Paper Chemistry… It’s more common than you think!

Presentation for IMFA – March 2015:
The Importance of Monitoring Chemistry and Charge Balance
In Thermoforming of Cellulose Fibers

March 2015
Alternative pulping – Elephant Paper

One elephant =>
Approximately 115 sheets of paper per day.
- Elephant is (literally) the digester
- No chlorine is required
- No harsh chemicals required for pulping

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Objective:
(maximize productivity; minimize downtime and waste)

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Traditional raw materials – North America
(Managing fiber sources used to be easier.)

Black Spruce
White Pine
Birch
Aspen (Cloquet)
Loblolly Pine (plantation)
Slash Pine
Yellow Poplar
Cottonwood

March 2015
The Future – Part 1 –

- Corn stalk residue
- Wheat straw pulps

The Future – Part 2 –

- Industrial hemp
- Bagasse fiber
- Sawgrass

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The Future – Part 3: Recycled content –

Eucalyptus

The Future – Part 4: Filler pulps –

Semi-mechanical pulps

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The Future – Part 4 (fillers: Hamburger Helper)

Kaolin
Bentonite
Titanium Dioxide

Calcium Carbonates

<table>
<thead>
<tr>
<th>PCC</th>
<th>GCC</th>
</tr>
</thead>
</table>

March 2015
<table>
<thead>
<tr>
<th>Past/Present</th>
<th>Future</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tree-based/Virgin</td>
<td>Recycled; non-tree based</td>
</tr>
<tr>
<td>Chemical pulping</td>
<td>Mechanical pulping</td>
</tr>
<tr>
<td>Low colloidal materials</td>
<td>High colloidal / dissolved materials content</td>
</tr>
<tr>
<td>bleached</td>
<td>Unbleached / deinked / reprocessed</td>
</tr>
<tr>
<td>Consistent in properties</td>
<td>Inconsistent in properties (recycled)</td>
</tr>
<tr>
<td>Clean</td>
<td>Dirty/Contaminated</td>
</tr>
<tr>
<td>Low silica levels</td>
<td>High silica levels</td>
</tr>
<tr>
<td>Good physical properties</td>
<td>Moderate to poor physical properties</td>
</tr>
</tbody>
</table>

Much harder to manage, due to high trash levels
Trash – Grouch's Like It, but...

- It stays dissolved only at first...
- And then it drops out of solution at the worst possible time...
  - Scaling
  - Deposits on tooling
  - Blocked vacuum lines
  - Foaming (stable; doesn’t go away)
  - Contamination in the press-forms

Grouch's tend to be negative.
Trash Components (negatively-charged in solution; colloidal in nature)

Fiber fines types

“Fiber-like”
- Ray
- Cut fiber

“Fibrillar”

“Split fibers”

M. Hubbe

Xylan + derivatives

Galactoglucomannan + derivatives

Lignin + derivatives

Shives

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Other, un-natural trash components from broke/recycled fiber sources

Dispersants from latexes, mineral fillers and other colloidal substances (negatively-charged)

Dissolved minerals (carbonates, talc, clays, silicas – negatively-charged)

Starch and other polymeric binder and adhesive materials

Adhesives from tapes and PS label stock

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What happens when anionic trash levels are high

Retention vs. Anionic Colloids

Clay content (%)

0 5 10 15

Contaminants (mg/g fiber)

0 1 2 4 6 8 10

TMP handsheets
20% clay
0.5% PEI

Kraft lignin
Sulfite lignin

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Another problem – Formation

High anionic trash levels => ugly, clumpy paper; dewaterers poorly despite high porosity

Controlled anionic trash => smoother, more aesthetically-pleasing; drains easily

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MAJOR issue – drainage / energy consumption

• Molded fibers retain more water after processing
  – Reactive size takes longer to cure
  – Other chemicals (ex. Fluorochemicals) work poorly, due to insufficient cure

• Higher temperatures =>
  – Greater energy consumption
  – Scorched forms; poorer aesthetics
A Bad Example from the world of Fluorochemistry

Wet end (Actual)

Fluorochemical: Cationic (+)

Pulp

Anionic trash / colloid
Resin, inorganic particle, etc.

The FC adsorbs on both pulp, fines and anionic trash

Oil and grease resistant paper

Machine Wire

H₂O

Wasted fluorochemical & trash solids

Poor OGR; less fluorochemical retained

Ca(CO₃)₂

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H₃C

COOH

CH₃(CH₂)₄CH=CHCH₂CH=(CH₂)₇COOH
Pretreatment of Anionic Trash Neutralization (using a cationic polymer fix agent)

Wet end

Cationic polymer

Cationic fluorochemical

Fluorochemical Absorbed on pulp

Better performance, due to better retention of the FC

Machine Wire

Neutralized trash & solids

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Oil and grease Resistant box or plate
Dealing with the anionic trash

- Popular cationic fix agents
  - PAAE
  - EPIDMA and other polyamines
  - PolyDADMAC
  - polyethylene imines (PEIs)
  - Cationic PAM

- For difficult applications (ex. BCTMP)
  - Polyethylene Oxide
  - Blends of cationic fix agents

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Best tools for management of charge balance in furnish

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Zeta Potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle.

