Fines from deinked pulp: Effect of contaminants on their bleachability and on the pulp final brightness

The importance of metals management is emphasized

By L. Lapierre, D. Pitre and J. Bouchard

Abstract: We recently reported that the over-all brightness and bleachability of deinked pulp (DIP) fines were substantially lower than for the long fibre fraction. It was unknown, however, what caused the poor bleaching response of DIP fines. This work led us to conclude that two factors coming from external contamination were the main cause for the poor bleaching response of DIP fines and low brightness ceiling: high effective residual ink and high level of transition metals, specifically iron.

METHOD
All chemical charges are expressed as percentage of pulp, oven dry (o.d.) basis; PAPTAC standard methods were used.

Fractionation: The small-scale fractionation process was carried out in a float wash-type fractionator [2], where a screen separated fibres primarily on the basis of length; separation by flexibility was a secondary effect [4].

Metal Management: Acid (A) and chelation (Q) stages were performed at 2% consistency for one hour at 50°C and followed by thorough washes with deionized water. The pH of the A-stage was adjusted with H₂SO₄ to 1.50 ± 0.05 or 2.50 ± 0.05. The pH of the Q-stage was adjusted with H₂SO₄ to 5.3 ± 0.3, and a 0.60% charge of EDTA was applied, unless otherwise indicated.

Bleaching Procedures:
— Washing: After each of the various bleaching treatments, the pulp was washed by diluting (to 1% consistency), then thickened. The fines samples were thickened by centrifuging.
— Peroxide bleaching: The peroxide bleaching stages were performed at 8% consistency using, except where indicated, a bleach liquor consisting of: 3.0% H₂O₂, 2.5% NaOH, 0.20% DTPA, 3.0% Na₂SiO₃ and 0.20% MgSO₄ if following an A-stage, or 0.050% MgSO₄ if following a Q-stage. Details are given in [2].
— Hydrosulphite bleaching: The sodium hydrosulphite stages (Y) had a charge of 0.5% Na₂S₂O₄ on pulp at a pH of 5.5 (adjusted with sulphuric acid), and performed for 30 minutes at 60°C. Details are given in [2].

RESULTS, DISCUSSION
A look at the characterization of DIP, TMP, UNP:UMG, and their fractions, are discussed below.

Fibre Length Distribution: Bauer-McNett: Figure 1 shows the Bauer-McNett histogram of the unfractionated DIP, TMP and UNP:UMG. Fines represented the largest fraction in all the pulps (Fig. 1). The UNP:UMG had the highest per-
percentage of fines because of contributions from fillers and coating materials. The DIP sample had the lowest P200 value because soluble material had been removed during the flotation applied to this sample in the mill.

The Bauer-McNett profiles of the long fractions of the three pulps obtained after float wash fractionation were very similar (Fig. 2). The largest contributions came almost equally from the R-14, 14/28 and 28/48 fractions. The float wash fractionator segregated between 85 and 89% of the fines material present in each sample.

Metal Ion Profile: The metal ion profiles of the initial unfractionated pulp samples, and of the long and short fibre fractions are shown in Table I. Most of the metal concentrations in the initial pulps were higher than those in the long fractions, and lower than those in the short fractions, indicating that the metals were concentrated in the fines. The exception was manganese, which appears to be washed out during fractionation, causing the original pulps to have higher manganese levels than those found in either fraction.

Calcium and magnesium were present in the fractions in concentrations that obeyed a mass balance. Iron was a special case; it obeyed a mass balance for DIP, but the TMP and UNP:UMG fines contained more iron than a mass balance predicted. The expected concentrations of iron in the original TMP and UNP:UMG, as determined by adding the contributions from the long and short fractions, were twice as much as the actual measured concentrations. We believe that the fines adsorbed iron that was present in the water used for dilution in either a flotation cell or a float wash fractionator. This would explain why TMP and UNP:UMG fines collected by the float wash fractionator were enriched in iron and why the DIP fines, having been floated at the mill and enriched in iron prior to fractionation, did not lose or gain any more iron.

Bleaching DIP TMP UNP:UMG
Unfractionated pulp Untreated 55.1 56.5 60.8
QP or APY (+11.8) (+17.6) (+11.3)
Long fractions Untreated 53.8 53.4 57.5
QP or APY (+20.9) (+23.0) (+17.5)
Fines Untreated 47.7 52.6 56.9
QP or APY (+8.0) (+17.8) (+11.9)

TABLE I. Metal ion profile (ppm).

