Wet end chemistry- filler

Wood and Paper Science
Chungbuk National University
Use of fillers in papermaking

- Properties of fillers
- Effect on paper properties
- Effect on the papermaking process
Use of fillers

- Fillers
  - Fine, white pigment powders
  - Manufactured from natural minerals or synthetically
  - Also some organic pigments
- Added into the fiber stock
  - Fill out the empty space between fibers, smooth the surface
  - Printing and writing papers

### Examples of paper product filler contents

<table>
<thead>
<tr>
<th>Product</th>
<th>Filler Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Newsprint</td>
<td>0-15 %</td>
</tr>
<tr>
<td>SC gravure paper</td>
<td>20-32 %</td>
</tr>
<tr>
<td>LWC base paper</td>
<td>6-10 %</td>
</tr>
<tr>
<td>Wallpaper</td>
<td>8-15 %</td>
</tr>
<tr>
<td>Mechanical catalogue paper</td>
<td>5-10 %</td>
</tr>
<tr>
<td>Wrapping base paper</td>
<td>5-20 %</td>
</tr>
<tr>
<td>Woodfree printing paper</td>
<td>10-25 %</td>
</tr>
<tr>
<td>Woodfree writing paper</td>
<td>10-25 %</td>
</tr>
<tr>
<td>Corrugated board</td>
<td>2-10 %</td>
</tr>
<tr>
<td>Wallpaper board</td>
<td>2-10 %</td>
</tr>
</tbody>
</table>
Why fillers are used?

- Economy
  - Most fillers are cheaper than fibers
  - Except specialty pigments

- Improve smoothness and printability (functional)
  - Formation, opacity, dimensional stability, gloss, (brightness)

Laufmann, M., Fillers for Paper – A Global View
Trends in using fillers

Europe

Uncoated Wood-free
100g / m²

SC - paper
60g / m²

% 40
30
20
10

1980 1990 2000 (est.)
1980 1990 2000 (est.)

Opacity

grammage, g/m²
Use of minerals in papermaking

Source: Ian Wilson: Filler and Coating Pigments for Papermakers

Use of calcium carbonate and clay in papermaking

<table>
<thead>
<tr>
<th>industry, Mt</th>
<th>1980</th>
<th>1990</th>
<th>2000</th>
<th>2005</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCC</td>
<td>0.2</td>
<td>1.2</td>
<td>4.9</td>
<td>5.75</td>
</tr>
<tr>
<td>GCC</td>
<td>3.4</td>
<td>6.2</td>
<td>10.0</td>
<td>11.6</td>
</tr>
<tr>
<td>Clay</td>
<td>8.5</td>
<td>10.2</td>
<td>13.5</td>
<td>15.1</td>
</tr>
</tbody>
</table>

Source: www.paperhedge.com/pdf/05minerals_data.pdf
Filler grouping

- Fillers
  - Clay, talc, GCC ja PCC
  - cheap

- Specialty pigments
  - Titandioxid (TiO₂), calcinated clay, gypsum, silica pigments, organic pigments
  - expensive
  - Give some special properties/combination of properties
  - Used minor amounts together with fillers
Properties of fillers and effect on paper quality
Properties of fillers

- Missing bonding ability
- Important properties for papermaking
  - Morphology
    - Particle size and shape
    - Specific surface area
    - Particle size distribution
  - Density
  - Chemical properties of the surface
  - Optical properties
    - Refractive index / Light scattering
    - Brightness/Colours
  - Absorption properties (oil, ink, etc.)
  - Chemical inert/solubility
  - Charge
  - Purity
  - Price