For paper furnishes: Dispersed particles are cellulose; fines; granules of minerals (carbonates, talcs, etc.)

Diagram showing the ionic concentration and potential difference as a function of distance from the charged surface of a particle suspended in a dispersion medium.
<table>
<thead>
<tr>
<th>Zeta potential [mV]</th>
<th>Stability of colloidal substances in solution</th>
<th>Implications for paper formation</th>
<th>Implications for retention</th>
</tr>
</thead>
<tbody>
<tr>
<td>from 0 to ±5</td>
<td>Rapid coagulation or flocculation</td>
<td>Best formation; fine grain structure</td>
<td>Optimal first pass retention</td>
</tr>
<tr>
<td>from ±10 to ±30</td>
<td>Incipient instability</td>
<td>Okay, but some loss of formation and grain observed.</td>
<td>Good first pass retention</td>
</tr>
<tr>
<td>from ±30 to ±40</td>
<td>Moderate stability</td>
<td>Formation beginning to suffer; dissolved substances present</td>
<td>Fair first pass retention; dissolved substances present</td>
</tr>
<tr>
<td>from ±40 to ±60</td>
<td>Good stability</td>
<td>Mediocre formation and drainage; lumpy paper</td>
<td>Mediocre first pass retention; moderate dissolved materials</td>
</tr>
<tr>
<td>more than ±61</td>
<td>Excellent stability</td>
<td>Poor formation; drainage; high moisture levels</td>
<td>Low first pass retention; high trash levels</td>
</tr>
</tbody>
</table>

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Typical fix agent curve for virgin pulps

- Ideal for retention is in blue region (aka the “dielectric point”)
  - Zeta potential of -5 to +5 mV
  - Fix agent efficiency decreases near the dielectric region
Typical fix agent curve for recycled pulp (OCC)

- OCC = Succotash
  - Kraft linerboard
  - Groundwood corrugate
- Complex / nonlinear relationship between cationic demand and zeta potential
  - Sometimes the CD titrator lies!

Dielectric region: 0.30-0.45% PAAE

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Fix agent curve for blended pulp

- Complex / nonlinear relationship between cationic demand and zeta potential
- Cationic demand actually INCREASES inside the dielectric region before “flipping” fully cationic
Step 2 – use of proflocculents and drainage aids

- **Anionic PAM**
  - Causes fibers to flocculate together
  - Use judiciously (to avoid poor formation)

- **Colloidal silica**
  - Increases internal surface area
  - Increases porosity for better sheet drainage

Note: pro-flocc & silica combo often used for continuous papermaking as above

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Scale formation:

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pH – known to be an issue for some treatment chemicals

Water pH used for dilution

Acidic Neutral Alkaline

Additive #1
(Stable pH under 5.5)

Additive #2
(Stable pH under 5.5)

Additive #3
(Stable pH over 6.0)

Unstable

Unstable

Unstable
Stable foam:
(Adding a defoamer doesn’t solve the problem!)

Does not get better with time or defoamer addition

Better; does not require defoamer

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These are bad news whenever / wherever they occur! Stable foam is often the result of this, in combination with other system components.

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Problem furnish example (again from the world of fluorochemistry): Precipitated calcium carbonate

Two different cationic fluorochemicals: 62-64 GSM; commercial 62/38 furnish; EPIDMA fix; 1% PCC

Two different cationic fluorochemicals: 133-139 GSM; commercial 62/38 furnish; EPIDMA fix; 1% PCC

The improved buffer system for FC #2 made the difference here.
Problem furnish example #2 – softwood / uncoated freesheet waste fiber blend

Recycled has high ash content – but better buffer for #2 helps
Key Points:

- This is a competitive industry
- There are pressures not to use trees anymore
  - Economic
  - Environmental

- Replacement fibers are often not as good as trees
  - Lacking in physical properties
  - Loaded with anionic trash, fillers, dirt, glue, flies, staples, silica, etc.
  - Need to adjust chemistry to compensate for negative charge in solution

- Thermoformers need to watch the following w/ new school fiber sources
  - charge potential (they tend to be negative)
  - pH (tends to be higher than before)
Key Points:

• **A focus on chemistry can only help**
  – Coagulant / proflocculent / colloidal silica packages are available; can
    • Manage anionic trash
    • Ensure fines retention
    • Optimize formation
    • Improve energy efficiency

• **However, need to consider compatibility of chemicals in use**
  – pH variations can cause “kick-out” of components
  – “kick-out” leads to foam (bad); precipitates (worse);
    • Need for costly machine shutdowns / cleanings; lost production time
    • Premature tooling changes
  – Some chemicals are shear-sensitive; prone to scale formation or deposits on machine
  – Very important consideration for fluorochemicals (often the most expensive component)
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AGC Chemicals Americas -

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