<table>
<thead>
<tr>
<th></th>
<th>DIP</th>
<th>TMP</th>
<th>UNP:UMG</th>
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<tbody>
<tr>
<td>Ca</td>
<td>1500</td>
<td>1400</td>
<td>1100</td>
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<tr>
<td>Fe</td>
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<td>30</td>
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<td>Mg</td>
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<td>120</td>
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<td>Mn</td>
<td>11</td>
<td>45</td>
<td>20</td>
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<th>DIP</th>
<th>TMP</th>
<th>UNP:UMG</th>
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<tbody>
<tr>
<td>Ca</td>
<td>1350</td>
<td>1100</td>
<td>910</td>
</tr>
<tr>
<td>Fe</td>
<td>45</td>
<td>15</td>
<td>33</td>
</tr>
<tr>
<td>Mg</td>
<td>210</td>
<td>105</td>
<td>130</td>
</tr>
<tr>
<td>Mn</td>
<td>3</td>
<td>0.6</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>DIP</th>
<th>TMP</th>
<th>UNP:UMG</th>
</tr>
</thead>
<tbody>
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<td>Ca</td>
<td>2000</td>
<td>2100</td>
<td>1600</td>
</tr>
<tr>
<td>Fe</td>
<td>560</td>
<td>170</td>
<td>550</td>
</tr>
<tr>
<td>Mg</td>
<td>440</td>
<td>170</td>
<td>240</td>
</tr>
<tr>
<td>Mn</td>
<td>7</td>
<td>11</td>
<td>10</td>
</tr>
</tbody>
</table>

Bleachability of Pulps and Pulp Fractions: Table II lists the ISO brightness of the pulps and those of the long and short fractions before and after QPY or APY; these two sequences led to the same results. The brightness gains are in parentheses.

Unbleached unfractionated pulps were always brighter than their fractionated components and unbleached fines had the lowest brightness due to their high lignin content and, in the case of DIP, high ERIC values (450 ppm). The higher brightness of the unfractionated pulps indicated that the positive effect of fines on light scattering is greater than their negative effect on light absorption.

After bleaching, the long fraction pulps were the brightest. The brightness gains show that these pulps responded best to the bleaching chemicals.

The final brightnesses of the long fraction pulps were relatively independent of the fibre source (ISO brightnesses after QPY: DIP, 74.7%; TMP, 76.4%; and UNP:UMG, 75.0%, for an over-all average of 75.4 ± 0.9%). However, the final brightnesses of the bleached unfractionated pulps were always brighter than their fractionated components and unbleached fines had the lowest brightness due to their high lignin content and, in the case of DIP, high ERIC values (450 ppm). The higher brightness of the unfractionated pulps indicated that the positive effect of fines on light scattering is greater than their negative effect on light absorption.
tionated pulps differed: DIP had the lowest ISO brightness at 66.9%, followed by UNP:UMG at 72.1% and TMP at 74.1%. The same order was seen for the ISO brightnesses of the bleached fines; DIP, 55.7%; UNP:UMG, 68.8%; and TMP 70.4%.

The above results indicate that the low final brightness of the DIP after QPY was a direct consequence of the poor bleachable and low brightness of the DIP fines. To confirm this, we measured the ISO brightness of DIP and TMP furnishes, consisting of the bleached (QPY) long fraction mixed with their respective bleached (QPY) fines counterparts, in ratios ranging from 70:30 to 100:0 long fraction:fines. The results, Fig. 3, show that the 100:0 DIP furnish had an ISO brightness of 75.1%, while the 70:30 DIP furnish had a brightness of 66.4%, a drop of 8.7 brightness points. Under the same conditions with TMP, the ISO brightness went from 76.7% to 74.7%, a drop of only 2.0 brightness points.

**Fines Bleachability:** The bleachability of the fines of the three furnish materials, obtained from the float wash fractionator, was evaluated for the following bleaching sequences: Y, QY, AY, P, QP, AP, QPY and APY. Again, A and Q treatments were equivalent and thus tabulated together. Table III summarizes these bleaching results.

**TABLE III. ISO brightness (%) of the short fractions (fines) obtained after different bleaching sequences (brightness changes are in parentheses).**

