brightness of pulps produced by near-neutral deinking chemistry is on average 1-2 points lower after flotation than when an alkaline deinking chemistry is used in the pulper [27]. The lower pulp brightness value with near-neutral deinking chemistry (**Fig. 8**) can be attributed to the lower bleaching capacity of Na_2SO_3 as compared to H_2O_2 , as residual ink concentration after 5-min flotation was very similar with either alkaline or near-neutral deinking chemistries (**Fig. 9**). A postbleaching stage with hydrosulfite could restore brightness and luminosity to acceptable levels. Because water-based pigments, in particular black pigments, are unbleachable, the amount of chemicals required to bleach the fibrous elements to attain the target brightness becomes impractically high.

Dirt specks

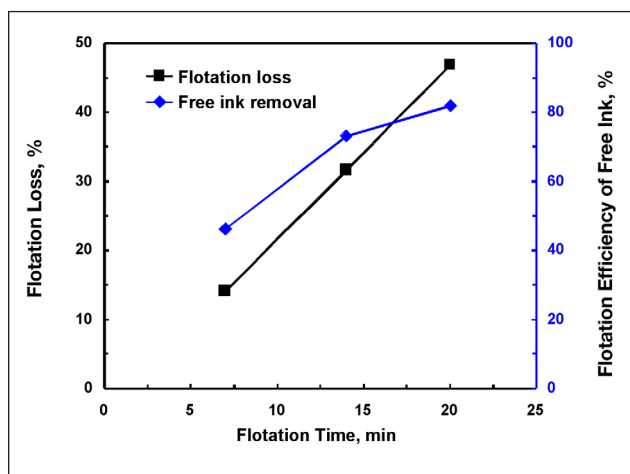
The effect of inkjet-printed ONP on pulp cleanliness was assessed from image analysis measurements made on hyperwashed pulps. In **Fig. 10**, pulp speckiness is expressed as physical dirt area. For fresh papers, the physical dirt area was quite low and inkjet-printed ONP had no major effect, in agreement with other deinkability studies [2,4,5], although paper aging dramatically increased the physical dirt area. The physical dirt area considerably decreased with inkjet ONP ratio in the paper furnishes, which indicated that aging inkjet ONP had a less negative effect on pulp cleanliness than that of offset ONP. The results in **Fig. 10** also show that deinking chemistry, alkaline or near-neutral, was not an important factor in pulp cleanliness.

Filtrate darkening

Filtrate darkening is used in the INGEDE method to assess fil-



11. Filtrate darkening as function of inkjet ONP.



12. Flotation efficiency and flotation yield loss as function of flotation time for fresh paper.

trate quality of deinked pulp. **Figure 11** shows that the filtrate darkening increased with inkjet ONP ratio. Paper blends with 12% and more inkjet ONP had filtrate darkening values exceeding the INGEDE upper threshold, making them unsuitable for deinking.

Flotation loss

To test the effect of flotation time on flotation loss, a flotation test was carried out for an extended time using a fresh paper blend with 18% of inkjet-printed ONP. As **Fig. 12** shows, flotation loss increased linearly with flotation time, indicating that the loss of fiber and filler in the froth was solely caused by entrainment in the interbubble water [23]. After 20-min flotation, 80% of the free and floatable ink was removed, but 46% of solid materials were rejected from the flotation cell. Because the population of unfloatable ink was removed in the calculation of flotation efficiency, the value of 80% is somewhat misleading because the largest fraction of removed ink particles originated from the offset inks. Flotation perfor-

mance and yield loss when the blend contains a large proportion of inkjet ink would not be acceptable in a deinking plant.

In summary, inkjet inks were easily dislodged from the fiber surface during repulping; however, the very small, detached ink particles were prone to redepositing on the surface of the fiber lumens. Moreover, the conventional flotation chemistry was ineffective at agglomerating these tiny ink particles and rendering them hydrophobic. The presence of fibers in the inkjet ink suspensions hampered the action of agglomerating agents. Total, bound, and residual ink concentrations all increased with inkjet-printed ONP ratio in the recovered paper whereas speckiness was reduced, especially for aged prints. Brightness, flotation efficiency, and flotation rate constant decreased with inkjet ONP ratio. With more than 10%–15% of inkjet-printed ONP in the blend, filtrate darkening was much higher than the upper threshold set by INGEDE to declare a print unrecyclable.

DISCUSSION

The scope of our work was to compare the deinking behaviour of pigmented inkjet inks with flexographic inks that we had studied extensively in the 1990s [7,13,14,19,34]. Because we tested a single formulation of inkjet ink printed on one source of newsprint paper substrate, it is clear that these limited results cannot lead to general conclusions on the deinkability of all formulations of pigmented inkjet inks. Composition of paper surface and of inkjet ink affected the deinkability of inkjet prints, as they did for flexographic prints; nevertheless, deinking behavior of the inkjet-printed paper was very similar to that of the numerous flexographic prints tested in the past. Hence, introduction of significant amounts inkjet-printed paper in typical blends used for newsprint manufacturing is likely to be as problematic as flexographic prints for the recycling industry. Our recent findings support the conclusions of European studies [1,2,4,5] that inkjet prints have such poor deinkability that a commercial deinking system would not be able to handle more than 10% of inkjet-printed paper substrates in the blend. One noteworthy difference between our work and the European studies was our effort to mimic best mill practices in North America. We have confirmed that short pulping is beneficial for papers printed with oil-based inks, as well as for papers printed with water-based inks [13,14] including pigmented inkjet inks. Because all mills in Canada with batch, helical pulpers have been employing the short pulping time strategy for nearly 10 years now, no further improvement in inkjet deinking can be expected from the pulping procedure. We have also shown that there is little beneficial effect on inkjet-print deinking when near-neutral deinking is used instead of conventional alkaline chemistry. Despite the adoption of short pulping time and neutral or near-neutral deinking, a recycling plant would still be adversely affected by the presence of inkjet prints.