Size comparison of wire mesh hole, fiber and filler particle

- Filler particle: 0.002-0.01 mm
- Wire mesh hole: 0.2 mm
- Fiber: 1-3 mm

Affect
- Processability
- Process
- Product
Particle shape

- Shape
  - platy
  - spherical
  - needless
  - (cubical, aggregates)
- Aspect ratio, a.r. (or shape factor) = L/T
  - Platly: diameter/thickness
  - Rods, needles: length/thickness

http://www.specialtyminerals.com
Scalenohedral
rhombohedral

\[ a=b=c \]

\[ \alpha \neq \beta \neq \gamma \neq 90^\circ \]
Particle size distribution

- PCC has narrow PSD
- GCC has broad PSD

- PCC: 0.7 micron
- GCC: 0.7 micron

http://www.specialtyminerals.com
Optical properties

- Optical properties are depending on
  - Chemical composition
  - Particle size distribution
  - Particle shape
  - Refractive index
- Brightness
  - High diffuse reflection at all wavelengths
  - Mineralogy
  - Purity
- Opacity – light scattering
  - Refractive index – specific to each material
  - Particle size
Effects on paper quality

- Why?
  - Small particle size
  - Density
  - Surface area
  - Missing bonding capacity
  - Shape of particles
  - Surface properties

- How?
  - Filler break down the fiber network
  - Filler properties have effect

Wood fiber and filler densities

- Holocellulose: 1541 kg/m³
- Lignin: 1387 kg/m³
- Kaolin: 2600 kg/m³
- Calcium carbonate: 2650 kg/m³
- Precipitated: 3900 kg/m³
- Titanium dioxide: 3900 kg/m³
Effect on optical properties

- Contact of light and paper
  - Specular reflection - gloss
  - Scattered reflection - brightness
  - Permeance - opacity
  - Absorption – color
- Light changes its direction at interfaces
- The scattered reflection depends on:
  - Optical surface area
  - Refractive index
  - Thickness of the material layer
Factors affecting optical properties

- Light scattering and absorption coefficients of components
- Ratio of components
- Grammage
- Properties of filler
  - Diffuse reflectance
  - Lack of bonding capacity
  - Specific surface area
- Effect on brightness is depending on the used fiber raw material
Effect on fiber network and structure of the paper

- Fiber network
  - Very bulky
  - Lot of empty space
  - Layered structure
- Filler particle in fiber network
  - How does it settle
  - Particle size and shape

Filling  Insertion  Expansion
Effects on strength properties

- Caused by decreased amount of fiber-fiber bonding
- Effect on tearing strength by high filler contents
- Decreased breaking strain
- Dimensional stability increases
- Unbound filler
  - Surface strength
  - Linting
  - Dusting

Effect of filler content on tensile and tear strength
Effect on paper structure

- Bulk
  - Density of the filler
- Thickness
  - Particle shape
  - Particle size
Effect of filler properties on properties of paper
Particle shape

Gloss as a function of filler particle size

SC offset paper, ash content 25 %, 50 % of filler particles < 2μm

Effect on calendering

![Graph showing gloss as a function of filler particle size](image1.png)

![Effect on calendering graph](image2.png)
### Particle size

<table>
<thead>
<tr>
<th>FILLER TYPES</th>
<th>APS (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>kaolin -- hydrous</td>
<td>0.2 ---- 2.0</td>
</tr>
<tr>
<td>kaolin -- calcined</td>
<td>0.7 ---- 1.5</td>
</tr>
<tr>
<td>CaCO$_3$ -- ground</td>
<td>0.7 ---- 3.0</td>
</tr>
<tr>
<td>CaCO$_3$ -- precipitated</td>
<td>0.3 ---- 3.0</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.2 ---- 0.4</td>
</tr>
<tr>
<td>talc</td>
<td>1.5 ---- 10.0</td>
</tr>
<tr>
<td>silica, silicate</td>
<td>0.1 ---- 3.0</td>
</tr>
</tbody>
</table>

**Light scattering coefficient as a function of filler particle size**

SC offset paper, ash content 2%.
aspect ratio of filler 11.