<table>
<thead>
<tr>
<th>Bleaching Sequence</th>
<th>DIP</th>
<th>TMP</th>
<th>UNP:UMG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>47.7</td>
<td>52.6</td>
<td>56.9</td>
</tr>
<tr>
<td>Y</td>
<td>49.4</td>
<td>56.5</td>
<td>—</td>
</tr>
<tr>
<td>(+1.7)</td>
<td>(+3.9)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>QY or AY</td>
<td>54.4</td>
<td>59.5</td>
<td>—</td>
</tr>
<tr>
<td>(+6.7)</td>
<td>(+6.9)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>P</td>
<td>45.4</td>
<td>62.6</td>
<td>57.5</td>
</tr>
<tr>
<td>(-2.3)</td>
<td>(+10.0)</td>
<td>(+0.6)</td>
<td>—</td>
</tr>
<tr>
<td>OP or AP</td>
<td>50.0*</td>
<td>66.5</td>
<td>67.2</td>
</tr>
<tr>
<td>(+2.3)</td>
<td>(+13.9)</td>
<td>(+10.3)</td>
<td>—</td>
</tr>
<tr>
<td>QPY or APY</td>
<td>55.7*</td>
<td>70.4</td>
<td>68.8</td>
</tr>
<tr>
<td>(+8.0)</td>
<td>(+17.8)</td>
<td>(+11.9)</td>
<td>—</td>
</tr>
</tbody>
</table>

* A 1.2% EDTA charge was applied in the Q-stage and 0.2% MgSO₄ added in the P-stage, a departure from the procedure described in the experimental section.

FIG. 3. ISO brightness of DIP and TMP furnishes, consisting of the bleached (QPY) long fraction mixed with their respective bleached (QPY) fines counterparts, in ratios ranging from 70:30 to 100:0 long fraction:fines.

Other than the difference in ERIC value, the DIP fines contained significantly more iron than the TMP fines. The exceptionally high concentrations of iron in the fines, especially the DIP fines, significantly reduced the bleaching efficiency of hydrox sulphite. Hydrox sulphite bleaching was less efficient for DIP fines than for TMP fines (ISO brightness gain of 1.7% vs. 3.9%, respectively). As a result, when the Y-stage was preceded by a metal-management stage, hydrox sulphite bleaching efficiency was restored giving ISO brightness gains of 6.9 and 6.7 points for DIP and TMP fines, respectively.

The high level of metals in the DIP fines fraction prevented any benefit from peroxide bleaching. Without a metal-management stage, a P-stage caused a brightness loss: the peroxide residual was nil and the high pH causedalkali darkening of the pulp. The best P-stage results occurred following either an acid wash at pH 1.5 or a Q-stage using a 1.2% charge of EDTA, twice the amount required for the unfractionated pulp and the long fractions. At this dosage, the magnesium in the pulp was also depleted and needed to be replenished for optimal peroxide bleaching efficiency. The metal-management stages decreased the iron concentration by about 100 ppm (from 560 to 460 ppm), with the subsequent peroxide stage giving an ISO brightness 4.6 points higher than the case with no pre-treatment, for a net ISO brightness gain of only 2.3 points.

The TMP fines, which had an Fe content 3.5 times less than that of the DIP fines (i.e., 170 ppm vs. 560 ppm), responded much better to peroxide bleaching than DIP fines. Even without a metal-management stage, the ISO brightness gain was 10 points. A metal-management stage provided an additional ISO brightness gain of ~4 points, similar to the benefit observed with the DIP fines.

A metal-management stage clearly improved the P-stage to a greater extent than the Y-stage, demonstrating the greater sensitivity of hydrogen peroxide towards transition metals.

A QPY/APY stage brought the final ISO brightness of the TMP fines to 70.4% (a gain of ~18 brightness points), and of the DIP fines to 55.7% (a gain of 8 brightness points). The effectiveness of the Y-stage decreased when preceded by an efficient P-stage; the two stages do not

Using the following equations,

\[
\text{Brightness} = 1 + k_f s - (2k_f s + (k_f s)^2)^{1/2}
\]

\[
k_{(fines+ink)} = k_{fines} + k_{ink}
\]

\[
k_{fines} = 21.9 \text{ m}^2/\text{kg}, \quad s_{fines} = 21.9 \text{ m}^2/\text{kg}
\]

where \(k\) is the absorption coefficient, \(s\) the scattering coefficient, \(k_{ink}\) the ink concentration, and \(k_{fines} = 15000 \text{ m}^2/\text{kg}\) [1], one can calculate the effect of ink on brightness.

The DIP fines had an ISO brightness of 47.7%, a scattering coefficient, \(s_{fines}=21.9 \text{ m}^2/\text{kg}\), and the ink concentration \(k_{ink} = 15000 \text{ m}^2/\text{kg}\). We calculated that \(k_{(fines+ink)} = 28.7 \text{ m}^2/\text{kg}\). For the ink-containing DIP fines to gain 8.0 brightness points over-all and reach 55.7%, the brightness of the DIP fines alone would have to be 63.0% i.e., \(k_{(fines+ink)} = 21.9 \text{ m}^2/\text{kg}\) and \(k_{ink} = 6.8 \text{ m}^2/\text{kg}\). If ink was absent, then \(k_{fines} = 21.9 \text{ m}^2/\text{kg}\), and the inkless brightness would be 52.2%.