Other means to enhance deinkability of inkjet ink include

altering the deinking process or the flotation collector chemistry, or both. On the process side, the two-loop deinking system has been advocated as the means to solve this problem [9]. In an industry that is struggling to survive, cost-cutting measures are a necessity. With essentially no capital available and a second loop that is costly to operate, this measure is simply not practical. Moreover, when a significant fraction of inkjet inks is unfloatable, a second flotation step becomes obviously of no value. Furthermore, higher material losses (7%–8%) are economically and environmentally sound only when it is a necessity (e.g., in tissue manufacturing). A more attractive approach, often promoted by water-based ink manufacturers, is to alter the collection chemistry to promote the agglomeration of submicron and even nano-size ink pigments by nonionic and/or charged polymers or minerals. This simple concept has been tried repeatedly by numerous researchers and has only led to modest improvement in water-based ink removal. We have shown that the presence of flocs of fibers in water-based ink suspensions hampers the action of agglomeration agents [34]. Also, numerous positive claims of a universal ink collector equally effective for oil- and water-based prints have been made by chemical and water-based ink suppliers, but these have not met expectations in the mills.

Because the solutions tried at the pilot and mill scales for enhancing the deinkability of flexographic inks have had limited success [8] despite considerable effort, it is likely that a different approach must be adopted to tackle the poor deinkability of pigmented inkjet prints. Ideally, printing should produce a macroscopic inkjet film on the paper surface. During recycling, the pulping action should dislodge the film from the paper surface and break it into pieces large enough to be properly processed in a deinking plant. Some sort of bonding agent or primer has been reported to enhance print quality and promote the coherence of an inkjet print [6]; this approach is in line with our own views. To make inkjet ink prints floatable, small pigments applied to the paper substrate must contain a coadditive that will provide sufficient cohesiveness to the print so that after drying and later processing in a repulper, they will not fall below a critical size that renders their capture by air bubbles impossible from a hydrodynamic standpoint. Moreover, the degree of coherence of the printed film will have to be defined because a cohesive print (like that produced by dry toners) may cause cleanliness issues when it is too thick [35]. Development of the proper formulation of inkjet inks will require the active participation of recyclers, papermakers, ink makers, and printer manufacturers. Otherwise, the different groups may express conflicting views to defend their own interests, which are particularly harmful and counter-productive when such views are based on perceptions rather than facts.

CONCLUSIONS

We carried out deinkability tests with different ratios of inkjet-printed ONP in paper furnishes under alkaline and

near-neutral deinking chemistries with fresh and aged papers. The method used for the evaluation is in line with current deinking practices in North American recycling plants (helical pulper, very short pulping time, and optimal flotation collector). We found that inkjet inks were easily dislodged from the fiber surface during repulping; however, the very small, detached ink particles were prone to redeposit irreversibly on the surface of the fiber lumens. Moreover, conventional flotation chemistry (calcium soaps of fatty acids), which is still considered to be the best approach, was found to be ineffective at agglomerating these tiny ink particles and rendering them hydrophobic. As for flexographic inks, the presence of fibers in the inkjet ink suspensions hampered the action of agglomerating agents. Total, bound and residual ink concentrations all increased with inkjet-printed ONP ratio in the recovered paper whereas speckiness was reduced, especially for aged prints. Brightness, flotation efficiency, and flotation rate constant decreased with inkjet ONP ratio. With more than 10%-15% of inkjet-printed ONP in the blend, filtrate darkening was much higher than the INGEDE upper threshold for deinking suitability of a print. Thus, even under more favorable conditions than INGEDE Method 11 for handling highly dispersible inks, our conclusions were very similar to those of European researchers. Pigmented inkjet inks are likely to be incompatible with the current deinking technology. The

exact percentage of inkjet-printed paper that a mill can tolerate is difficult to estimate from laboratory tests because the results represent a best-case scenario; however, the percentage of 10% proposed by CTP appears to be reasonable.

The best approach to avoid inkjet prints eventually becoming an issue for the recycling industry is to alter cohesiveness of the print produced by this technology. Presently, the prints do not have sufficient cohesion to withstand the forces imparted to it in the pulper. To reach this objective, the best strategy would be to add some form of agent to the ink that would promote film formation on paper surface. **TJ**

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ABOUT THE AUTHORS

The topic of our research is an important issue for paper recycling plants, and the conclusions we reached were very similar to those of European researchers. Because of some difficulties in obtaining inkjet-printed ONP from manufacturers, we printed newspapers using a representative pigmented inkjet ink.

We discovered that the inkjet ink is very similar to water-based flexo ink; therefore, pigmented inkjet inks are likely to be incompatible with the current deinking technology. As a result, there is likely a need to convince manufacturers to produce deinkable inkjet inks.



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Editor's Note – In the next PPR supplement to TAPPI Journal, scheduled for February 2012, we will feature the 2011 Wayne Carr Best Paper winner, "A first online analyzer for stickies and macrocontaminants." Co-authored by Michelle Ricard, Denise Filion, Sylvain Gendron, Gilles Dorris, Natalie Page (FPInnovations) and Carlos Castro (Evanic SA), this paper was presented at the 2010 TAPPI PEERS Conference in Norfolk, VA, USA.

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