![Graph showing light scattering coefficient as a function of filler particle size](image)
Particle shape

![Graph showing the relationship between print through and filler loading for different materials.](image)

- Calcium Silicate 55g/m²
- Calcined Clay 55g/m²
- Calcium Silicate 45g/m²
- Calcined Clay 45g/m²
Particle size

3D graph showing the relationship between tensile index (N m/g) and filler content (%) and particle size (μm).
Particle size and shape

Graph 1: Base Sheet Bendtsen Porosity (ml/min) vs. Filler Loading Level (%)
- Chalk
- UK kaolin
- Brazil kaolin
- PCC

Graph 2: Porosity (ml/min) vs. Filler Content (%)
- Coarse calcium carbonate
- Coarse clay
- Medium-coarse talc
- Fine calcium carbonate
- Fine clay
Particle size and shape

![Graph showing the relationship between mean particle size and tensile index. The graph compares Scaleno PCC, Rhombic PCC, and Aragonite PCC.](image)

![Graph showing the relationship between filler content and tensile index. The graph compares Fine sPCC, Coarse sPCC, Fine iPCC, Coarse iPCC, Fine GCC, and Coarse GCC.](image)
Particle size and shape

Sheet Opacity (%)

% filler in sheet

Filler Loading (wt%)

Opacity

- 1.2µm PCC-s
- 2.2µm PCC-s
- 0.8µm GCC
- 1.5µm kaolin
- 0.3µm TiO2

Calcium Silicate 55g/m²
Calcined Clay 55g/m²
Calcium Silicate 45g/m²
Calcined Clay 45g/m²
Importance of particle size and shape

Light scattering ⇒ optical properties
- Optimal particle size 0.2 - 0.3 μm (high refractive index)
- Practically 0.4 – 0.5 μm (low refractive index)
- Porous aggregate ⇒ micropores
- Particle size distribution
  - Narrow ⇒ higher scattering
- Gloss
  - Fine particles
  - Platy, needles
- Affect also strength properties and printability

Effects of finer particle size

Paper Properties | Pigment Properties
---|---|---|---
Finer particle size | Steeper PSD | Aggregated Crystal Structure
Optics | + | + | +
Strength | - | + | -
Bulk | - | +/- | +
Stiffness | - | +/- | -
Porosity | - | +/- | +
Specific surface area

- Fiber: SSA = 1 - 2 m²/g
- Fiber fines: SSA = 6 - 8 m²/g
- Filler: SSA = 4 - 20 m²/g

50X magnification

<table>
<thead>
<tr>
<th>FILLER TYPES</th>
<th>SSA (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>kaolin -- hydrous</td>
<td>10 -- 25</td>
</tr>
<tr>
<td>kaolin -- calcined</td>
<td>15 -- 25</td>
</tr>
<tr>
<td>CaCO₃ -- ground</td>
<td>2 -- 12</td>
</tr>
<tr>
<td>CaCO₃ -- precipitated</td>
<td>3 -- 25</td>
</tr>
<tr>
<td>TiO₂</td>
<td>7 -- 12</td>
</tr>
<tr>
<td>talc</td>
<td>9 -- 20</td>
</tr>
<tr>
<td>silica, silicate</td>
<td>45 -- 75</td>
</tr>
</tbody>
</table>

fibers = 1 -- 2 m²/g
fiber fines = 6 -- 8 m²/g
Specific surface area

- 70% fiber: SSA = 1.5 m²/g
- 15% fines: SSA = 7.4 m²/g
- 15% filler: SSA = 11.7 m²/g

Graph showing the breaking length as a function of the percentage of filler in the sheet.
Other important properties of fillers

- Abrasion (on paper machine, printing)
  - Hardness
  - Particle size
  - Particle shape
  - Impurities
- Purity
  - brightness
  - solubility
  - Surface properties
- Other
  - Availability
  - Uniform quality
  - Price