During the QPY sequence, \(k_{ink}\) of black ink remains unchanged and therefore, for the ink-containing DIP fines to gain 8.0 brightness points over-all and reach 55.7%, the brightness of the DIP fines alone would have to be 63.0% i.e., \(k_{fines} = 21.9 \text{ m}^2/\text{kg}\) and \(k_{ink} = 6.8 \text{ m}^2/\text{kg}\). If ink was absent, then \(k_{fines} = 21.9 \text{ m}^2/\text{kg}\), and the inkless brightness would be 52.2%.
perfectly complement each other [6].

— Fines from UNP:UMG: The fines from UNP:UMG (Table III) had the highest brightness due to their origin (30% bleached magazine at an ISO brightness of 68%, and 70% of newsprint at an ISO brightness of 60.4%). The ERIC value of the UNP:UMG fines was 125 ppm, higher than the 75 ppm for the TMP fines, but lower than the 450-ppm of the DIP fines. The 30% DIP content in the UNP could explain this intermediate ERIC value.

Due to their prior bleaching history, high Fe concentration and ink carried over from recycling, the UNP:UMG fines bleachability was intermediate to those of the DIP and TMP; however, their final brightness was only slightly lower than that of the TMP fines.

The peroxide bleaching response was poor when it was not preceded by a metal-management stage (only 0.6 of a brightness point); however, it was still better than the DIP fines response (~2.3 brightness points), but less than the TMP fines response (10.0 brightness points). A metal-management stage improved the ISO brightness gain following peroxide bleaching by nearly 10 points, to 67.2%. The ISO brightness increase was between that of DIP (2.3 brightness points) and TMP (13.9 brightness points), but the final brightness was similar to that of the TMP. The maximum ISO brightness gain was 11.9 points following a QP-stage, less than the 17.8 brightness points gain for TMP but greater than the 8.0 brightness points for DIP. The maximum ISO brightness attained for the UNP:UMG fines was 68.8%, close to the 70.4% value for the TMP fines, and definitely higher than that of the DIP fines (55.7%).

We can conclude that fines that have never been through printing respond well to bleaching reagents, provided they are treated with a metal-management stage. For each furnish, the ratio of the maximum ISO brightness gains of the fines (Table III) over that of the original pulps (Table II) were 0.68 for DIP (8.0/11.8), 1.01 for TMP (17.8/17.6) and 1.05 for UNP:UMG (11.9/11.5), which illustrates again how the high ERIC of the DIP fines limited the final brightness gain of the unfract-ionated pulps.

It is interesting to note that the long fractions of the DIP and UNP:UMG had similar brightness gains and final brightnesses (Table II), while their fines bleachability differed significantly. Therefore, the processing of the pulp into paper did not significantly affect its bleachability, as noted previously by Galland et al. [7]. However, the printing process did affect the bleachability due to the poor deinking of the fines.

CONCLUSION

Ink was extremely difficult to detach and seemed to be permanently bound to the DIP fines; it was the major factor limiting their brightness gain.

Iron had a strong affinity for fines. Without a proper metal-management stage, their high level of iron decreased the performance of hydrosulphite bleaching. The peroxide bleeding efficiency on fines from UNP:UMG or DIP was practically nil without an acid wash or a chelation stage.

Therefore, even if fines have a higher percentage of lignin than the long fraction, they can nevertheless be bleached to high brightness if they are not contaminated by ink. To bleach DIP to high brightness, either fines have to be removed or a process to detach and remove ink from fines is necessary.

The fines that had been processed, for example, through a paper machine, had a brightness ceiling similar to the fines that had not been processed, as long as ink was absent from that process.

LITERATURE


Résumé: Nous avons récemment présenté un rapport indiquant que la blancheur et l’aptitude au blanchiment des fines de pâte désen-crée (PDE) étaient en général substantiellement inférieures à celles de la fraction de fibres longues. Nous ne savions pas à ce moment ce qui avait entrainé la pauvre réponse des fines de PDE aux agents de blanchiment. Nous avons conclu que deux facteurs liés à la contami-nation externe étaient la cause principale de la pauvre réponse au blanchiment et au faible degré de blancheur maximale des fines de PDE : un taux effectif élevé d’encre résiduelle et une forte quantité de métaux de transition, principalement le fer.


Keywords: FINES, DEINKED STOCK, BRIGHTNESS, BLEACH-ABILITY, CONTRARIES, TRANSITION METALS.