### Table: Filler Type and Wire Wear

<table>
<thead>
<tr>
<th>Filler Type</th>
<th>Wire Wear*</th>
<th>Internal Abrasion**</th>
</tr>
</thead>
<tbody>
<tr>
<td>kaolin - hydrous</td>
<td>1 -- 6</td>
<td>50 -- 300</td>
</tr>
<tr>
<td>kaolin - calcined</td>
<td>15 -- 30</td>
<td>1000 -- 1500</td>
</tr>
<tr>
<td>CaCO₃ - natural</td>
<td>3 -- 15</td>
<td>300 -- 650</td>
</tr>
<tr>
<td>CaCO₃ - precipitated</td>
<td>2 -- 9</td>
<td>20 -- 600</td>
</tr>
<tr>
<td>TiO₂</td>
<td>10 -- 30</td>
<td></td>
</tr>
<tr>
<td>talc</td>
<td>3 -- 5</td>
<td></td>
</tr>
<tr>
<td>silica, silicate</td>
<td>5 -- 13</td>
<td></td>
</tr>
</tbody>
</table>

*Einlehner Abrasion (mg. of wire loss)  
**Needle Abrasion (µg. of needle wear)  
+ unfilled paper = 50 -- 200µg. of needle wear
Process effects of the use of fillers
Effect of the use of fillers

- Fine particle size
- Higher density than fibers
- High surface area (light reflecting surface)
- Price

- Lack of bonding ability
- Shape and surface properties
- Minimal water binding to filler

- Advantages
  - Cost-effectiveness
  - Price
  - Improved drainability and better dewatering in the wire section
  - Printability (smoothness)
  - Ink absorption
  - Dimension stability

- Drawbacks
  - Decreased strength properties
    - Runnability
  - Abrasion
  - Poor retention
  - Two sidedness
  - High amount of filler in circulation water
Effect on papermaking process

- Density
  - Sedimentation of filler particles
  - Separation in centrifugal field
- Particle size
  - Poor retention
  - Increased consumption of paper chemicals
- Hardness
  - Abrasion of wires
  - Depends also on impurities

Pigments enrich in centrifugal cleaning plant rejects

1. stage reject
2. stage reject
3. stage reject
4. stage reject
5. stage reject
6. stage reject
Effects on process

- Lack of bonding
  - Demands on fiber raw material
  - Dusting
- Better water removal
  - Minimal water binding to filler
  - Higher solid content at the wire section and after the pressing
  - Depends on particle size

![Graph showing drainage rate vs. weight percentage under 2 μm with different filler amounts (3% and 6%) and comparison to no filler case.](image-url)
**Charge of the filler particles**

- \( \zeta \)-potential values of fiber and fillers

<table>
<thead>
<tr>
<th>Material</th>
<th>pH</th>
<th>( \zeta )-potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber</td>
<td>4</td>
<td>-15</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>-25</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>-30</td>
</tr>
<tr>
<td>Clay</td>
<td>5</td>
<td>-20</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>-30</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>4</td>
<td>-9</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>-28</td>
</tr>
<tr>
<td>Chalk</td>
<td></td>
<td>-20</td>
</tr>
<tr>
<td>PCC + excess of Ca(^{++})</td>
<td></td>
<td>+12</td>
</tr>
<tr>
<td>Talc</td>
<td>4</td>
<td>-10</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>-20</td>
</tr>
<tr>
<td>Silica</td>
<td>5</td>
<td>-40</td>
</tr>
</tbody>
</table>

Most of the fillers have negative charge on their surface.
Absorption of cationic additives
⇒ Effect on \( \zeta \)-potential
Charge of filler

(16% filler level)

FILLER RETENTION (%) vs. ZETA POTENTIAL (mV)

r = .900
Retention

- Increase of filler content in circulation water
- Uneven z-directional filler distribution
- Abrasion of wire
- Consistency variations
Treatment of fillers

- Dispersing in water
  - Use of dispersing agents
  - Anionic dispersing agents or NaOH
- Screening
- Pumping into the paper stock
- Special treatments to increase retention
  - Grinding of GCC in present of cationic polyelectrolyte
  - Cationizing of Clay
Selection of fillers and use in different paper grades
Ideal filler

- Chemical character ➞ unsoluble
- Retention ➞ effective use
- Spectral reflectivity independent on wavelength ➞ brightness
- Physical properties ➞ low abrasion, bulk
- Particle size 0.2 – 0.3 μm ➞ opacity
- High reflective index ➞ opacity
- Low price ➞ economy

Compromises are needed!
Selection of filler

- Final result?
- Process?
- Demands from customer?
- Functions of filler?
- Which filler fulfills these demands?
- Which filler is most economical and fulfills these demands?

**Advantages**
- Paper brightness
- Opacity
- Drainage
- Drying
- Flatness
- Fiber replacement
- Cost

**Limitations**
- Sizing
- Dusting
- Stiffness
- Strength
- Bulk

Evaluating the cost-benefit of using filler and advantages and disadvantages on paper properties ⇒ the optimal filler content
## Selection of filler

### PAPER PROPERTY/WET END ENHANCEMENT

<table>
<thead>
<tr>
<th>Property</th>
<th>Fillers To Be Considered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brightness</td>
<td>Calcium carbonate, aluminum trihydrate, amorphous silicas and silicates, 90 brightness and calcined clay. (At low addition levels) titanium dioxide - theoretically any material brighter than pulp.</td>
</tr>
<tr>
<td>Opacity</td>
<td>Titanium dioxide based on refractive index. For other materials, fine particle size, high surface area, high aspect ratio and high bulk are desirable - most PCC fillers. In some cases, off-white materials can be beneficial.</td>
</tr>
<tr>
<td>Smoothness</td>
<td>All fillers, providing there is a minimum of coarse particles or agglomerates present.</td>
</tr>
<tr>
<td>Lower Chemical Demand</td>
<td>Large particle size PCC and GCC fillers, air-float clay, talc. In general larger particle size and / low surface area is desirable.</td>
</tr>
<tr>
<td>Printability</td>
<td>Same as for smoothness - calcium carbonate, aluminum trihydrate, talc, calcined clay, and the amorphous silicas and silicates for added ink receptivity.</td>
</tr>
<tr>
<td>Ink Holdout</td>
<td>Amorphous silicas and silicates, precipitated calcium carbonate, delaminated and calcined clay, talc.</td>
</tr>
</tbody>
</table>
### Table 4. Filler pigments in different printing paper applications

<table>
<thead>
<tr>
<th>Type of Paper</th>
<th>Ash Content, %</th>
<th>Clay, %</th>
<th>GCC, %</th>
<th>PCC, %</th>
<th>Talc, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Newsprint*</td>
<td>&lt;15</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td></td>
<td>Can be used</td>
</tr>
<tr>
<td>Machine-finished specially (MFS)</td>
<td>&lt;15</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Supercalendered offset (SCO)</td>
<td>&lt;35</td>
<td>&lt;35</td>
<td>&lt;10</td>
<td>&lt;20</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Supercalendered rotogravure (SCR)</td>
<td>&lt;35</td>
<td>&lt;35</td>
<td>&lt;10</td>
<td>&lt;20</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Lightweight coated offset (LWCO)†</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>High-brightness lightweight coated (HB LWC)†</td>
<td>&lt;12</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Medium-weight coated (MWC)†</td>
<td>&lt;10</td>
<td>&lt;22</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>WFU†</td>
<td>&lt;10</td>
<td></td>
<td>&lt;10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WFC†</td>
<td>&lt;15</td>
<td>&lt;15</td>
<td>&lt;15</td>
<td></td>
<td>Pitch talc</td>
</tr>
</tbody>
</table>

Adapted from Haarla 2002.

* Most of the ash comes from recycled fiber in newsprint, if the main raw material is recycled paper.
† A part of the ash comes from coated broke in coated paper.
Lumen loading

Filler into the lumens of fiber (inside of the fiber)
- With mechanical energy
- Precipitation
  - Better strength
  - More filler can be used, optical properties
  - Good retention
  - Preparing magnetic fibers (Fe$_3$O$_4$)
Preflocculation

- Pre-treatment of filler with polyelectrolyte
- Controllable forming and breakdown of the flocs
- Better strength
- Higher filler content
- Good strength/opacity properties
- Better retention